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Tetraethylenepentamine-Grafted Magnetic Polymer Composite as Promising Sorbent for CO₂ Capture

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Abstract

In this study, magnetic porous glycidyl methacrylate and ethylene glycol dimethacrylate copolymer (mP) grafted with tetraethylenepentamine (mP-TEPA) obtained in a two-step procedure was tested as the CO₂ sorbent. The morphological, textural, structural, and thermal characterization of the sample was determined by scanning electron microscopy with energy-dispersive X-ray analysis (SEM-EDS), mercury intrusion porosimetry (MIP), nitrogen physisorption at 77 K, Fourier transform infrared spectroscopy in ATR mode (FTIR-ATR), X-ray photoelectron spectroscopy (XPS), elemental analysis, and thermogravimetric analysis (TGA). The effects of thermodynamic and kinetic parameters, as well as the adsorption/desorption mechanism on the CO₂ sorption ability of mP-TEPA, were investigated using a pulse gas chromatographic method. Under optimal adsorption conditions, the CO₂ sorption capacity reached 6.20 mmol CO₂/g (6.20×10^{-2} mmol CO₂/m²). Temperature-programmed desorption (TPD) experiments were conducted to calculate the activation energy of CO₂ desorption. The low desorption activation energy of 18.80 kJ/mol and high desorption rate, with stable CO₂ uptake after ten adsorption/desorption cycles, suggest that mP-TEPA is a potentially excellent sorbent for CO₂ adsorption.

Keywords: adsorption; carbon dioxide; magnetic polymer; amino-functionalized

1. Introduction

The huge consumption of fossil fuels has resulted in sharply rising levels of anthropogenic CO₂ emissions, leading to serious linkage problems associated with global warming and climate change [1,2]. Due to the significant diversity of emissions sources in terms of volume, composition, and industrial characteristics, the development of high-efficiency carbon capture and storage technologies becomes crucial for achieving carbon neutrality [3]. Among the current methods, CO₂ capture via adsorption is increasingly recognized as a highly promising method due to its straightforward implementation, environmental safety, and low energy requirements [4]. Various types of adsorbents can be potentially used for CO₂ capture, such as zeolites [5], activated carbon [6], metal–organic frameworks (MOFs) [7], etc. CO₂ capture relies on either physical (e.g., electrostatic) or chemical interactions with the adsorbate, and the captured carbon dioxide can be subsequently recovered by increasing the temperature or reducing the pressure [8]. However, the search continues for materials capable of meeting challenging requirements, such as high CO₂ capacity, fast kinetics, selectivity, chemical and thermal stability, reusability, efficiency, and low cost, and



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it remains an ongoing challenge as well as a key focus of current research efforts in material science and environmental engineering.

One of the most promising approaches is to combine highly CO₂-philic amines and porous organic polymers (POPs) as solid support [9]. The introduction of various amine groups into porous materials results in sorbents with high CO₂ capture capacity, selectivity, regenerability, and stability [10]. The amino groups can be introduced into POPs by direct synthesis of monomers with incorporated amino groups, or by post-functionalization of polymer by amine impregnation [11]. Over the past few decades, amine-functionalized adsorbents have been extensively investigated for CO₂ capture due to their high adsorption capacity, selectivity, and rapid kinetics [12]. Among the studied materials, polyethyleneimine (PEI) supported on metal–organic frameworks (MOFs) [13], PEI-mesoporous silica composites [14], and PEI grafted onto polypropylene fibers [15] have demonstrated significant potential. The incorporation of primary and secondary amino groups, such as ethylenediamine (ED), N'-dimethylethylenediamine (mme), diethylenetriamine (DETA), and tetraethylenepentamine (TEPA), enhances CO₂ adsorption even under humid conditions [13]. Additionally, innovative approaches have been reported, including magnetic nanoparticles functionalized with amino groups [16] and acrylonitrile-grafted viscose fibers aminated with teta [17]. These investigations demonstrate the adaptability of amine-functionalized adsorbents and their promising capability for effective CO₂ capture across various material systems.

Porous copolymers based on glycidyl methacrylate (GMA) are highly attractive solid supports for the removal and detection of both inorganic and organic pollutants from various media. The surface chemistry and porosity of GMA-based polymers can be adjusted by the reaction of nucleophilic addition of different reagents (hydroxyl, mercapto groups, hydroxyl, primary and secondary groups) on the epoxy group of the GMA molecule, and adjusted to different applications [18]. Over several decades, we have systematically investigated the effect of copolymerization conditions on the preparation of the macroporous poly(GMA-co-EGDMA) copolymer, based on GMA and ethylene glycol dimethacrylate (EGDMA). We focused on how these conditions influence porosity, functionalization, detection capabilities, and the efficiency of removing metal ions, organic compounds, dyes, and radionuclides from aqueous solutions [18–21]. With controllable surface chemistry and textural properties (porosity and specific surface area), high thermal stability, and versatile functionalization, these materials are especially promising for advanced applications such as CO₂ capture. A limited number of studies have explored amino-functionalized GMA-based polymers specifically for CO₂ adsorption. Notable examples include a terpolymer of GMA, tert-butyl methacrylate (TBMA), and trimethylolpropane triacrylate (TMPTA) [22] and a terpolymer of GMA, methyl methacrylate (MMA) and EGDMA [23] prepared via suspension polymerization, as well as poly(glycidyl methacrylate) (pGMA) homopolymer [24]. These studies highlight the potential of GMA-based polymers as versatile platforms for CO₂ capture, particularly when functionalized with amino groups that enhance adsorption capacity and selectivity.

The main objective of this study is to investigate the CO₂ adsorption/desorption performance of an amino-grafted magnetic GMA-based porous copolymer (mP-TEPA) prepared through suspension copolymerization followed by TEPA grafting. The adsorbent was comprehensively characterized in terms of its morphological, textural, structural, and thermal properties using scanning electron microscopy with energy-dispersive X-ray analysis (SEM-EDS), mercury intrusion porosimetry, nitrogen adsorption/desorption measurements, Fourier transform infrared spectroscopy in ATR mode (FTIR-ATR), X-ray photoelectron spectroscopy (XPS), elemental analysis, and thermogravimetric analysis (TGA), respectively. The CO₂ uptake, adsorption equilibrium or near-equilibrium proper-

ties, thermodynamics and kinetics, and adsorption/desorption cycle stability of mP-TEPA were investigated in detail over a range of CO₂ partial pressures and adsorption temperatures. The activation energy of CO₂ desorption from the mP-TEPA composite was determined using a method based on derivative thermogravimetric analysis with a fast Fourier transform filter.

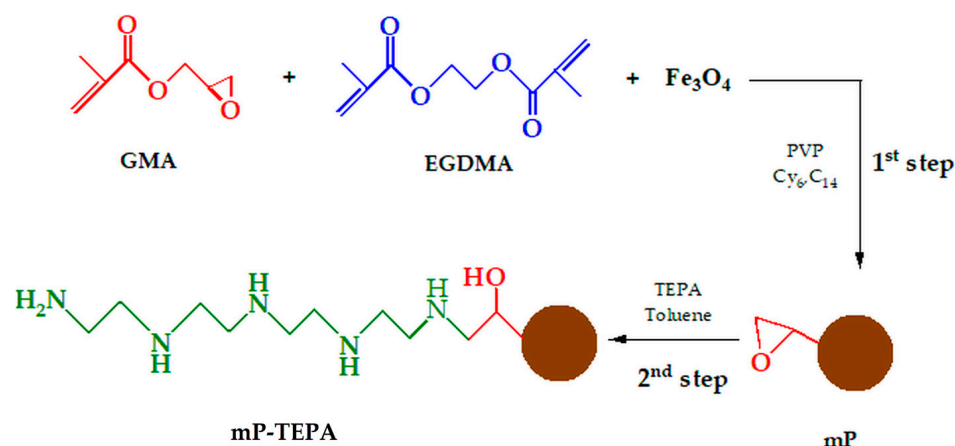
2. Materials and Methods

2.1. Chemicals

All chemicals used for magnetic sorbent synthesis and functionalization were analytical grade products and used as received. GMA, cyclohexanol (Cy₆), and 1-tetradecanol (C₁₄) were obtained from Merck (Darmstadt, Germany). EGDMA, 2,2'-Azobis(2-methylpropionitrile) (AIBN), magnetite (nanopowder with particle size 50 nm, ≥ 98% trace metals basis), and TEPA were supplied from Sigma-Aldrich (Hamburg, Germany). Poly(N-vinyl pyrrolidone) (PVP, Kollidone 90) was purchased from BASF (Ludwigs-hafen, Germany). Toluene and ethanol were obtained from Zorka Pharma (Šabac, Serbia).

