## B. TECH. PROJECT REPORT On MgO@SiO2 based Materials for CO2 Adsorption

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DISCIPLINE OF METALLURGY ENGINEERING AND MATERIALS SCIENCE INDIAN INSTITUTE OF TECHNOLOGY INDORE December 2019

# MgO@SiO2 based Materials for CO2 Adsorption

## A PROJECT REPORT

Submitted in partial fulfilment of the requirements for the award of the degrees

## of BACHELOR OF TECHNOLOGY in METALLURGY ENGINEERING AND MATERIALS SCIENCE

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> *Guided by:* **Dr. Dhirendra Kumar Rai**



## DISCIPLINE OF METALLURGY ENGINEERING AND MATERIALS SCIENCE INDIAN INSTITUTE OF TECHNOLOGY INDORE December 2019

## **CANDIDATE'S DECLARATION**

We hereby declare that the project entitled "MgO@SiO<sub>2</sub> based materials for CO<sub>2</sub> adsorption" submitted in partial fulfilment for the award of the degree of Bachelor of Technology in 'Discipline of Metallurgy Engineering and Materials science' completed under the supervision of Dr. Dhirendra Kumar Rai, Assistant Professor, Discipline of Metallurgy Engineering and Materials Science, Indian Institute of Technology Indore is an authentic work.

Further, we declare that we have not submitted this work for the award of any other degree elsewhere.

#### Signature and name of the students with date

## **CERTIFICATE by BTP Guide(s)**

It is certified that the above statement made by the students is correct to the best of my/our knowledge.

#### Signature of BTP Guide with date and their designation

## **Preface**

This report on "MgO@SiO<sub>2</sub> based materials for CO<sub>2</sub> adsorption" is prepared under the supervision of Dr. Dhirendra Kumar Rai, Discipline of Metallurgy Engineering and Material Sciences, Indian Institute of Technology Indore.

Increasing CO<sub>2</sub> levels is a topic that holds the attention of the world. Polyethyleneimine (PEI) is a weak basic aliphatic polymer with repeating units composed of amine groups, is functionalized with MgO@m-SiO<sub>2</sub>. These amines have active centres to absorb and interact with CO<sub>2</sub>. For CO<sub>2</sub> capture, linear and branched polyethyleneimine both have been used and are frequently impregnated over porous materials like MgO and SiO<sub>2</sub> to get maximum CO<sub>2</sub> adsorption. The synthesis and performance towards CO<sub>2</sub> capture application have been investigated for three materials; MgO-PEI, m-SiO<sub>2</sub>-PEI and MgO@m-SiO<sub>2</sub>-PEI.

Through this report, we have tried to give a comprehensive study of CO<sub>2</sub> adsorption of MgO-PEI, m-SiO<sub>2</sub>-PEI and MgO@m-SiO<sub>2</sub>-PEI. We have tried to the best of our abilities and knowledge to explain the content in a lucid manner

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#### **Abstract**

In this study, porous and hierarchical polyethyleneimine (PEI) functionalized MgO@m-SiO<sub>2</sub> microspheres have been studied for CO<sub>2</sub> capture application. In this regard, the performance of the overall material has been investigated for three materials; (i) MgO-PEI, (ii) mesoporous SiO<sub>2</sub> (m-SiO<sub>2</sub>)-PEI and (iii) MgO@m-SiO<sub>2</sub>-PEI, towards CO<sub>2</sub> capture application. A simple precipitation-ageing-calcination method, the Stober method and a straightforward grinding followed by heat treatment is used to synthesise MgO, m-SiO<sub>2</sub>, MgO@m-SiO<sub>2</sub> respectively. MgO-PEI, m-SiO<sub>2</sub>-PEI and MgO@m-SiO<sub>2</sub>-PEI are prepared by wet impregnation method. The powder X-ray diffraction (PXRD), field emission scanning electron microscopy (FESEM), and N<sub>2</sub> adsorption-desorption isotherm characterisation techniques have been investigated to conform the material's synthesis. It has been observed that the MgO, m-SiO<sub>2</sub> and MgO@m-SiO<sub>2</sub> has a porous hierarchical structure, agglomerated mesoporous structure and porous clustered structures respectively. The obtained BET specific surface area of MgO, m-SiO<sub>2</sub> and MgO@SiO<sub>2</sub> is 119.5 m<sup>2</sup>/g, 1152.9 m<sup>2</sup>/g and 96.1 m<sup>2</sup>/g respectively. After the PEI functionalization on MgO, m-SiO<sub>2</sub> and MgO@m-SiO<sub>2</sub>, the BET surface area gets decreased substantially due to the pore filling effect caused by PEI. In order to perform a comparative performance analysis, CO<sub>2</sub> adsorption study was also performed for MgO, m-SiO<sub>2</sub> and MgO@SiO<sub>2</sub> separately. The enhanced CO<sub>2</sub> adsorption capacity of 0.9 mmol/g at 298 K for MgO-PEI, 0.8 mmol/g at 298 K for m-SiO<sub>2</sub>-PEI was observed and 0.3 mmol/g at 298 K for MgO@m-SiO<sub>2</sub>-PEI, which is 2.1 times higher than the MgO, 1.5 times lesser than SiO<sub>2</sub> and 1.1 times higher than MgO@m-SiO<sub>2</sub>. Investigations suggest that the use of PEI causes improvement in MgO but not in m-SiO<sub>2</sub>, and MgO@m-SiO<sub>2</sub> on the CO<sub>2</sub> adsorption capacity.

