



Polyethyleneimine (PEI) Functionalized Metal Oxide Nanoparticles Recovered From the Catalytic Converters of Spent Automotive Exhaust Systems and Application for CO₂ Adsorption

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A novel CO₂ sorbent was prepared from the catalytic converters of spent automotive exhaust system by modifying with polyethyleneimine (PEI) through wet impregnation method. The prepared sorbent was characterized by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), X-ray diffraction (XRD) and Brauer-Emmett-teller (BET) analysis before and after functionalization. Different PEI loadings were employed to study the adsorption performance of as-prepared sorbent. The characterization results showed no significant change in the structure, but the surface area was decreased after modification with amine groups. The adsorption was remarkably improved by increasing the PEI loading. The optimal PEI loading on the as-prepared sorbent was 60 wt.%. At optimal PEI loading, the CO₂ adsorption reached to 101.3 mg (g sorbent)⁻¹ at 70°C and partial pressure of 100 kPa. Further PEI loading had a negative effect on the adsorption. The CO₂ adsorption capacity increased to 125.2 mg (g sorbent)⁻¹ in the presence of 1 vol.% of the H₂O moisture. Results confirmed the high performance of novel sorbent compared to other porous sorbents such as carbon-based materials. Adsorption/desorption cycles revealed that the PEI-impregnated sorbent can be satisfactorily regenerated after CO₂ adsorption process.

Keywords: spent catalytic converter, polyethyleneimine, multi-metal oxides, CO₂ adsorption, functionalizability

INTRODUCTION

Fossil fuels had a drastic increase in CO₂ emissions during past two centuries by a rapid increase of the world population and industrial activities (Dutcher et al., 2015; Li et al., 2015; Lee et al., 2016; Sanz-Pérez et al., 2016; Hu et al., 2017). The greenhouse effect results from the disruption in carbon balance in earth's atmosphere leads to environmental impacts on the biological ecosystems (Mofarahi et al., 2008; Songolzadeh et al., 2014; Pasięka et al., 2015; Figueiredo et al., 2016; Irani et al., 2016; Luis, 2016; Singh et al., 2016). Therefore, academic and industrial communities have focused on developing promising methods to mitigate the CO₂ concentration to standard levels

(Lin et al., 2014; Shekhah et al., 2014; Wang J. et al., 2015). CO₂ is known as the most prevalent greenhouse gas which need to be significantly decreased through various approaches such as pre-combustion, post-combustion and oxy-fuel combustion. Among them, post-combustion CO₂ capture has received a wide attention from the scientific society due to the most popularity in the industrial processes. There are different procedures to reduce the CO₂ emissions including aqueous solutions of amine (Maleki et al., 2018), membrane separation (Rezazakemi et al., 2011), hybrid systems and sorbent adsorption (Irani et al., 2018b,c).

Amine solution is commonly used in the industrial processes including gas sweetening in the natural gas refining plants. There are various amine solvents employed in the acid gas absorption including MDEA, DEA, MEA and a mix of mentioned solvents. MDEA play a significant role due to high absorption capacity and thermal and mechanical stability. However, amine solvents are restricted by some phenomenon including foaming, degradation, carbamate formation, toxicity and volatility (Ghasemi et al., 2020).

The adsorption process is known as an effective method for separation of CO₂ in industrial applications. One of the most promising ways to separate the CO₂ is adsorption by porous materials (Silva et al., 2017; Gil et al., 2018; Prasetyo et al., 2018). Porous materials have many remarkable features including stability, reusability, high surface area, the minimal energy requirement for regeneration and selectivity for the desired molecules (Nugent et al., 2013). Porous solid adsorbents such as metal oxides (Cuéllar-Franca and Azapagic, 2015; Gunathilake et al., 2016), porous carbon based materials, metal-organic frameworks (MOFs) (Irani et al., 2018b), covalent organic frameworks (COFs) (Didas et al., 2015; Huang et al., 2016) and zeolites (Lee and Park, 2015; Kim et al., 2016) have been separately investigated. Recently, studies have been focused on the CO₂ separation using functionalized such adsorbents with amine-based compounds to form a composite (Best et al., 2018; Du et al., 2018). This functionalization process resulted in some excellent features such as high CO₂ selectivity, ability to regeneration and excellent adsorption capacities. Amine functionalized solid adsorbents have shown the CO₂ adsorption through separate or simultaneous chemical and physical bond formation as well as pore diffusion (Fan et al., 2018). Amine-modified adsorbents are prepared by various strategies including grafting nitrogen based groups on the solid surface, physical impregnation of solid sorbents with polyethyleneimine (PEI) and nitrogen-doping of some materials with gaseous NH₃. Metal oxides have been widely modified with some organic functional groups to be employed in various applications such as catalysis, separation, drug delivery and bioactivation (Jung et al., 2016; Hu et al., 2017; Molavi et al., 2018). PEI (branched structure) is the most frequently used amine for CO₂ adsorption by solids because of its amine-rich structure (Jung et al., 2018; Peng et al., 2018). Carbon-based materials are the most prevalent sorbents used in various studies to investigate the CO₂ adsorption capability. Irani et al. studied modified carbon nanotubes/tetraethylenepentamine for CO₂ adsorption and the results showed the sorption capacity of 5 mmol/g-sorbent at 60°C (Irani et al., 2017).

Car industry annually generates a high amount of spent car catalysts which resulting in economic and environmental consequences. Automotive catalytic converters emerged in mid-1970s in the United States to reduce the emission of cars. This catalyst mainly contains platinum or a combination of platinum and palladium to convert the hydrocarbons and CO to H₂O and CO₂. Other main elements available in these catalytic converters are rhodium and gold (Sabegh et al., 2018). However, automotive industry suffers from some disadvantages such as non-renewability of these metals, high price and the environmental impacts related to their extraction. There is promising interest toward the recovery of these metals from spent car catalytic converters which result in the economic and environmental consequences (Jimenez de Aberasturi et al., 2011). Recovering the platinum metal groups (PMGs) has been focused by researchers in recent year. In a typical recovery process, PGMs can be extracted from scraps through melting and collecting them by collector metals including copper. In another process, scraps are dissolved in strong acid and metals are collected (Jimenez de Aberasturi et al., 2011).