2.2. Synthesis of Amino-Grafted Magnetic Polymer Composite

The magnetic amino-grafted copolymer was obtained from a two-step procedure, according to Scheme 1. In the first step, magnetic porous polymer (mP) was prepared by suspension polymerization of GMA (40 wt.%) and EGDMA (60 wt.%) in the presence of magnetite (2 wt.%). The aqueous phase containing PVP was first heated, after which the monomer mixture, AIBN, and inert components (cyclohexanol and 1-tetradecanol) with dispersed magnetite were added and stirred to achieve uniform dispersion, following the procedure described elsewhere [21]. For the second step, post-functionalization of mP with amine was performed in a typical procedure, i.e., 2.5 g of mP and 20 g of amine was added to 75 cm³ of toluene and heated under stirring at 80 °C for 6 h. The amino-grafted copolymer (mP-TEPA) was filtered, washed with ethanol and dried under vacuum at 50 °C.



Scheme 1. Synthesis of mP composite (first step); mP-TEPA composite (second step).

2.3. Instruments

Scanning electron microscopy (SEM, JEOL JSM-6460LV, JEOL Ltd., Tokyo, Japan) was used to observe the morphology of polymer samples. Prior to SEM measurements, the samples were covered with a very thin layer of gold in a high-vacuum evaporator. An EDS system (Oxford Instruments XMax SDD, 20 mm², Oxford Instruments Nanoanalysis, UK) integrated with a JEOL JSM-6460 LV scanning electron microscope was employed for elemental identification.

Textural characteristics of both polymer samples were determined using complementary techniques: mercury intrusion porosimetry (MIP) and low-temperature N₂ physisorption. MIP measurements were performed using a high-pressure apparatus 2000 (Carlo Erba, Milan, Italy) within the pressure range of 0.1 to 2000 bar. This range enables the determination of pore diameters between 14.7 µm and 7.5 nm. Prior to MIP analysis, the sample was dried in an oven at 40 °C for 16 h. Subsequent degassing was carried out under vacuum for 2 h directly inside a CD-3 dilatometer, located within Hg-filling position of a Macropore Unit 120 (Carlo Erba, Milan, Italy). Nitrogen physisorption measurements were conducted at 77 K using an Autosorb 6300 XR-XR-XR apparatus (Anton Paar GmbH, Graz, Austria). Sample preparation involved degassing at the designated preparation port for 2 h at room temperature, followed by an additional 16 h at 40 °C, both performed at a residual pressure of <0.1 mPa. The Brunauer–Emmett–Teller (BET) method [25] was applied for specific surface area (SSA_{BET}) determination, adhering to Rouquerol recommendations [26], while micropore volume (V_{mic}) and mesopore volume (V_{mes}) were determined by the Dubinin–Radushkevich method [27] and the Barrett, Joyner, and Halenda (BJH) method [28], respectively. All textural data were processed using the Kaomi software package, version 2.03 (Anton Paar GmbH, Graz, Austria).

Fourier transform infrared (FTIR) analysis was carried out in ATR mode using Nicolet 6700 spectrometer (Thermo Scientific, Waltham, MA, USA) over the range of 400–4000 cm^{−1} with a resolution of 4 cm^{−1}. X-ray photoelectron spectroscopy (XPS) was employed to investigate the surface chemical composition using a PHOIBOS 100 analyzer (SPECS, Berlin, Germany) operating with a monochromatized dual Al/Ag X-ray source. The full-scan spectra were obtained with Al Kα radiation at an energy increment of 0.5 eV under FAT 40 conditions. For detailed spectral analysis, high-resolution scans were acquired at reduced pass energy (FAT 20) using an energy step of 0.1 eV. Elemental analysis (C, H, N) was performed by the Vario EL III device (Elementar Analysensysteme GmbH, Langenselbord, Germany). Elemental composition was calculated from multiple determinations of elemental analysis within ±0.2% agreement.

Thermal stability of the synthesized samples was investigated by thermal gravimetric analysis (SDT Q600 analyzer, TA Instruments, New Castle, DE, USA). The experiments were carried out in N₂ atmosphere (flow rate: 100 cm³/min) and heated at 20 °C/min up to 700 °C.

2.4. CO₂ Adsorption and Desorption Tests

CO₂ adsorption and desorption experiments were conducted on amino-grafted samples mP-TEPA (0.0150 g) in a dynamic flow system, using a pulse gas chromatographic method with a homemade apparatus equipped with a TCD detector (Shimadzu GC-8A gas chromatograph, Shimadzu, Kyoto, Japan). To achieve the highest accuracy in the GC pulse gas chromatography system, CO₂ was introduced through a gas sampling valve with a calibrated loop. The loop volume was 0.1 mL, and this value is always corrected to STP conditions. The GC was set to the most sensitive parameters for CO₂ detection: carrier gas He (99.999%) at a constant flow rate of 40 mL/min, packed column Porapak Q (80/100 mesh), length 2 m, column temperature isothermal at 60 °C, injector temperature 100 °C, and detector temperature 150 °C. Data processing was performed using Shimadzu i-PeakFinder Integration (Shimadzu, Kyoto, Japan), an automated algorithm that handles baseline drift and accurately defines peak boundaries. Quantification of CO₂ was carried out using the Shimadzu method of absolute calibration with 1/x weighting, which provides the best accuracy across a range of CO₂ concentrations. The GC system is equipped with Zero-Dead-Volume (ZDV) fittings, which eliminate unswept spaces that cause peak tailing. The GC system set in this way ensures the determination of CO₂ concentration with an

error of less than 0.5%. The samples were placed in a fixed-bed tubular reactor made of stainless steel, with dimensions of 6 mm (outer diameter), 4 mm (inner diameter), and 115 mm (length). The samples were positioned in the central zone of the reactor on a quartz wool holder, with thermocouples at the top and bottom of the reactor bed. For adsorption experiments, the sample was exposed to pulses of 0.1 mL CO₂ injected into a carrier gas stream (He, 2400 mL/h) at 20 °C. For temperature-programmed desorption tests, the sample was presaturated with CO₂ at 20 °C. Desorption was then performed at heating rates of 10, 20, 30, 40, and 50 °C/min, in the temperature range 20–200 °C, with holding at 200 °C for 2 min after desorption. The regenerability test was performed using ten CO₂ adsorption–desorption cycles, consisting of adsorption at 20 °C until saturation and desorption from 20 to 200 °C (heating rate 30 °C/min), with a 2 min retention at 200 °C and subsequent cooling to 20 °C. For the sake of comparison, all adsorption–desorption and regeneration tests were also performed for the mP sample. All experiments were repeated three times.

3. Results and Discussion

3.1. Characterization of mP-TEPA

Since practical application and CO₂ adsorption performances of amino-grafted porous sorbent strongly depend on its characteristics such as morphology, particle chemistry (amine groups content and location), and pore structure (specific surface area, specific pore volume, pore size and distribution), a detailed characterization of amino-grafted porous samples was performed.

SEM analysis (Figure 1) revealed that the mP copolymer particles obtained by suspension polymerization are spherical and distinctly porous, with a rough surface morphology characteristic of this type of material. After amine functionalization, SEM images confirmed that the overall particle morphology was preserved, while the surface irregularities and porous structure remained clearly visible. Cross-sectional images indicated a well-developed internal porosity both before and after modification. The presence of amine functional groups was further confirmed by EDS analysis, with nitrogen detected both on the particle surface (2.2 mass. %) and within the cross-section (1.7 mass. %). These results confirmed that the amino groups were successfully incorporated in the mP structure, on the cross-section and on the inside the cavities and pores as well.

The porosity parameters, i.e., the values of specific pore volume, V_{tot-Hg} , and pore diameter which corresponds to half of the pore volume, $D_{V/2}$, were read from the pore size distribution curves determined by mercury intrusion porosimetry, while the specific surface area, SSA_{Hg} , was calculated as the sum of incremental specific surface areas from the pore size distribution curves (Figure S1) as described in the literature [29] assuming cylindrical pore shape. The values of porosity parameters are presented in Table 1.

Table 1. Porosity parameters of the mP and mP-TEPA samples obtained by mercury intrusion porosimetry.