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## **Chapter 1: Introduction**

The continuous surge in the emissions of greenhouse gases which include carbon dioxide, methane, nitrogen oxide is a rising concern. These greenhouse gases absorb the sun's energy and keep the earth warm. However, the increase of these gases, especially carbon dioxide, creates an excess of greenhouse gases that trap additional heat. This trapped heat leads to severe environmental issues such as global warming, melting ice caps, climate change and rising ocean levels. The drastic rise in carbon dioxide emissions has been linked with the increasing dependence on fossil fuels for energy production. The projections of the International Energy Agency show that we will be overly dependent on fossil fuels for energy until the year 2030<sup>[1]</sup>. There is a severe need for strategies to reduce carbon dioxide content in the global atmosphere.



Image courtesy: https://ourworldindata.org/co2-and-other-greenhouse-gas-emissions **Figure 1**: Annual CO<sub>2</sub> emissions by world region

There are many  $CO_2$  capture systems, such as solvent-based chemisorption, solid-based physisorption, carbonate looping and oxyfuel process. Such traditional technologies for largescale capture have been commercially accessible for over 50 years. They are focused on the separation of  $CO_2$  from flue gases by the use of cryogenic coolers and amine scrubbers, which are energy-intensive and are not cost-effective for carbon emissions reduction<sup>[2]</sup>. The physisorbents have the advantage of low energy consumption for regeneration, but their drawback is their low  $CO_2/N_2$  selectivity, which has limited their applications. An exciting approach toward improving sorbent's  $CO_2$  selectivity is to tune the ultra-micropore size to improve adsorption potential energy meticulously. An ideal sorbent should have a hierarchical structure, in which the ultra-micropores will present high selectivity and capacity, while the mesopores are essential for letting fast gas diffusion<sup>[3]</sup>.

Metal oxides are likely alternatives for CO<sub>2</sub> adsorbents, and they have excellent potential in the future due to their easy accessibility and favourable thermodynamic characteristics<sup>[4]</sup>. MgO is a non-toxic, environmentally friendly white solid mineral that occurs naturally. The adsorption capacity and higher surface reactivity make it an appropriate adsorbent for cations and anions from aqueous solution due to its favourable electrostatic attractive mechanisms<sup>[5]</sup>. MgO has been commonly explored for CO<sub>2</sub> capture and has been recognised as one of the most promising adsorbents for CO<sub>2</sub> adsorption together with CaO<sup>[4]</sup>. A notable benefit of these materials is the possibility of integrating them into hybrid systems such as SiO<sub>2</sub>(*a*)TiO<sub>2</sub>, MgO(*a*)SiO<sub>2</sub> or of modifying their surfaces with selected compounds that increase their adhesion to a particular group of pollutants<sup>[6]</sup>. The advancement of MgO@SiO<sub>2</sub> materials for CO<sub>2</sub> sorption is advantageous because MgO has shown high capacity and affinity toward CO<sub>2</sub> at ambient, and flue gas conditions, which after merging with SiO<sub>2</sub> can be considerably increased due to the high active surface area and well-developed porosity of the composite sorbents<sup>[7]</sup>. MgO@SiO<sub>2</sub> type of nanocomposites has drawn much attention because of its potential in the modification and protection of the core particles with suitable shell materials to achieve suitable performance. Nowadays, considerable efforts have been centred on the assembly of core-shell nanocomposites with mesoporous silica<sup>[8]</sup>.

Polyethyleneimine (PEI) is a weakly basic aliphatic polymer with repeating units comprised of one amine group and two carbon aliphatic CH<sub>2</sub>CH<sub>2</sub> spacers. Linear polyethyleneimines contain all secondary amines, in contradiction to branched PEIs which include primary, secondary and tertiary amino groups. These are widely used in various products like adhesives, detergents, water-treatment agents, and cosmetics<sup>[9]</sup>. For sufficient encapsulating material, a stable matrix with high surface matrix area and few organic amine radicals are frequently needed to take full use of the designed adsorbent. The matrix for CO<sub>2</sub> encapsulating plays the role of backer for the amine species to keep the products in a stable and solid-state. This property helps to facilitate transportation, storage, reduce corrosivity and volatility. The amines are the active centres to absorb and interact with CO<sub>2</sub>. For CO<sub>2</sub> capture, linear and branched polyethyleneimine both have been used and are frequently impregnated over porous materials like MgO and SiO<sub>2</sub> to get maximum CO<sub>2</sub> adsorption. Song *et al.* reported

the preparation of m-SiO<sub>2</sub> impregnated with PEI for CO<sub>2</sub> capture and CO<sub>2</sub> adsorption capacity as high as 3 mmol g<sup>-1</sup> was obtained at 75 °C<sup>[10]</sup>. They also found that the use of m-SiO<sub>2</sub> had a synergetic effect on the adsorption of CO<sub>2</sub> by PEI. After loading the PEI into the m-SiO<sub>2</sub> pore channels, the adsorption capacity of the m-SiO<sub>2</sub> was increased substantially.