In this study, a novel cost-effective sorbent was prepared and studied as a high performance support for CO₂ capture. Multi-metal oxides were recovered via a cost-effective, green sol-gel procedure from catalytic converters of spent exhaust systems. The obtained multi-metal oxide was used as a novel adsorbent after modifying with PEI. Multi-metal oxide mixture was fully characterized before and after the functionalization process; and the different PEI loading, adsorption temperature, and CO₂ partial pressure effects were studied using a thermogravimetric analyzer (TGA).

EXPERIMENTAL

Materials

Spent catalytic converters of exhaust systems were obtained by Iran and Research center of Auto parts and components company (ITRAC Co.) to recover the metal oxide *nanoparticles as a novel solid CO₂ adsorbent*. Other materials found in this study with their source and specifications are summarized in Table 1.

Recovering Process of Metal Oxides From Spent Catalytic Converters

Following the crushing and milling catalytic converters of spent exhaust systems and obtaining the utmost particle

TABLE 1 | Materials used in this study and their source and specifications.

Chemical name	Molecular formula	Purity	Supplier
Polyethyleneimine (branched)	CH ₃ N(CH ₂ CH ₂ OH) ₂	>99%	Sigma-Aldrich
Hydrochloric acid	HCl	37%	Merck
Potassium permanganate	KMnO ₄	>99%	Sigma-Aldrich
Hydrogen peroxide	H ₂ O ₂	30%	Sigma-Aldrich
Sodium nitrate	NaNO ₃	>99%	Sigma Aldrich
Sulfuric acid	H ₂ SO ₄	>99%	Sigma Aldrich

size of 0.1 mm, the obtained powder was transferred to a beaker (250 ml) accompanied by addition of 10 ml of distilled water, 10 ml of HNO₃ and 25 ml of HClO₄ and 10 ml of HF. Then, the solution was cooled right down to ambient temperature after heating at 120°C for 3 h. Heating and cooling process was repeated while 25 ml of HCl was added to the solution. A larger beaker (500 ml) containing 300 ml distilled water was prepared and top of the solvent of the former beaker was transferred into it. Afterward, the NH₃ solution was added dropwise to separate the elements from the mixture. After collecting, washing and drying the solid part, a solution containing sufficient level of nitric acid was prepared.

Finally, 10 g gelatin was included with a 100 ml deionized water container to be able to synthesize metal oxide nanoparticles. The container was heated at 80°C, while the solution prepared in the earlier stage was added into the container until obtaining a mild brown color. The ultimate product was calcined at 500°C for 4 h to acquire metal oxide nanoparticles.

Preparation of PEI-Loaded Metal Oxide Nanoparticles

In order to prepare the PEI functionalized metal oxide nanoparticles, wet impregnation method was employed (Liu J. et al., 2012; Wang W. et al., 2015; Martín et al., 2016). For this specific purpose, PEI (in a desired amount) was dissolved in 20 ml of methanol under stirring for 15 min. Then, 0.5 g of metal oxide nanoparticles were added to the solution. The mixture was continuously stirred at 50°C for 3.5 h, followed closely by sealing at 50°C for 12 h. Afterward, the resultant slurry was dried at 80°C to obtain the amine modified sorbent. The as-prepared sorbent was impregnated with the different mass fraction of PEI (30, 40, 50, 60, and 70 wt.%). The morphology of recovered sorbent was characterized before and after impregnation with PEI. X-ray diffraction (XRD) pattern was performed using Xpert MPD diffractometer. Field emission scanning electron was recorded by a Tuscan MIR3 LM. The thermal stability was examined with TGA (Perkin-Elmer). Finally, FT-IR absorption was employed on a Bruker ISS-88 to verify the sorbent nature.

CO₂ Adsorption and Regeneration Process

CO₂ adsorption measurements of PEI functionalized MMO nanoparticles were performed by TGA (Pyris 1, PerkinElmer TG analyzer, United States) (Lee et al., 2015). In this task, the specified amount (10 mg) of PEI impregnated MMO was placed into an alumina crucible. The temperature was changed from room temperature to 100°C with an interest rate of 5°C/min under a natural N₂ flow (50 ml/min) to eliminate the adsorbed CO₂ and moisture available in the structure. Then, after cooling the sample to the required temperature (25, 40, 65, 70, 90°C), N₂ flow was switched to CO₂ (pure) or CO₂/N₂ (mixture) and any change in the sample weight was simultaneously recorded. To be able to desorption measurements, the gas

flow was switched to N₂ (pure) with a temperature rate of 10°C/min to 110°C.

RESULTS AND DISCUSSION

Characterization of Pristine MMO and PEI Functionalized MMO Recovered From Spent Car Catalytic Converter

FESEM-EDS analysis was performed to study the morphological structure of nanoparticles and verify amounts and types of metals available in the structure of the sorbent. As shown in **Figure 1**, a porous structure has been verified as a result of chemical composition of the coat which will be mainly Al₂O₃ and ZrO₂ nanoparticles. Different size range (9–60 nm) of the cubic crystalline particles is due to the presence of CeO₂, MgO, and ZrO₂ compounds in the structure. The higher degree of oxygen detected in the structure is definitely an indicator of the accessibility of metals within their oxide form that will be desired for amine modification. Aluminum is the absolute most prevalent substance in the structure of as-prepared sorbent, while the automotive catalytic converters are often formed by an alumina-coated ceramic structure to aid the platinum group metals (PGMs) (Jimenez de Aberasturi et al., 2011). The SEM images of PEI modified MMO reveal a retained structure after modification. However, the meso and micro-pores are blocked after functionalization because of the presence of amine groups in the structure. The EDS analysis verifies the clear presence of N atoms in the structure after modification by the amine.