Sample	SSA_{Hg} , m ² /g	V_{tot-Hg} , cm ³ /g	$D_{V/2}$, nm
mP	107	1.18	82
mP-TEPA	90	1.13	67

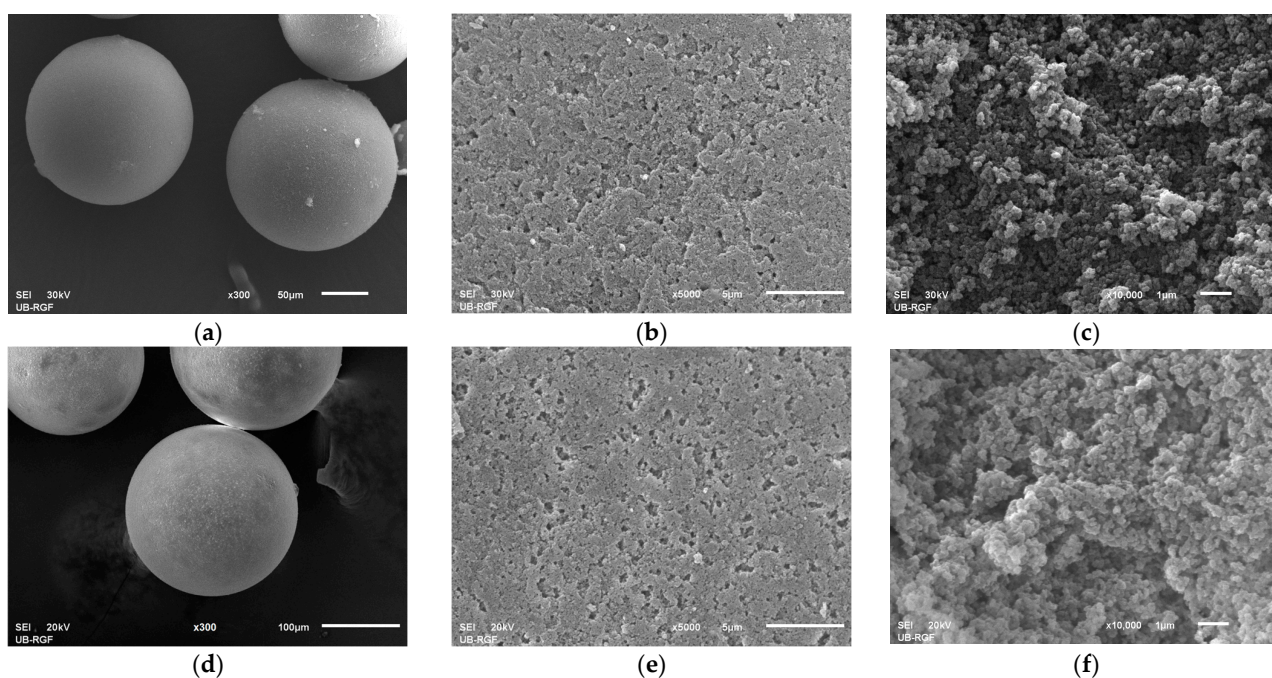


Figure 1. SEM microphotographs of mP: (a) particle appearance (magnification 300 $\times$); (b) particle surface (magnification 5000 $\times$); (c) cross-section of the particles (magnification 10,000 $\times$), and SEM microphotographs of mP-TEPA: (d) particle appearance (magnification 300 $\times$); (e) particle surface (magnification 5000 $\times$); (f) cross-section of the particles (magnification 5000 $\times$).

As seen, the initial sample, mP, is macroporous in nature ($D_{V/2} > 50$ nm). Amino-grafting has a notable impact on porosity parameters, especially on specific pore areas and for pore diameter. Following the modification, a slight decrease in specific surface area (from 107 to 90 m²/g) and pore diameter (from 82 to 67 nm) was observed. These changes suggest the formation of narrower pores and partial pore blockage, reflecting a measurable effect of amino-grafting on the porous structure. Furthermore, the cumulative pore volume distribution curves for both samples exhibit an inverse S-shaped profile and do not reach a plateau. The increase in the volume of the intruded mercury exists in the entire region of the investigated diameters, including the segment of mesopores below 50 nm. The absence of a plateau even at the smallest measurable pores (7.5 nm) indicates the likely presence of smaller mesopores in mP and mP-TEPA, which remain undetected at the maximum applied intrusion pressure of 2000 bar. To address this limitation and investigate the potential presence of even smaller features, including micropores, N₂ physisorption was employed as a complementary technique. This approach is essential because, while mercury intrusion porosimetry is the gold standard for quantifying the macroporous framework, N₂ physisorption provides the necessary resolution for the entire meso- and micropore range where MIP reaches its technical limit. Conversely, N₂ analysis often fails to accurately quantify large macropores where isotherms do not reach a plateau near $p/p_0 = 1$, making the two methods mutually reinforcing. The results of the N₂ physisorption measurements are summarized in Table 2, with the corresponding adsorption–desorption isotherms shown in Figure S2.

Table 2. Textural parameters of the mP and mP-TEPA derived from N₂ physisorption measurements.

Sample	SSA_{BET} , m ² /g	C_{BET}	V_{micr} , cm ³ /g	V_{mesr} , cm ³ /g
mP	118	64.5	0.017	0.341
mP-TEPA	100	46.2	0.013	0.310

Physisorption isotherms for both samples (Figure S2) exhibit highly similar characteristics. The isotherms are characterized by a small but visible uptake in the low relative pressure region ($p/p_0 < 0.05$), indicative of micropore filling. This is followed by a nearly linear increase in the p/p_0 region corresponding to monolayer formation and subsequent multilayer adsorption. A sharp, pronounced increase in adsorbed volume is observed at high relative pressures ($p/p_0 > 0.9$), which is attributed to the unrestricted filling of large mesopores and macropores within the material structure. Based on the characteristics of the adsorption branch, both isotherms are classified as Type II according to the IUPAC nomenclature [30], which is typically associated with macro- or nonporous materials. However, the results obtained from SEM and MIP exclude the synthesized materials from the nonporous category, confirming their substantial macroporous structure (overall pore volume $\approx 1.2 \text{ cm}^3/\text{g}$).

A notable feature, atypical for an ideal Type II isotherm (which is expected to be reversible), is the presence of a subtle but noticeable hysteresis loop in the desorption branch. While such loops are occasionally linked to capillary condensation in nanovoids formed by weak contacts between weakly bound or unbounded nanoparticles, this is dismissed in the current case. Since the final material form consists of discrete, spherical beads far larger than sub-micron dimensions ($\approx 200 \text{ }\mu\text{m}$), the quantified microporosity and mesoporosity (Table 2) must be considered an inherent feature of the individual beads rather than an artifact of particle–particle contact. The presence of hysteresis, therefore, confirms the complex porous texture of the synthesized materials, suggesting the coexistence of all pore categories within the bead structure, albeit with large differences in their overall abundance.

The large mesopore volume quantified in the N_2 analysis ($V_{\text{mes}} \approx 0.4 \text{ cm}^3/\text{g}$) without a plateau at higher p/p_0 values (characteristic of Type IV) suggests that this volume is primarily due to the mesoporous segments of the overall macropore structure, where the progressive filling of widening pores prevents the stabilization of the adsorbed volume prior to the final condensation near $p/p_0 = 1$. All measured textural parameters confirm the general trend observed by MIP regarding the partial reduction in textural properties upon functionalization of the mP macropolymer with the amine group. The specific surface area (SSA_{BET}) values determined by N_2 physisorption are slightly higher than the corresponding values determined by MIP ($118 \text{ m}^2/\text{g}$ vs. $107 \text{ m}^2/\text{g}$ for mP, and $100 \text{ m}^2/\text{g}$ vs. $90 \text{ m}^2/\text{g}$ for mP-TEPA). This difference can be attributed to the contribution to the total specific surface area from the portion of pores (diameter width $< 7.5 \text{ nm}$) that are inaccessible to the MIP technique at applied pressures. Regarding the reliability of the MIP data for these specific materials, the potential for artifacts arising from skeletal compression or non-elastic deformation, often a concern for “soft” polymers, must be considered. However, the highly crosslinked nature of the GMA-based framework provides the necessary structural rigidity to withstand the intrusion pressures. This is further evidenced by the good agreement in the trends observed between MIP and N_2 physisorption, as both techniques consistently show a reduction in surface area and pore volume following the amino-grafting process. This consistency confirms that the quantified changes reflect real textural modifications within the beads rather than artifacts caused by pressure-induced structural collapse.