X-ray diffraction (XRD) patterns of nanoparticles show the Bragg's peaks in the product range of 2Theta values between 5° and 90°. The presence of Al₂O₃ and Au particles were completely confirmed in the line with the standard patterns. The sample shows the exact same diffraction peaks with lower intensities after impregnation which indicates the retained structure after modification process, and intensities of the peaks became lower with increasing the PEI contents (Zaman et al., 2010; Strunk et al., 2011; Cortes Vega et al., 2017; **Figure 2**). According to EDS analysis presented in **Figure 1**, The catalyst has a porous structure which could be in association with the chemical composition of the coat (mostly Al₂O₃, ZrO₂). The cubic crystalline particles, which are in the different size ranges between 9 and 60 nm, are assigned to CeO₂, ZrO₂, MgO compounds. The higher amount of Oxygen (42.06 wt%) show that the detected elements such as Al, Au, Ce, Zr, Si, Mg and Ba are available in their oxide form. Because the car catalytic converters are formed by an alumina-coated ceramic structure which supports the PGMs, So, aluminum must be the most prevalent substance in the prepared catalyst.

FT-IR spectroscopy showed two bands at 3600 and 3199 cm⁻¹ which are caused by O-H bonds. As inferred from **Figure 3**, the bands at 2099 and 1652 cm⁻¹ are linked to H-O-H bonds. The peak at 1072 cm⁻¹ is attributed to the Al-O-H (Liu C. et al., 2012). The clear presence of Alumina in the structure is completely

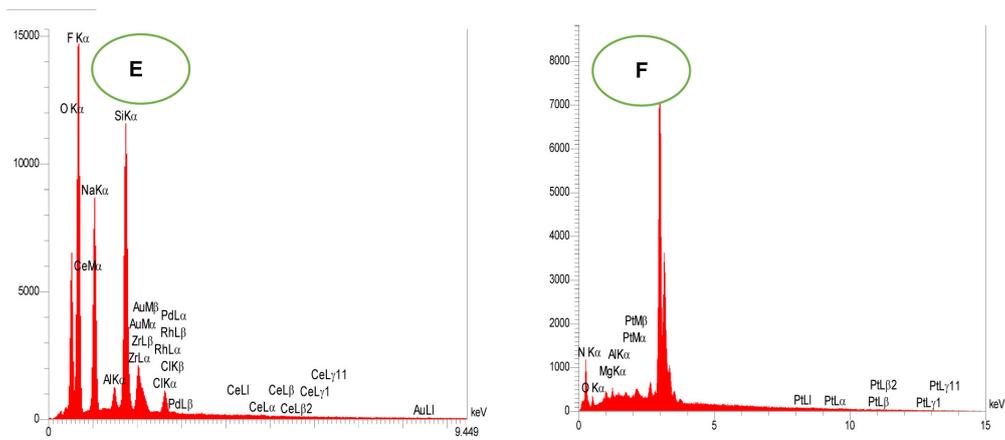
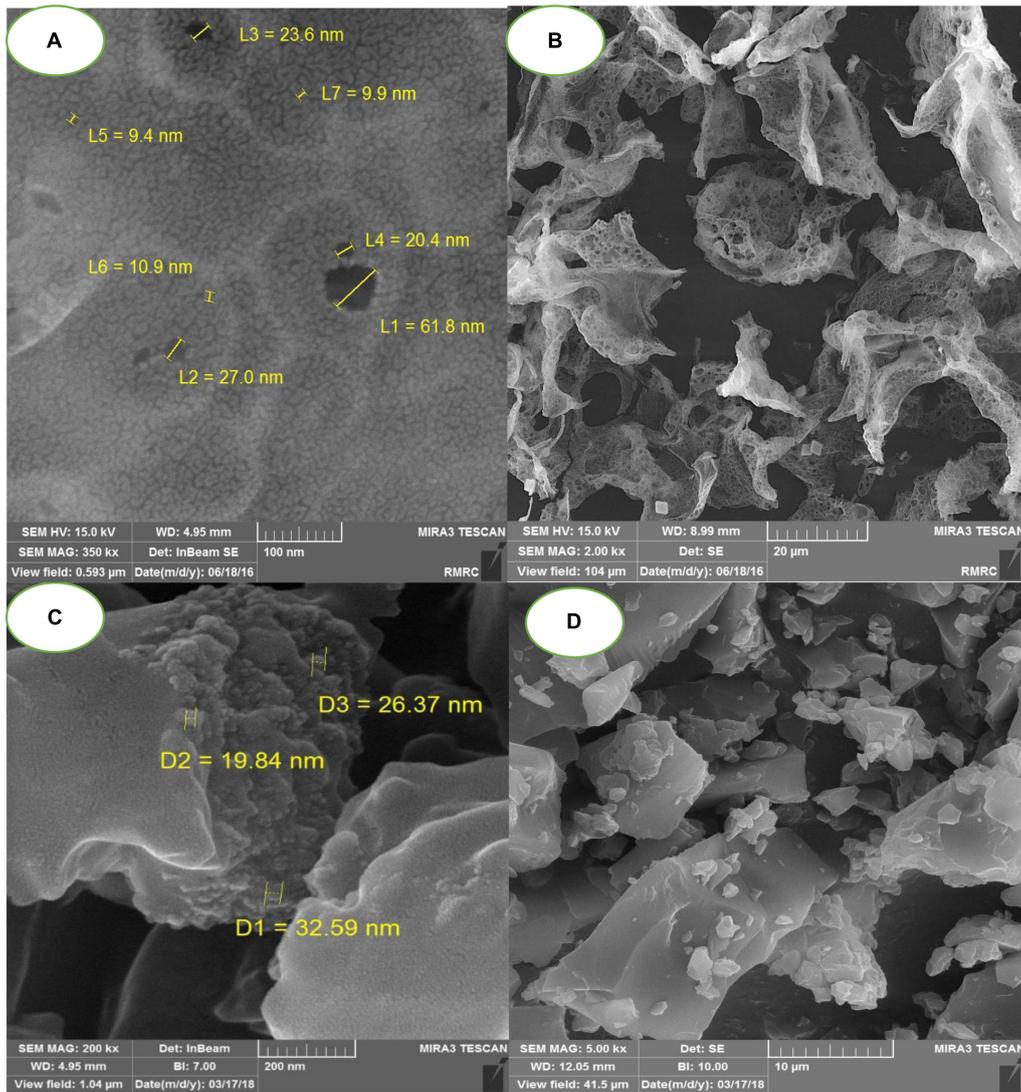
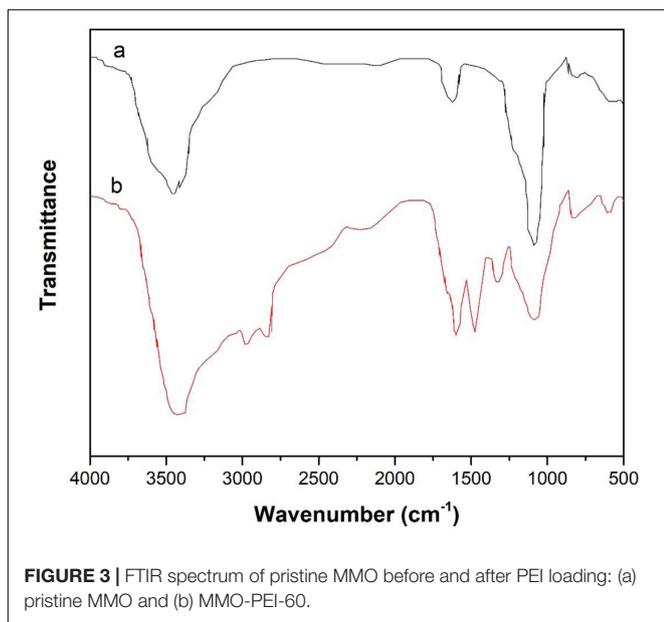
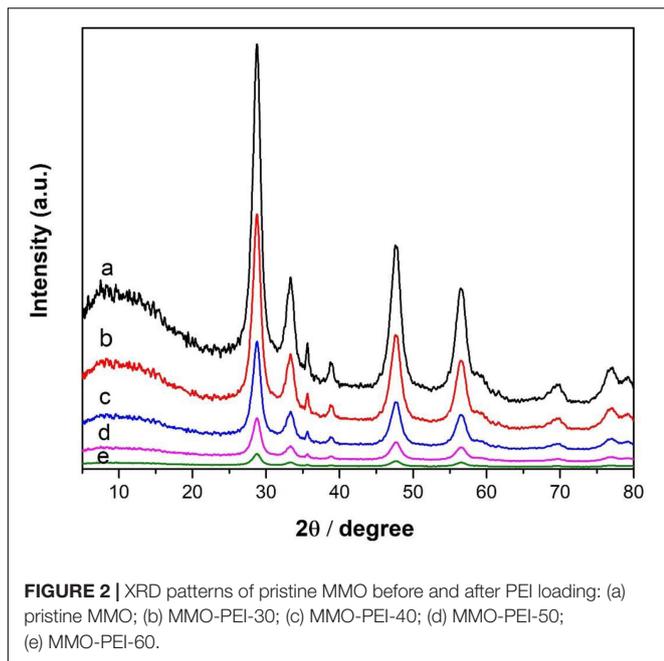
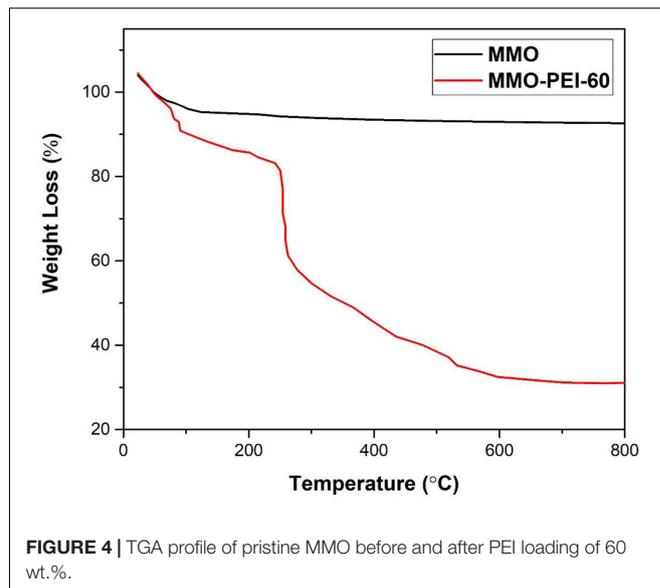


FIGURE 1 | SEM images of (A,B) pristine MMO, (C,D) MMO-PEI-60, EDS analysis of recycled multi-metal oxide prepared from the spent car catalytic converter (E) and EDS analysis of 60 wt.% PEI loading (F).



confirmed by these bands obtained in the FT-IR analysis. Ce-O stretching vibration is verified by bands at 848 and 521 cm^{-1} . The bands round the 1700 cm^{-1} verify the current presence of metal oxides in the structure (Liu C. et al., 2012). The presence of PEI could be observed via FT-IR spectra. There are two important bands after functionalization emerged by amine groups. The absorption peak at 1556 cm^{-1} is attributed to stretching vibration along with symmetric and asymmetric bending vibration of the NH_2 group. The stretching vibration of the CH_2 groups at the absorption band of 2945 cm^{-1} demonstrates the successful loading of PEI which is also verified by literature (Thi Le et al., 2014; Niu et al., 2016; Irani et al., 2018b).