Finally, the analysis of textural changes reveals a noticeable reduction in the C_{BET} constant for the amino-grafted material (mP-TEPA). The C_{BET} constant, a known indicator of the adsorbent–adsorbate interaction energy, reveals that the binding energy of the first N_2 layer is lower in the modified sorbent compared to the pristine polymer. More importantly, this reduction in the C_{BET} value supports the conclusion that the modification of the base polymer was successfully performed on the surface, as intended.

The chemical structure of the samples, and the functionalization and efficient incorporation of magnetite were confirmed by FTIR. The FTIR spectra of mP and mP-TEPA are shown in Figure 2. The peaks characteristic of GMA-based copolymers at 1255, 905, and 850 cm^{-1} (symmetric and asymmetric stretching vibrations of epoxy groups in GMA), 1725 cm^{-1} (carbonyl stretching vibrations), 2996 and 2952 cm^{-1} (C–H stretching vibrations in methyl and methylene groups), and 1450 and 1390 cm^{-1} (C–H bending vibrations in methyl and methylene groups) were observed in the FTIR spectra of mP and mP-TEPA [31,32]. In the FTIR spectra of mP and mP-TEPA, a band at 590 cm^{-1} was observed, which can be attributed to Fe–O vibrations [33].

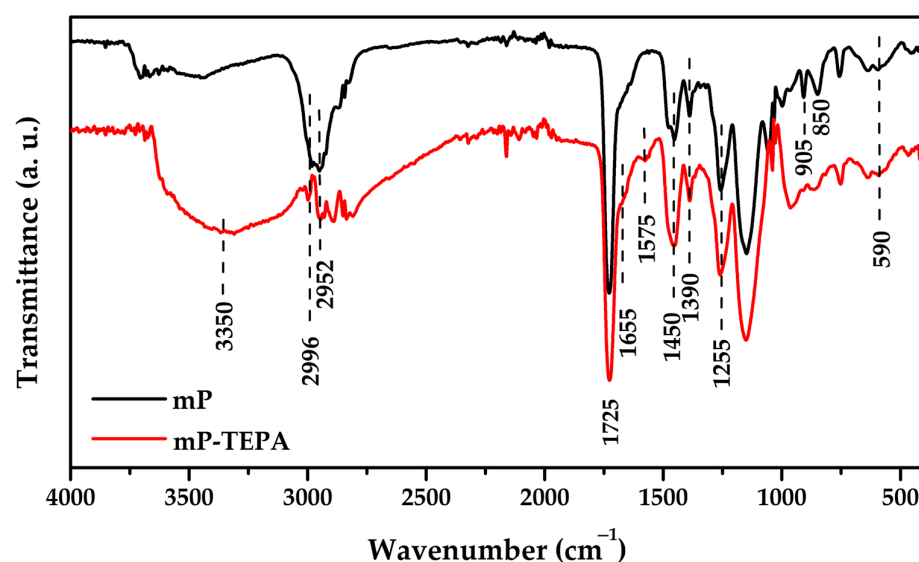


Figure 2. FTIR spectra of investigated samples.

In the spectra of the amino-grafted sample, a wide and strong band appears at 3350 cm^{-1} , which can be ascribed to the overlapping of the stretching vibrations (N–H and O–H) for $-\text{NH}$, $-\text{NH}_2$, and $-\text{OH}$ groups [34]. Additionally, two new peaks at 1655 cm^{-1} (appearing as a shoulder) and 1575 cm^{-1} , assigned to N–H bending vibrations, were detected in mP-TEPA [20].

XPS analysis was employed as an additional technique to confirm the structure of the synthesized magnetic polymer composite. The full-scan XPS spectra of mP and mP-TEPA (Figure 3a) showed characteristic peaks corresponding to C 1s, O 1s, and Fe 2p at ~ 286 eV, ~ 530 eV, and ~ 710 eV, respectively [35]. The presence of Fe 2p detected in the full-scan XPS spectra, along with the characteristic Fe–O vibration observed in the FTIR spectrum at 590 cm^{-1} , confirms the successful incorporation of magnetic nanoparticles into the copolymer matrix. As illustrated in Figure S3, these nanoparticles provide magnetic properties to the obtained composite, by its response to an external magnetic field, thus facilitating and highlighting its potential for practical applications. After modification, a new peak N 1s was observed at ~ 400 eV [36]. For a detailed analysis of the active sites, a high-resolution N 1s spectrum of mP-TEPA was recorded. As shown in Figure 3b, the N 1s spectrum was deconvoluted into two peaks at 398.8 eV and 400.8 eV, indicating the presence of primary and secondary amino groups, respectively [37]. The results of the XPS analysis are in agreement with the FTIR results, confirming the successful TEPA grafting on the mP composite.

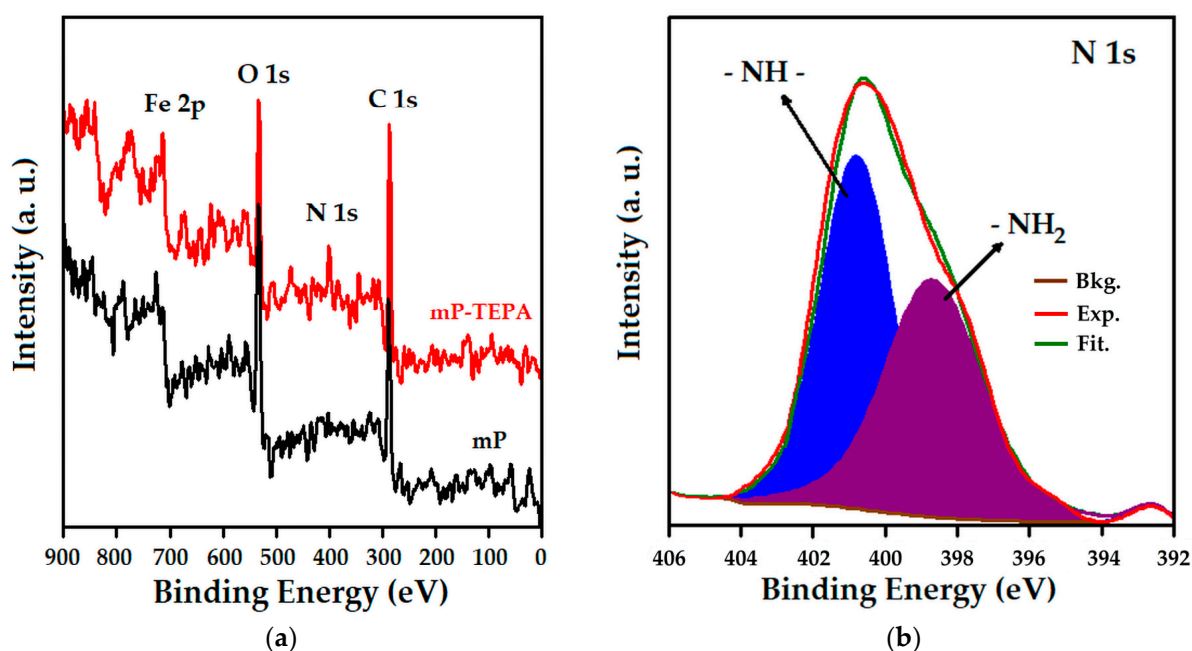


Figure 3. (a) Full-scan spectra of mP and mP-TEPA and (b) high-resolution N 1s spectrum of mP-TEPA.

To quantify the total amount of amino groups incorporated in the structure of the amino-grafted sample, CHNS analysis was performed. The concentration of amino groups in mP-TEPA, corresponding to the moles of amine functional groups per gram of sorbent, was calculated from the nitrogen content determined by CHNS analysis (5.53%), yielding a value of 3.95 mmol/g. The concentration of amino groups (C_{AG}) was calculated according to Equations (1) and (2):

$$C_{lig} = \frac{\omega_{\%}}{100 \cdot A(N) \cdot n} \quad (1)$$

$$C_{AG} = n \cdot C_{lig} \quad (2)$$

where C_{lig} (mmol/g) is the concentration of ligand (TEPA) in amino-grafted composite, ω_N (%) is the nitrogen content determined by CHNS analysis, $A(N)$ is the atomic mass of nitrogen (14.01 g/mol), and n is the number of nitrogen per ligand (TEPA) molecule.

In order to evaluate the thermal stability of mP and mP-TEPA, thermogravimetric analysis was performed. The TG curves of mP and mP-TEPA are presented in Figure 4. The main thermal parameters, such as the temperatures corresponding to 5% and 50% weight loss ($T_{5\%}$ and $T_{50\%}$), the final degradation temperature (T_{end}), the temperatures of maximum weight loss (T_{max}), the related weight loss (Δm), and residue, are summarized in Table 3.

Table 3. Thermal parameters of the mP and mP-TEPA.

Sample	$T_{5\%}$, °C	$T_{50\%}$, °C	T_{end} , °C	T_{max1} , °C	Δm_1 , wt. %	T_{max2} , °C	Δm_2 , wt. %	T_{max3} , °C	Δm_3 , wt. %	Residue, wt. %
mP	256	334	435	259	0.27	339	82.02	408	13.62	2.13
mP-TEPA	245	346	548	267	0.67	371	72.81	556	21.70	1.96

As seen from the TG curves, the $T_{5\%}$ of mP is approximately 10 °C higher than that of mP-TEPA, indicating an earlier release of adsorbed water molecules in the modified sample. This behavior can be attributed to the smaller pore diameter of mP-TEPA (67 nm) compared to mP (82 nm), as well as the introduction of polar amino groups, which likely

increases its hydrophilicity and facilitates water desorption at lower temperatures [38]. However, the modified sample exhibits higher thermal stability in the main degradation stage, as evidenced by the increased T_{50} and T_{end} values compared with mP.

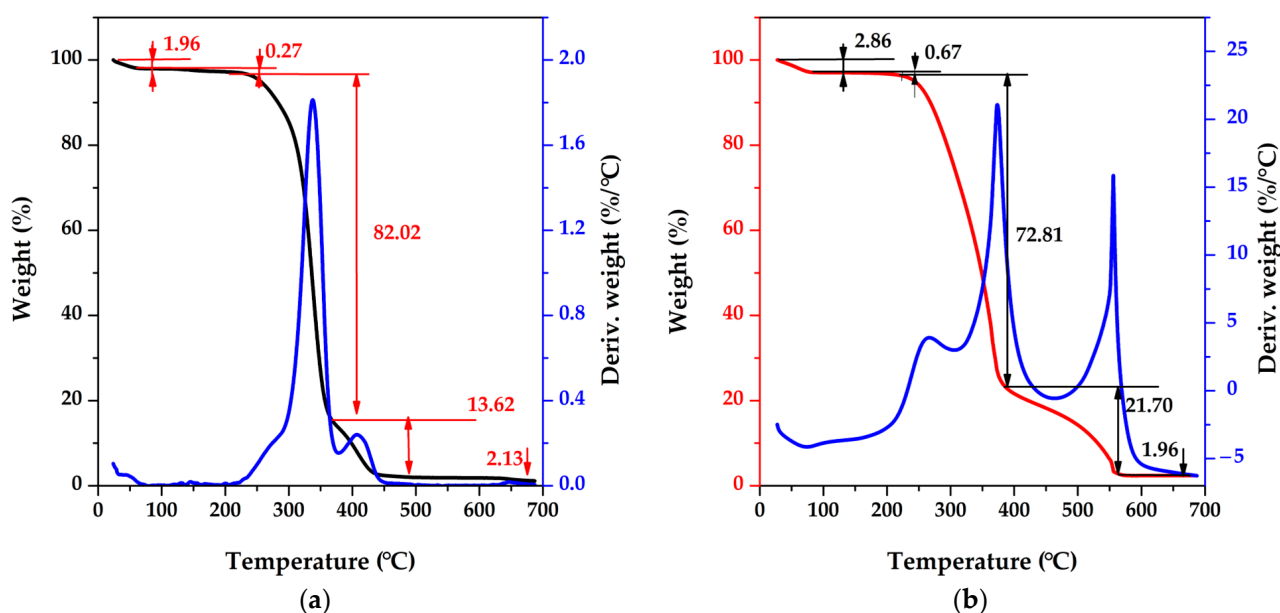


Figure 4. TG and DTG curves of (a) mP and (b) mP-TEPA.

At the same time, the DTG curves of mP and mP-TEPA indicate that both samples undergo a three-step degradation process in an N_2 atmosphere, which is characteristic of methacrylate polymers [39,40]. As seen, both mP and mP-TEPA exhibit a weight loss below 100 °C, which may be attributed primarily to the removal of physically adsorbed water and solvents [41]. The first degradation step was observed in the range of 200–300 °C with T_{max1} at 259 and 267 °C for mP and mP-TEPA, respectively. This is ascribed to the decomposition initiated at weak bonds in epoxy groups, or aminating agent [38,40]. A major mass loss of approximately 80 wt.% for mP and 70 wt.% for mP-TEPA was recorded in the second degradation stage. This stage, attributed to the scission of ester functionalities, occurs within 300–380 °C with T_{max2} for mP at 339 °C and extends to 300–460 °C with T_{max2} for mP-TEPA at 371 °C [42]. The third step was observed at higher temperatures, with T_{max3} at 408 °C for mP and 556 °C for mP-TEPA, corresponding to the degradation through random scissions of highly crosslinked domain regions [39,42]. Thus, it can be seen from TG/DTG curves that amino-grafting significantly changed the material's resistance to thermal degradation.

3.2. CO_2 Adsorption/Desorption

The CO_2 uptake was determined using a pulse gas chromatography method. Before the CO_2 adsorption measurements, the adsorbent was treated in a helium stream for 2 h at 100 °C. After cooling in the helium stream to working temperatures, the adsorption cell was thermostated at 20 °C and CO_2 was pulsed into the helium stream. The samples adsorbed the CO_2 pulses until saturation occurred. In this case, the proportion of non-adsorbed CO_2 is determined. Figure 5 shows the dynamics of CO_2 capture on mP-TEPA polymer.

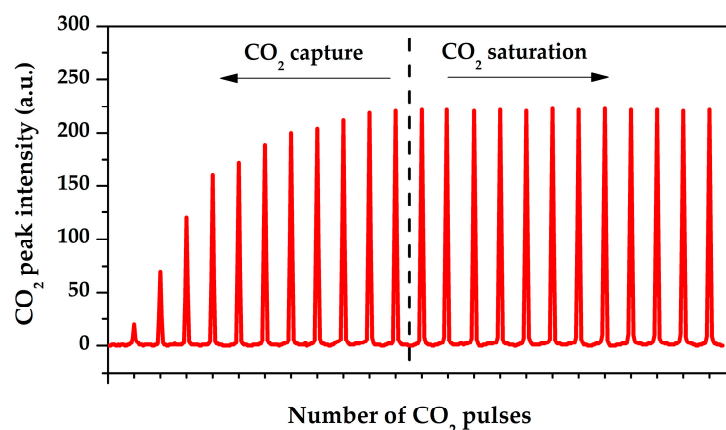


Figure 5. CO₂ capture determined by the pulse gas chromatography method (mP-TEPA loading: 0.0150 g; CO₂ adsorption temperature: 20 °C; CO₂ pulse volume 0.1 cm³).

The saturated adsorption capacity, defined as the CO₂ adsorption capacity per gram of adsorbent, of polymer mP-TEPA was 6.20 mmol CO₂/g, corresponding to a normalized value per unit area of 6.20×10^{-2} mmol CO₂/m². The saturated adsorption capacity of the mP copolymer was 1.78 mmol CO₂/g (1.51×10^{-2} mmol CO₂/m²), which is significantly lower than that of mP-TEPA. The amine efficiency, CO₂ adsorption capacity, and chemical structure of bare mP and mP-TEPA were compared with similar solid amine-polymer CO₂ adsorbents reported in the recent literature (Table 4).

Table 4. Comparisons with relevant solid amine-polymer material.

Adsorbent *	Temperature (°C)	CO ₂ Adsorption Capacity (mmol/g)	Final Degradation Temperature (°C)	Specific Surface Area (m ² /g)	Reference
PS-HA PS-AE PS-AEHA	15	2.98 3.30 3.71	~450	30 35 35	[43]
PAF-5-C=N-EDA PAF-5-C=N-DETA PAF-5-C=N-TETA	25	3.78 3.88 3.31	~650 **	1423 1224 1101	[44]
PP-2-EDA PP-2-DETA PP-2-TEPA PP-2-PEI	25	1.27 1.43 1.47 1.55	~550	1200 940 720 410	[45]
PAN-TEPA PAN-TETA	25	4.35 5.44	- -	- -	[46]
C-PDVB-0.3PEHA Meso-PDVB-0.3PEHA	30	2.73 3.66	~450	13 57	[47]
mP mP-TEPA	20	1.78 6.20	435 548	118 100	This work

* PEHA or HA—pentaethylenhexamine; EDA or AE—ethylenediamine; DETA—diethylenetriamine; TETA—triethylenetetramine; TEPA—tetraethylenepentamine; PEI—polyethylenimine; PS—Merrifield resin; PAF-5-C=N—porous aromatic framework; PP-2—porous polymers with two -CH₂Cl; C-PDVB—connected porous poly(Divinylbenzene); meso-PDVB—mesoporous Poly(Divinylbenzene). ** Estimated from TG curves reported in the literature.