Thermo-gravimetric analyzer profile, which was performed from 40°C to 800°C with a rate of 40°C/min, shows a mass loss (10–15%) peaks around 150°C, which is mainly due to the evaporation of moisture. According to **Figure 4**, TGA profile also shows a mass loss peak around 250 which is associated the decomposition of PEI. So, based on these observations, MMO-PEI tolerates the temperatures up to 250°C, which is desirable for regeneration process at 110°C. The as-prepared sorbent showed an acceptable stability compared to carbon-based materials such as graphene and CNTs. As reported (Irani et al., 2017), MWCNTs/TEPA with TEPA loading of 75 wt.% showed a similar thermal stability in comparison with the novel sorbent prepared in this study. Carbon-based materials are well-known for their high thermal and mechanical stability and the TGA profile confirmed the high thermal stability of the novel sorbent compared with carbon-based materials.

N_2 adsorption/desorption isotherms of MMO was also examined before and following the modification process by PEI. The hysteric loops observed at $0.2 < P/P_0 < 1$ indicates the mesoporous structure. As shown in **Figure 5**, obvious changes are determined after PEI loading as a result of presence of amine groups in the pore channels of MMO nanoparticles. So, decreases in N_2 capacity adsorption confirmed this fact that the pores were gradually filled by PEI molecules resulted in slimmer hysteric loops. According to **Figure 6**, the mesopores were centered at 1 nm. Therefore, increasing the PEI loading contributes to an entire filling in the pores (Samanta et al., 2012; Molavi et al., 2018). The decrease of pore size of MMO after PEI loading was because of the modification of amine groups on MMO. **Table 2** presents the specific surface area and total pore volumes for pristine MMO and functionalized MMOs. As inferred from **Table 2**, the total pore volume of mesopores as well as S_{BET} decreased with increasing the amount of PEI loading. So, impregnation of MMO with PEI triggered covering the micropores and mesopores of MMO with amine groups.

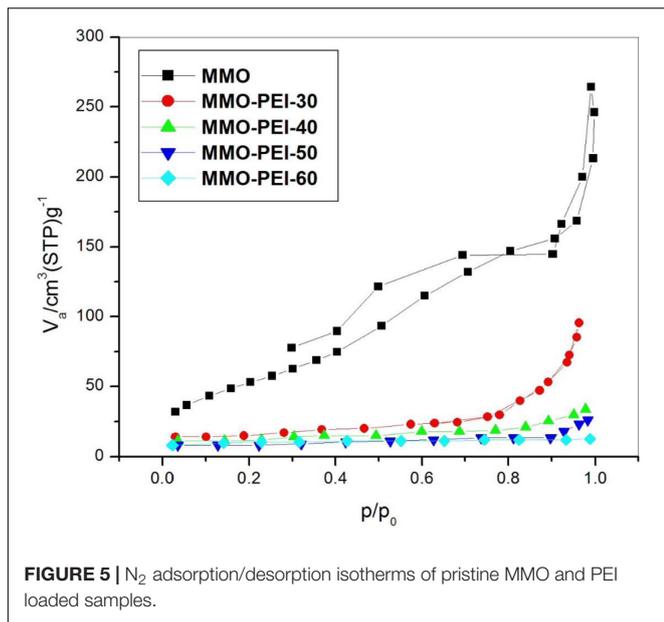


FIGURE 5 | N₂ adsorption/desorption isotherms of pristine MMO and PEI loaded samples.

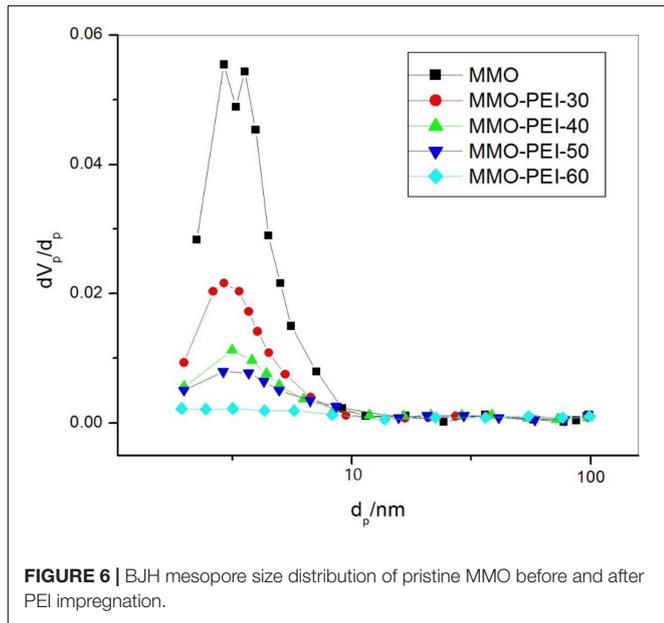


FIGURE 6 | BJH mesopore size distribution of pristine MMO before and after PEI impregnation.

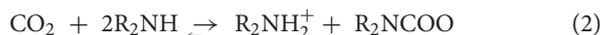
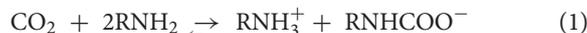
TABLE 2 | Textural properties of pristine MMO and PEI-MMO samples.

Specimens	S _{BET} (m ² /g)	V _{total} (cm ³ /g)	d _{p,peak} (BJH) (nm)
MMO	200	0.357	3.29
MMO-PEI-30	43	0.091	3.08
MMO-PEI-40	17	0.067	3.28
MMO-PEI-50	8	0.041	3.19
MMO-PEI-60	0.7	0.008	3.19

CO₂ Adsorption of MMO-PEI

After impregnation of MMO with amine groups, the modified surface comes with an affinity for acidic gases. CO₂ will react with PEI at first glance of MMO as opposed to inner PEI

(Irani et al., 2015). The adsorption capacity is mainly depended on the accessibility of amine groups on the surface sample to interact with carbon dioxide. More sites were provided after more loadings. However, too much PEI loading agglomerated together resulted in the hindered pores for adsorption. The reactions associated with CO₂ adsorption process are presented as follows.



The outcomes of CO₂ adsorption of modified MMO with various quantities of PEI at 70°C and in CO₂ partial pressure of 100 kPa are shown in Figure 7. Adsorption capacity was improved by increasing the total amount of PEI loading on the MMO. Actually, the interaction between PEI and CO₂ molecules will be through acid-base chemical reaction by increasing the loading of PEI onto MMO surface in accordance with to Eq. 1, 2. The utmost adsorption capacity as a function of time for pristine MMO was just 10.8 mg/(g sorbent). The adsorption capacity of MMO-PEI-30 increased significantly to 55.6 mg/g as a result of amine loading onto the surface of MMO. These observations confirmed the effective capture of CO₂ with amine loading. The adsorption capacity increased with increasing the PEI loading amount due to the presence of more amine sites available on the surface of the MMO (Irani et al., 2016). The maximum adsorption capacities for MMO-PEI-40 and MMO-PEI-50 was 76.3 and 81 mg/g, respectively. On the list of samples, MMO-PEI-60 showed the best CO₂ adsorption capacity. The adsorption capacity with this sample as a function of time was 101.3 mg/g. Further PEI loading generated a reduction in adsorption capacity. For MMO-PEI-70, the adsorption capacity decreased to 66.2 mg/g weighed against

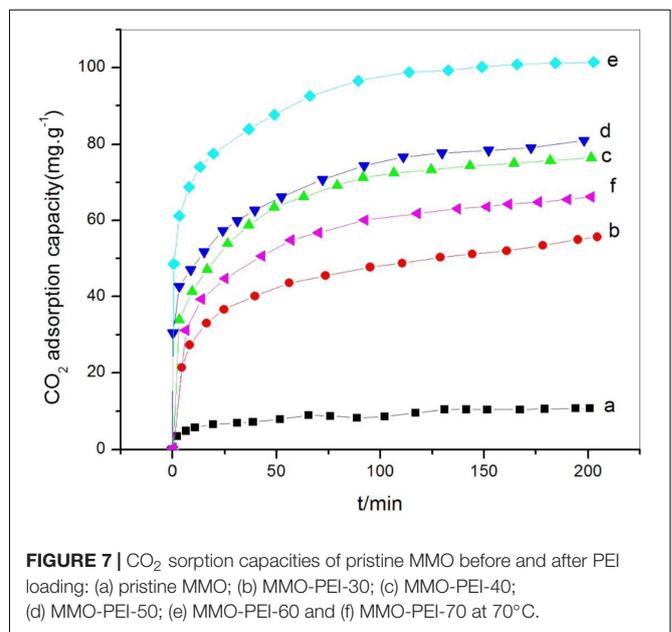


FIGURE 7 | CO₂ sorption capacities of pristine MMO before and after PEI loading: (a) pristine MMO; (b) MMO-PEI-30; (c) MMO-PEI-40; (d) MMO-PEI-50; (e) MMO-PEI-60 and (f) MMO-PEI-70 at 70°C.

MMO-PEI-60. Therefore, further PEI loading will cover the out lining of MMO and avoid the diffusion of CO₂ molecules in to the inner spaces modified MMO with amine groups, and so the accessible sorption sites will undoubtedly be reduced after further functionalization (Irani et al., 2017). Compared to the literature, results showed a high adsorption capacity of the sorbent so that the sample with the optimum performance (MMO-PEI-60) revealed the adsorption capacity of 101.3 mg/g-sorbents (Irani et al., 2017, 2018a).

In amine-based sorbents, the CO₂ adsorption capacity is affected directly by the total amount of amine loading. As shown in **Figure 8**, increasing the PEI loading features a positive effect on the CO₂ sorption. The CO₂ sorption risen up to 101.3 mg/g with increasing the PEI loading from 30 to 60 wt.%. Further PEI loading resulted in a reduced amount of CO₂ sorption capacity. This phenomenon could be linked to the reduced accessible amine sites available on the sorbent surface as a result of amine agglomeration.

Effect of Partial Pressure on CO₂ Adsorption Capacity

Figure 9 shows the adsorption capacity of MMO-PEI-60 at 70°C and in partial pressures of 7, 25, 50, 70, 80, and 90 kPa. Partial pressure had a positive effect on the adsorption capacity of samples. The maximum adsorption capacity was 92.7 mg/g in partial pressure of 90 kPa. Partial pressure has always a direct effect on both absorption and adsorption processes.

Effect of Temperature on CO₂ Adsorption Capacity

The adsorption capacity of MMO-PEI-60 was evaluated at different temperatures and in partial pressure of 100 kPa. As given in **Figure 10**, the adsorption capacity raised with increasing the temperature to 75°C. Increasing temperature

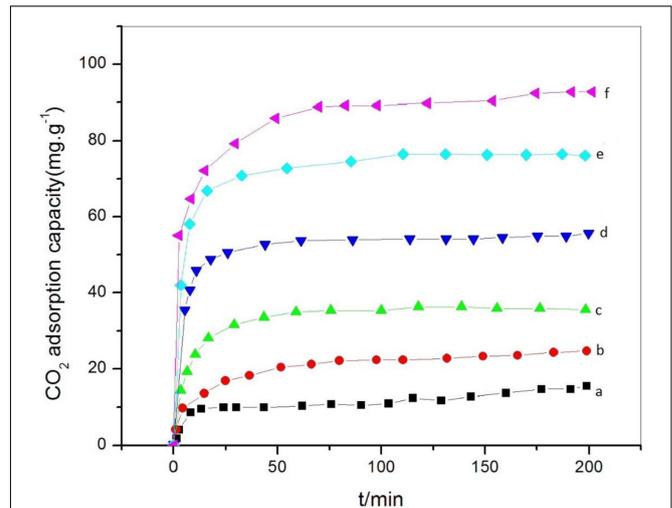


FIGURE 9 | CO₂ adsorption capacity of MMO-PEI-60 at 70°C and in partial pressures of (a) 7; (b) 25; (c) 50; (d) 70; (e) 80 and (f) 90 kPa.