As indicated by the results in Table 4, mP-TEPA outperforms several materials that possess significantly higher specific surface areas [44,45]. The discrepancy between SSA and CO₂ adsorption capacity in these predominantly microporous materials most probably arises from the inaccessibility of a substantial portion of the internal surface to the bulky modifier molecules. During the functionalization process, amine molecules can preferentially anchor at the pore entrances, leading to pore blockage. This phenomenon

effectively isolates the internal micropore volume, preventing the bonding of amino groups to the reactive sites of the support. Consequently, while the material may retain a high residual SSA after modification, it lacks the necessary active sites for CO₂ chemisorption within these restricted spaces. Furthermore, even if some amino groups are successfully introduced, their efficiency is often hindered by steric hindrance. The initial binding of CO₂ can induce conformational changes in the flexible TEPA chains, which, in the confined space of a micropore, creates a physical barrier that obstructs the diffusion of subsequent CO₂ molecules.

In contrast, the predominantly meso- and macroporous architecture of mP-TEPA bypasses these diffusion-related limitations. The larger pore diameters ensure both the successful loading of TEPA and the high accessibility of the resulting amine sites. This synergy between chemical functionality and structural openness accounts for mP-TEPA and achieves superior CO₂ capture performance compared to the high-SSA materials reported in Table 4.

When amines are analyzed with respect to their chemical structure, TEPA demonstrates a higher CO₂ adsorption capacity due to its high density of amine groups per molecule and an appropriate balance of chemical properties that enable effective reaction with CO₂. The linear structure of TEPA contains five amine groups, more than EDA (2), DETA (3), and TETA (4). This greater number of active nitrogen sites increases the possibility for reactions with CO₂, resulting in a higher CO₂ capture capacity. It was also shown that mP-TEPA had a better CO₂ adsorption capacity than adsorbents containing PEHA and PEI, even though PEHA has six amino groups per molecule and PEI is a polymer with a variable number of amino groups depending on its molecular weight and branching structure. TEPA has a lower viscosity than higher molecular weight amine PEHA or polymeric amine PEI when used as a liquid absorbent or as an impregnating reagent for solid supports. This enhances diffusion within the pores of support materials, increasing the accessibility of amine sites to CO₂ molecules and improving mass transfer efficiency, especially in solid adsorbents. In this way, TEPA offers a beneficial balance with more amine groups than the others, resulting in higher CO₂ adsorption efficiency. Compared to larger, more complex amines in some polymer support materials, TEPA's molecular structure provides a high degree of mobility, which helps minimize mass transfer resistance and permits more rapid adsorption kinetics. Furthermore, mP-TEPA has a substantially better CO₂ adsorption capacity than amine polymers with much higher specific surface areas [44,45].

For porous solid amine adsorbents, determining whether amine surface density (the number of amine groups per unit area) or specific surface area (the total area available on the support) is more important depends on whether the goal is to optimize the chemical reaction (efficiency) or total capacity (volume). Amine efficiency (η), defined as the molar ratio of captured CO₂ to the total moles of nitrogen (amine groups) in the sorbent, is a critical variable for the chemistry of CO₂ capture. For mP-TEPA, amine efficiency was calculated as $\eta = 6.2 \text{ mmol CO}_2/\text{g}/3.95 \text{ mmol N/g} = 1.57$. This η value exceeds the optimal efficiency for dry amines of 0.5 (carbamate formation) and for humid conditions of 1.0 (bicarbonate formation), suggesting that either the support material, mP polymer, contributes significantly to CO₂ capture through physical adsorption, or that the amine is deposited in multilayers deep on the surface. Amine surface density (σ), which indicates how crowded the amine groups are on the support surface, for the mP-TEPA sorbent was 23.67 N/nm². For mP-TEPA, which has a specific surface area of 100 m²/g, a typical monolayer of amine groups is about 4–5 N/nm² (exactly 4.73 N/nm²). A density of 23.67 N/nm² indicates that the amines are deposited approximately five layers deep on the surface. Therefore, the multilayered adsorption of CO₂ confirms that amine density is generally the more critical parameter for the mechanism of CO₂ capture, whereas specific

surface area acts as a theoretical limit of how much amine can be added without the amines stacking into thick, nonporous layers.

The lack of a compensatory effect of specific surface area on the number of sites for CO₂ adsorption arises because the capture process is governed by a CO₂ adsorption mechanism rather than by simple physical surface area. In this process, performance is primarily determined by the high density and accessibility of amine functional groups, rather than the basic topography of the sorbent. Consequently, this dominance of the adsorption mechanism ensures that the CO₂ adsorption capacity of TEPA is sufficiently high, making it a technically effective candidate for the intensive capture requirements of industrial flue gases. A good and energy-efficient CO₂ sorbent should have fast CO₂ desorption kinetics at a low temperature. A series of temperature-programmed CO₂ desorption (TPD) experiments were performed at different heating rates to determine the activation energy for the desorption of CO₂. Using the derived thermogravimetric analysis method, Equation (3) is as follows:

$$\ln\left(\frac{RT_p^2}{\beta}\right) = \frac{E_d}{R}\left(\frac{1}{T_p}\right) + \ln \frac{E_d}{k_o} \quad (3)$$

It can be linearized, and the slope of a curve $\ln(RT_p^2/\beta)$ vs. $1/T_p$ made it possible to calculate the desorption activation energy [48]. In Equation (1), R is the gas constant, T_p is the CO₂-TPD peak temperature, β is the heating rate (°/min), E_d is the activation energy for desorption (kJ/mol), and k_o is the desorption rate coefficient (1/min). Figure 6 shows the CO₂-TPD profiles obtained at different heating rates for the sorbents mP-TEPA and bare mP. Figure S4 shows the relationship between $\ln(RT_p^2/\beta)$ and $1/T_p$ for CO₂ desorption, including the calculated CO₂ desorption activation energy.

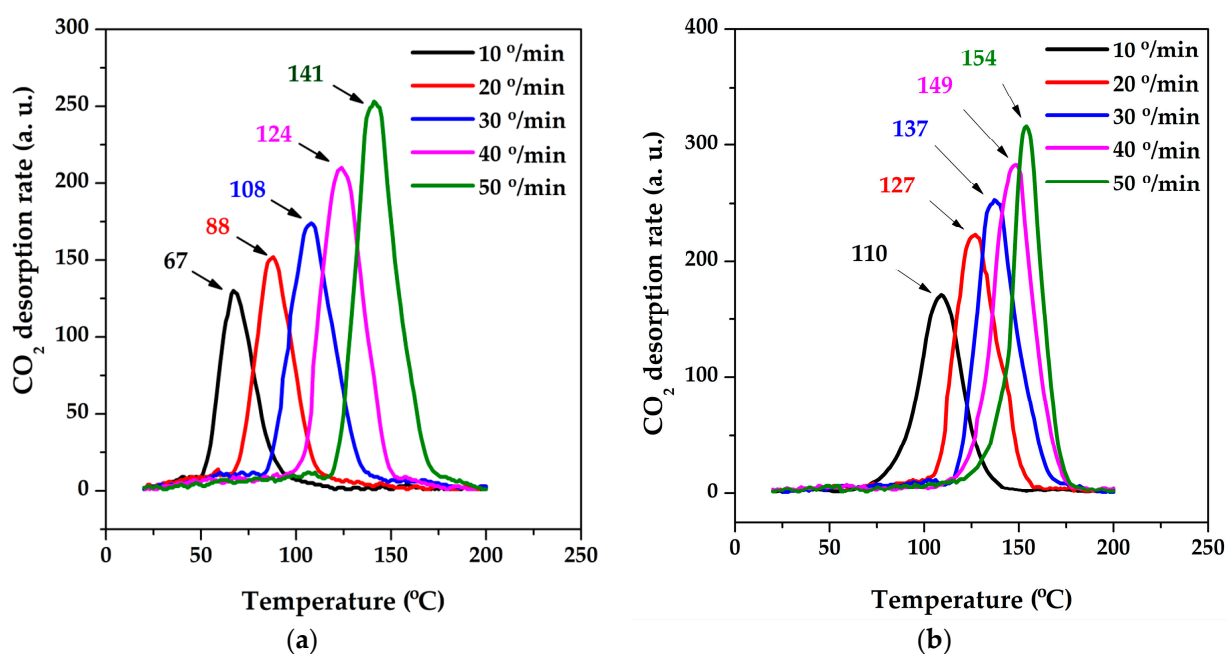


Figure 6. CO₂-TPD profiles of (a) mP-TEPA and (b) mP [Flow rate of carrier gas (He): 2400 mL/h; temperature regime: heating rates 10, 20, 30, 40, and 50 °/min for temperature increase from 20 to 200 °C, holding at 200 °C for 2 min; sorbent mass: 0.0150 g].