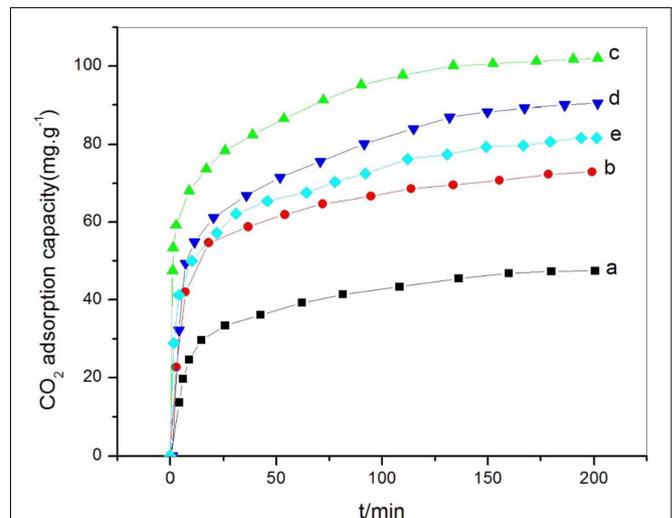


FIGURE 10 | CO₂ adsorption capacity of MMO-PEI-60 at (a) 20; (b) 40; (c) 70; (d) 85 and 100°C.

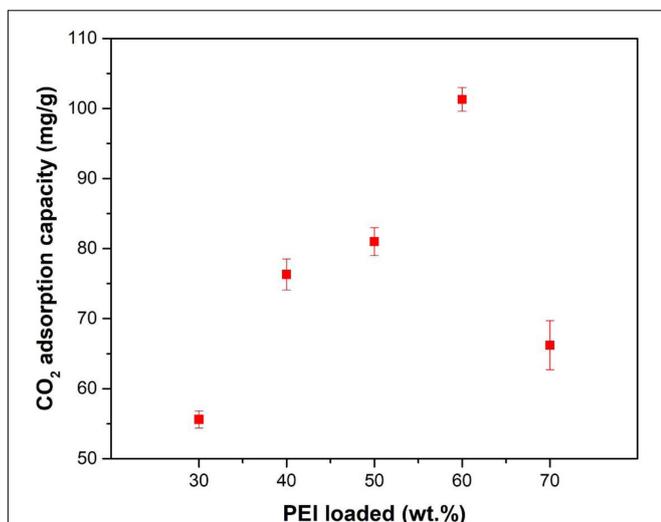


FIGURE 8 | The effect of PEI loading on the CO₂ adsorption capacity at 70°C and in CO₂ partial pressure of 100 kPa.

accelerated the amine molecules motion which led to the enhanced sorption capacity. However, the further increase in temperature triggered a slight decline in adsorption capacity because of the thermodynamic effects. In reality, at higher temperatures, desorption could be the dominant reaction compared to adsorption. CO₂ adsorption is controlled by kinetics at low temperature. Only at that array of temperature, PEI includes a high viscosity and adsorption capacity is reduced by this factor. At higher temperatures, the reaction is principally controlled by thermodynamic factors and active CO₂-affinity sites may be utilized. When the temperature raised up to 70°C, the equilibrium shifted to desorption process and adsorption capacity decreased. Two stage process can be observed for adsorption. The beginning sharp linear adsorption is due to

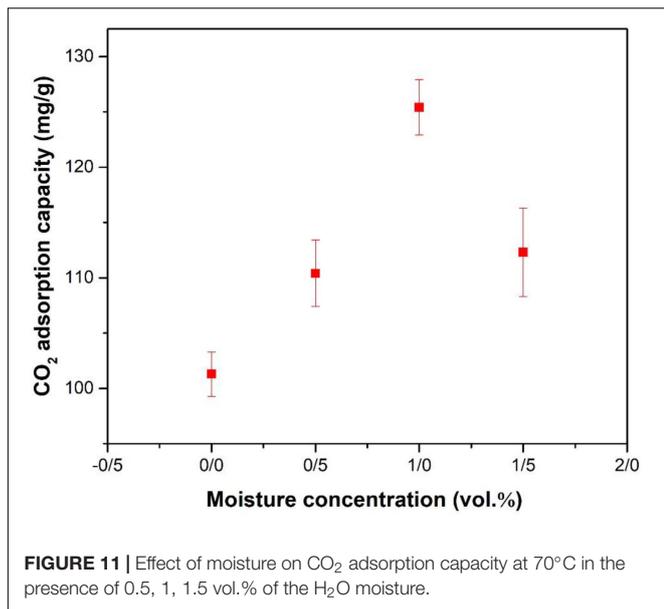
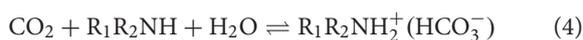
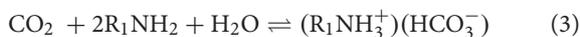


FIGURE 11 | Effect of moisture on CO₂ adsorption capacity at 70°C in the presence of 0.5, 1, 1.5 vol.% of the H₂O moisture.

the surface chemical reaction and the second is attributed to the slow diffusion stage. Therefore, at the beginning stage, the chemical reaction on the sample surface determines the adsorption rate. So, the perfect adsorption temperature for MMO-PEI-60 was 70°C in line with the effect of kinetics and thermodynamics.

Effect of Moisture on the CO₂ Adsorption Capacity

All types of gases typically contain some moisture; so, examination the aftereffect of presence of moisture is crucial for CO₂ adsorption measurement. As shown in **Figure 11**, addition of 1 vol.% resulted in increase in the CO₂ sorption capacity to 125.2 mg/g. Further concentration of moisture caused a lowering of CO₂ sorption capacity. This could be due to the occupying some accessible surface area by water molecules. As previously mentioned, under dry conditions, carbamates are the product of the reaction between amine groups and CO₂ molecule. In the current presence of the moisture, both bicarbonates could be formed when CO₂ molecule reacts with one amine groups (Irani et al., 2015, 2016; Guo et al., 2016). The reactions under wet conditions are presented as follows:



Determining the Selectivity of CO₂ Over N₂

Kinetic diameters for CO₂ and N₂ are 3.3 and 3.64 Å, respectively. However, coulombic forces are present in the interactions between CO₂ and amine groups. CO₂ shows a strong chemisorption and physisorption interactions with polar amine

groups. On the other side, N₂ only interacts via physisorption and intermolecular interactions (van der waals) (Shin et al., 2016). So, Henry’s law selectivity can be calculated through Toth model at low pressure (Bali et al., 2015).

$$Q = Q_{max}A^{(\frac{1}{n})}P(1 + AP)^{(\frac{1}{n})} \quad (5)$$

Where Q presents the gas capacity, Q_{max} is the maximum gas capacity, and A and n are constant values.