It should be noted that the activation energy values of CO₂ desorption for sorbent mP-TEPA are relatively low ($E_d = 18.80$ kJ/mol), with a value of 30.8 s^{-1} for the pre-exponential factor, which is determined from the intercept of the plot in Figure S4.

In the context of the experimental setup, pulse gas chromatography, CO₂-TPD with a He carrier gas stream, and thermogravimetric analysis (Kissinger analysis), the value of E_d can indicate whether a molecule is weakly held by physical forces (physisorption) or strongly bonded by chemical reactions (chemisorption). The E_d of 18.80 kJ/mol is close to the E_d values of 15.8 kJ/mol and 16.8 kJ/mol for the physisorbed CO₂ on TEPA-based MCM-41 [49] and on bi-amine-functionalized mesostructured silica nanospheres [50], respectively. Generally, E_d values below 20 kJ/mol suggest physisorption dominated by weak van der Waals forces, while higher values are associated with chemisorption involving stronger chemical bonding. An E_d of 18.80 kJ/mol clearly indicates physisorption rather than chemisorption. On the energy scale, chemisorption typically occurs at desorption energies E_d in the range of 50 to 200 kJ/mol [51–55]. The low E_d suggests that CO₂ can be desorbed very easily, often at moderate temperatures (<100 °C). The obtained activation energy of desorption of 18.80 kJ/mol typically corresponds to weak acid–base interactions between CO₂, which is a Lewis acid, and basic sites or hydroxyl groups (–OH) on the surface of mP-TEPA. The E_d in the range of 20–50 kJ/mol represents the involvement of both physisorption and weak chemisorption. This occurs in materials where CO₂ can interact with less accessible amine sites to form carbamic acid rather than stable carbamates. It is common in amine-impregnated sorbents where the pore size and structure influence the chemical reaction [56–58]. The calculated pre-exponential factor of 30.8 s^{−1} is extremely low for a fundamental chemical bond-breaking event. This suggests that desorption of CO₂ is a diffusion-limited process, where the rate is controlled by how fast CO₂ can move through a material, rather than by the chemical reaction itself. Also, this extremely low pre-exponential factor can be due to weak physical interactions where molecules are loosely held or physisorbed on the amine sites. This indicates that the CO₂ molecules are only weakly adsorbed on the active sites of mP-TEPA. In Figure S4, it shows a good linear fit with an acceptable R² coefficient of determination values (R² > 0.99), which justified the method for determining the value of the desorption activation energy at different heating rates. With a desorption activation energy of 18.80 kJ/mol, mP-TEPA enables the release of CO₂ at relatively low temperatures. Furthermore, mP-TEPA adsorbs CO₂ at 20 °C and desorbs CO₂ at 67 °C (at heating rates of 10 °C), which is a relatively small difference in CO₂ adsorption–desorption temperature. Considering the texture and porous structure of the adsorbent mP-TEPA, it seems that during CO₂ desorption, a greater quantity of CO₂ molecules may block the pore entrances and make the diffusion of CO₂ molecules through the inner pores of the sorbent more difficult. Bearing in mind the values of CO₂ adsorption capacity (6.20 mmol/g) and activation energy of CO₂ desorption (18.80 kJ/mol), it seems that a greater amount of CO₂ can inhibit the desorption process, and that CO₂ leaves the pore system at higher temperatures. In microporous materials, this value is often close to the isosteric heat of adsorption for physisorbed CO₂ interacting with the pore walls. CO₂ is frequently re-adsorbed multiple times as it leaves the pores, and this re-adsorption macroscopically slows the desorption rate, which is reflected in a relatively low E_d value of 18.80 kJ/mol and a pre-exponential factor of 30.8 s^{−1} for surface desorption kinetics. According to transition state theory (TST), a pre-exponential factor value of 30.8 s^{−1} indicates CO₂ physisorption and usually represents CO₂ trapped in pores or very weakly interacting with the surface [59].

To emphasize the role of mP copolymer grafting with the amine TEPA, all kinetic CO₂ adsorption–desorption parameters on the mP copolymer surface were determined using the same procedures as for mP-TEPA. The mP copolymer has a CO₂ adsorption capacity of 1.78 mmol CO₂/g, and a desorption activation energy of 42.10 kJ/mol with a pre-exponential factor of 10⁵, while CO₂ desorption in the temperature range of 10 to

50 °C/min occurs at TPD peak temperatures from 110 to 154 °C. The E_d value of 42.10 kJ/mol indicates an interaction that combines physisorption and weak chemisorption.

For a more detailed analysis of the interaction between CO₂ and mP-TEPA and mP sorbents, the desorption activation energy (E_d) was calculated using the Redhead equation [60], providing insights into the interaction strength between CO₂ and the adsorbent surface. The Redhead equation is presented as Equation (4):

$$E_d = RT_m \left[\ln \left(\frac{\beta T_m}{\nu} \right) - 3.45 \right] \quad (4)$$

where R is the gas constant (8.314 J/molK), T_m (K) is the peak desorption temperature, β (K/s) is the heating rate, and ν (s^{−1}) is the pre-exponential factor.

Redhead analysis was performed using pre-exponential factors determined by the Kissinger analysis. Pre-exponential factors of 30.8 s^{−1} and 10⁵ s^{−1} were applied for the mP-TEPA and mP samples, respectively. Table 5 summarizes the peak CO₂ desorption temperatures and desorption energies corresponding to different heating rates for the mP-TEPA and mP samples.

Table 5. CO₂ desorption characteristics for mP-TEPA and mP samples.

Sample	Measurements No.	T_m (K)	β (K/min)	E_d (kJ/mol)
mP-TEPA	1	340	10	25.06
	2	361	20	24.91
	3	381	30	25.30
	4	397	40	25.64
	5	414	50	26.18
mP	1	383	10	52.39
	2	400	20	52.68
	3	410	30	52.78
	4	422	40	53.47
	5	427	50	53.40

Table 5 shows the consistency of the E_d values for both samples. The mean E_d is 25.42 ± 0.51 kJ/mol for mP-TEPA and 53.94 ± 0.47 kJ/mol for mP (standard deviations < 1 kJ/mol). This demonstrates that these are two distinct, well-defined adsorption environments, not a spectrum of heterogeneous sites. The desorption energy level for mP-TEPA ($E_d \approx 25$ kJ/mol) is typical for CO₂ physisorption. For comparison, the heat of sublimation of CO₂ is approximately 28 kJ/mol [61], and the heat of liquefaction is approximately 17 kJ/mol [62]. An E_d in the 20–30 kJ/mol range indicates molecules held by weak van der Waals forces or very weak electrostatic interactions with surface dipoles. The consistency of the E_d values, together with the exceptionally low pre-factor ($\nu = 30.8$ s^{−1}), suggests a highly immobile state. Even though the bond is weak, the CO₂ molecules may be trapped in narrow pores or pore diffusion may slow down the desorption process. For the mP polymer, crossing the 40–50 kJ/mol threshold usually marks the transition from physical to chemical bonding [63,64]. This energy indicates that a true chemical bond has formed, though it is relatively weak. This is often attributed to CO₂ interacting with weak Lewis acid–base pairs. These species are stable at room temperature but decompose readily upon mild heating, as shown for mP polymer in the temperature range 383 to 427 K, Table 5. The applied pre-factor ($\nu = 10^5$ s^{−1}) is much lower than the recommended 10¹³ s^{−1} for Redhead analysis, but E_d remains consistent (52.94 ± 0.47 kJ/mol) over the entire temperature range. This confirms that the transition state involves a significant loss of rotational or translational freedom, which is consistent with the breaking of a

coordinated chemical bond. The results of Redhead analysis for mP-TEPA represent CO₂ filling the pores or physisorption, while for the mP polymer it can be attributed to weak chemisorption at the active sites. Although the Redhead method tends to give a slightly higher activation energy E_d than the Kissinger method due to different approximations and assumptions inherent in each method, the results of the Redhead method are completely analogous to those of the Kissinger method. For mP-TEPA, the diffusion of CO₂ is probably the controlling step of the overall process of CO₂ desorption. However, the mP-TEPA polymer has great potential for application in CO₂ capture processes with lower energy consumption. Further improvement in these systems should focus on the optimization of the porous and textural properties of sorbent.