Thus, Henry’s constant can be calculated as follows:

$$K = \frac{dN}{dp} = A^{(\frac{1}{n})}Q_{max} \quad (6)$$

So, the adsorption selectivity for x over y is calculated as

$$S_{x,y} = \frac{K_x}{K_y} \quad (7)$$

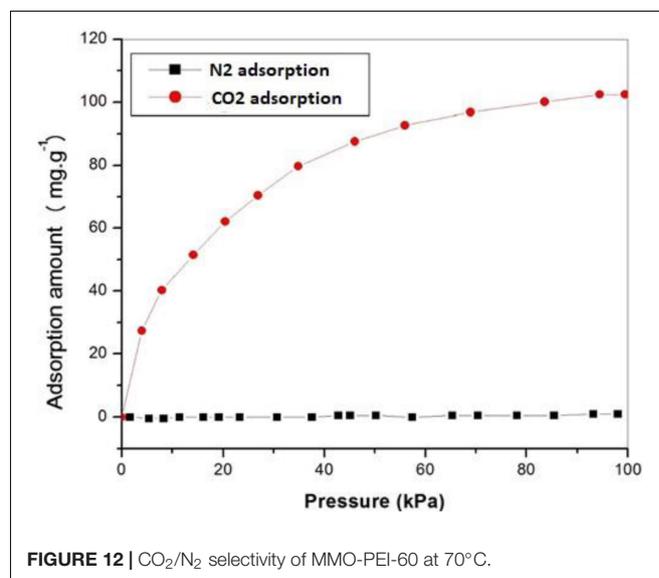


FIGURE 12 | CO₂/N₂ selectivity of MMO-PEI-60 at 70°C.

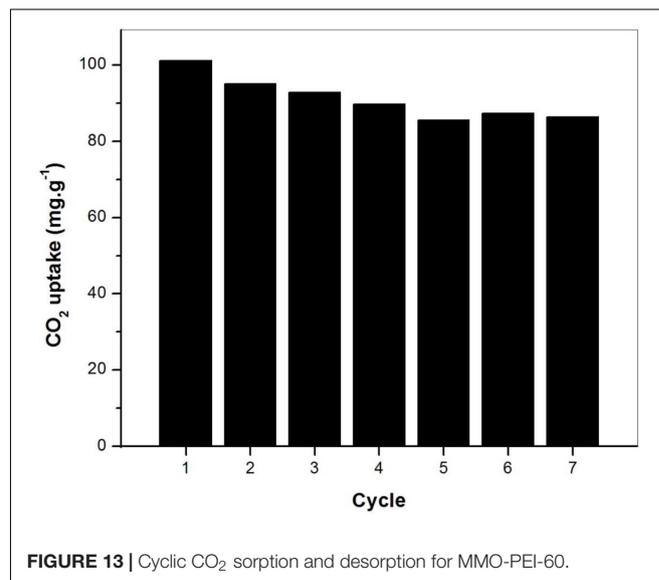


FIGURE 13 | Cyclic CO₂ sorption and desorption for MMO-PEI-60.

The selectivity of MMO-PEI-60 was calculated using the mentioned equations. **Figure 12** shows the CO₂ and N₂ adsorption isotherms of MMO-PEI-60 at 70°C and partial pressure range of 0 to 100 kPa.

The selectivity of MMO-PEI-60 toward CO₂ over N₂ was calculated as high as 50.2. This selectivity value confirms that MMO-PEI has a high affinity for CO₂ because impregnated amine groups lead to an enhancement in the interactions between CO₂ gases and the impregnated sorbents.

Regenability of the Sorbent

Cyclic CO₂ adsorption was performed at 70°C and partial pressure of 100 kPa to investigate the regeneration properties of the MMO-PEI-60. The regeneration process plays a critical role in the case of lowering the cost of power plants (Lee et al., 2016; Ntiamoah et al., 2016). The results of the regeneration measurements for MMO-PEI-60 over 7 cycles are shown in **Figure 13**. These results indicate that the MMO-PEI sorbents show a good stability and regeneration.

CONCLUSION

An inexpensive and recovered sorbent for CO₂ adsorption has been prepared from catalytic converters of spent exhaust systems and functionalized with polyethyleneimine through wet impregnation method. The thermal stability of sorbent and functionalized samples showed that the modified multi-metal oxides/PEI are stable below 250°C. The sorbent was treated by acid to increase the surface area. The PEI loading on the sorbent was optimized as 60 wt.% with maximum CO₂ sorption capacity

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of 101.3 mg (g sorbent)⁻¹ at 70°C and partial pressure of 100 kPa. Higher adsorption capacity was achieved by increasing the CO₂ partial pressure. The CO₂ adsorption capacity increased to 125.2 in the presence of 1 vol.% of the H₂O moisture. The selectivity of MMO-PEI-60 toward CO₂ over N₂ was calculated as high as 50.2. The regeneration measurements for MMO-PEI-60 over 7 cycles confirmed a good regenerability for modified MMO/PEI sorbent.

DATA AVAILABILITY STATEMENT

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation.

AUTHOR CONTRIBUTIONS

All authors listed have made a substantial, direct and intellectual contribution to the work, and approved it for publication.

SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fenrg.2020.00196/full#supplementary-material>

FIGURE S1 | EDS analysis of recycled multi-metal oxide prepared from the spent car catalytic converter.

FIGURE S2 | EDS analysis of 60 wt.% PEI loading.

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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