3.3. Regenerability

Successful industrial use of an efficient adsorbent requires a high adsorption and regeneration capacity during many adsorption–desorption cycles. Therefore, 10 adsorption–desorption cycles were performed to evaluate the regenerability of the absorbents, mP-TEPA, and mP. The results are shown in Figure 7.

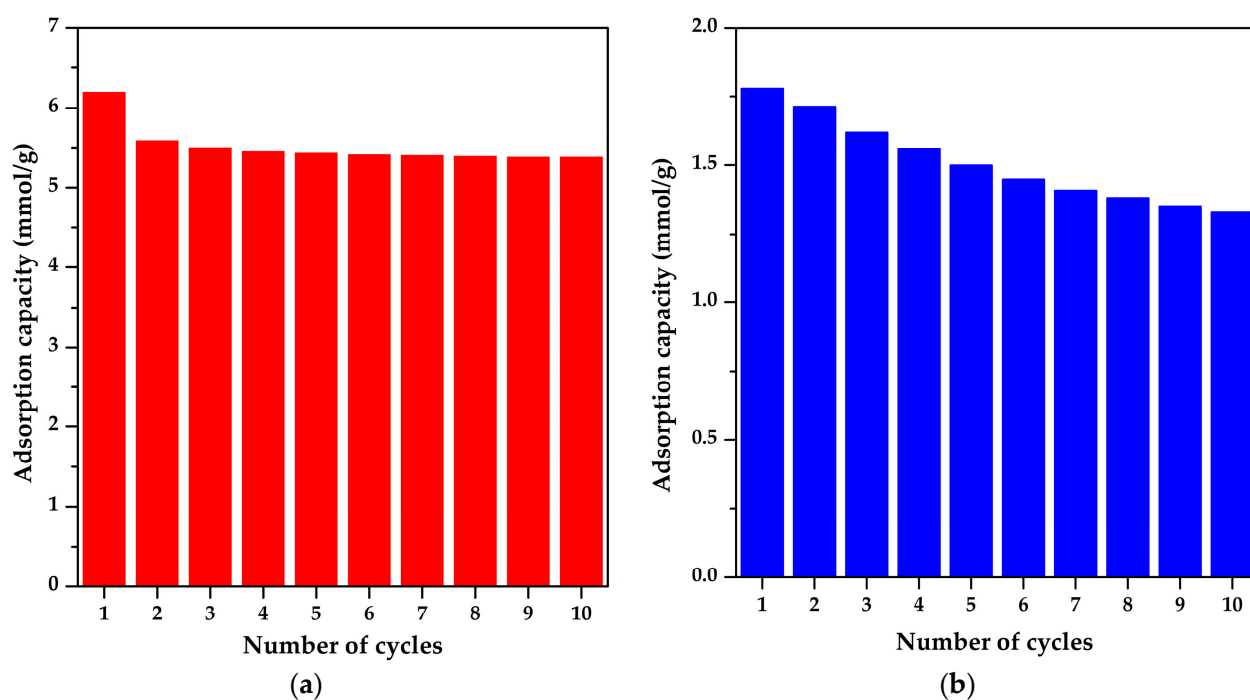


Figure 7. Adsorption–desorption properties of (a) mP-TEPA and (b) mP in ten repeated cycles of CO₂ adsorption. [Flow rate of carrier gas (He): 2400 mL/h; one cycle temperature regime: linear increase from 20 to 200 °C (heating rate 30 °/min), holding at 200 °C for 2 min, cooling to 20 °C; sorbent mass: 0.0150 g].

It is well-known that TEPA, a material with a high amine density (five nitrogen atoms per molecule), partially reacts with CO₂ through chemisorption to form a carbamate under dry conditions or a bicarbonate under humid conditions, although the overall process often involves a mixed mechanism of both chemisorption and physisorption. Accordingly, the 10% decrease in CO₂ adsorption capacity after the first regeneration (Figure 7a) could be due to a reaction between CO₂ and TEPA, which occupies the available adsorption sites. Considering that the maximum temperature during the regeneration cycle is 200 °C, and that TEPA is resistant to thermal degradation at temperatures above 200 to 250 °C, it appears that the volatilization of TEPA plays an important role in the reduction in CO₂ adsorption capacity. During the first regeneration cycle, TEPA volatilization is higher

than in subsequent cycles because TEPA molecules on the upper sorbent surface are less strongly bound to the mP polymer than those in the deeper layer of the initial mP-TEPA.

As shown in Figure 7b, the sorption capacity of bare mP decreases almost continuously with the increasing number of cycles, falling by 25% after 10 cycles. This decrease in sorption capacity for bare mP is significantly more pronounced than the 15.5% decrease observed for the mP-TEPA sorbent. At the start of the thermo-desorption cycles, the initial mass of both sorbents was 0.0150 g, and after 10 cycles of regeneration, their masses were 0.0149 g (<0.6%) for mP-TEPA and 0.0143 g (<4.7%) for bare mP. This is consistent with thermogravimetric analysis, which showed that amino-grafting significantly increased the resistance of the mP-TEPA sorbent to thermal degradation compared to the bare mP copolymer. The decrease in CO₂ adsorption capacity of the mP-TEPA sorbent is probably due to the volatilization of the amine TEPA, while in the case of the bare mP sorbent, the decrease in adsorption capacity is due to increased thermal degradation of the mP copolymer.

Several factors led to a decrease in CO₂ adsorption capacity, including the volatilization of amines during the adsorption–desorption cycle [10]. The boiling point of TEPA (380 °C) is much higher than the maximum temperature of 200 °C at which the mP-TEPA sorbent was treated. Consequently, mP-TEPA is very stable under temperature regime in the CO₂ desorption condition. Therefore, mP-TEPA seems to be a good choice for practical CO₂ capture applications due to its high CO₂ adsorption capacity and stable cyclic regeneration.

4. Conclusions

In this study, based on suspension polymerization, mP porous magnetic composite was successfully synthesized and subsequently functionalized to obtain TEPA-grafted magnetic GMA-based porous copolymer (mP-TEPA). The incorporation of magnetite into the structure of the porous composite, as well as the functionalization of mP by the introduction of primary and secondary amino groups, was confirmed by FTIR, XPS, and elemental analysis. The resulting mP-TEPA particles are spherical and highly porous, with a rough morphology where surface irregularities and the porous structure are clearly visible. The specific surface area of the mP-TEPA sorbent was 100 m²/g, with an average pore diameter of 67 nm. The saturated CO₂ capture capacity of the mP-TEPA polymer, determined by the pulse gas chromatography method, was 6.20 mmol CO₂/g, or, when normalized per unit area, 6.20×10^{-2} mmol CO₂/m². The relatively low value of the activation energy of CO₂ desorption for the mP-TEPA sorbent, E_d (18.80 kJ/mol), was obtained, while the sorbent exhibited high regenerability, with only 15.5% loss of CO₂ adsorption capacity after 10 cycles. Comparison with similar amino-grafted polymers showed that mP-TEPA was a promising material for practical applications as an efficient CO₂ sorbent, due to its high CO₂ adsorption capacity, optimal adsorption–desorption temperature characteristics, and stability during regeneration.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/separations13020056/s1>, Figure S1: Integral pore size distribution curves for mP and mP-TEPA; Figure S2: Adsorption/desorption isotherm measured at 77 K for (a) mP; (b) mP-TEPA; Figure S3: Response of the amino-grafted magnetic polymer composite mP-TEPA to an external magnetic field; Figure S4: Plot of $\ln(RT_p^2/\beta)$ vs. $1/T_p$.

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Conflicts of Interest: The authors declare no conflicts of interest.

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