In this experiment, we have used PXRD, SEM, FTIR, TGA, N2 isotherm and CO2 isotherm analysis methods to characterize our samples. X-ray diffraction is the elastic scattering of x-ray photons by atoms in a periodic lattice. XRD is based on the principle of Braggs law. The rays diffract through the crystal and into a detector, and the beam and detector are rotated through a range of angles XRD can be used to identify single crystals and to reveal the structure of single crystals. A crystalline sample is placed in the path of an X-ray beam. Fourier Transform Infrared Spectroscopy (FTIR) is an analytical technique used to identify organic, polymeric and in some cases, inorganic materials. FTIR Analysis measures the range of wavelengths in the infrared region that is adsorbed by a material. Scanning Electron Microscopy (SEM) is based on the principle that the accelerated electrons in an SEM carry significant amounts of kinetic energy and this energy is dissipated as a variety of signals produced by electron-sample interactions when the incident electrons are decelerated in the solid sample. Thermogravimetric Analysis (TGA) is performed by gradually raising the temperature of a sample in a furnace as its weight is measured on an analytic balance that remains outside of the furnace. In TGA, mass loss is observed, if a thermal event involves loss of volatile compounds. Brunauer-Emmett-Teller (BET) theory aims to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for a critical analysis technique for the measurement of the specific surface area of the materials.

## **Chapter 2: Experimental Section**

#### 2.1 Materials Used

Sodium carbonate, Magnesium chloride hexahydrate, Cetrimonium bromide (CTAB), Tetraethyl orthosilicate (TEOS), Polyethyleneimine, Aqueous ammonia (35%) are the materials used. Deionized water and Methanol are used as solvents.

#### 2.2 Synthesis of MgO hierarchical microspheres



Figure 2: Synthesis of MgO microspheres

MgO microspheres synthesised by the precipitation-ageing-calcination method. Initially, 12.5 mL of 1M Na<sub>2</sub>CO<sub>3</sub> dissolved in 12.5 mL of deionised water in a conical flask and subsequently 12.5 mL of 1M MgCl<sub>2</sub>.  $6H_2O$  dissolved in 12.5 mL of deionised water in another conical flask. Ultrasonication was carried out for 2 min to dissolve the material in deionised water. Formation of white precipitate occurs after adding 12.5 mL of 1M Na<sub>2</sub>CO<sub>3</sub> solution dropwise to the 2.5 mL of 1M MgCl<sub>2</sub>. $6H_2O$  solution at a flow rate of 2 drops per second. Then it is left to ageing for 2 h at 80 °C. After that, the centrifuge machine is used to wash the solution with deionised water for four times at 4000 rpm for 5 min. After centrifuge, the white material is transferred to a quartz tube and put in the electric-arc furnace for calcination at 500 °C for 5 h<sup>[11]</sup>.

#### 2.3 Synthesis of MgO-PEI

Wet impregnation method is used to prepare MgO-PEI. In this process, 0.1 g of PEI-600 (600 is the molecular weight of PEI) is added to the 3 mL of methanol in a beaker. Magnetic stirring is done for 2 h at 500 rpm at 40 °C. Afterwards, 0.2 g of MgO is added to the solution and stirred for 4 h at 500 rpm speed at 40 °C. The obtained product is dried for 12 h at 80 °C and then washed it with methanol through centrifuge for 3 times at 5000 rpm for 5 min. Then again, it is dried at 80°C for 12 h<sup>[12]</sup>.



Figure 3: Synthesis of MgO-PEI

#### 2.4 Synthesis of Mesoporous SiO<sub>2</sub>

The Stober method is used to prepare mesoporous  $SiO_2$  (m-SiO<sub>2</sub>). In this method, 0.88 grams of cetyl trimethyl ammonium bromide (CTAB) is dissolved in a mixture of 20 ml of deionised water and 10 ml of 35% aqueous ammonia at 35 °C. After complete dispersion of CTAB, 4 mL of Tetraethyl orthosilicate (TEOS) is added slowly to the solution under constant stirring. The mixture is stirred for 3 h at 400-500 RPM, and the gel formed after stirring is aged in a closed container at room temperature for 24 hours. The obtained product was washed through centrifuge seven times at 4000 rpm for 5 m and air-dried for 12 h. The obtained material is calcined at 550 °C for 6 h<sup>[13]</sup>.



Figure 4: Synthesis of mesoporous SiO<sub>2</sub>

#### 2.5 Synthesis of m-SiO<sub>2</sub>-PEI

Wet impregnation method is used to prepare m-SiO<sub>2</sub>-PEI. In this process, 0.1 g of PEI-600 is added to the 3 mL of methanol in a beaker. Magnetic stirring is done for 2 h at 500 rpm at 40 °C. Afterwards, 0.2 g of m-SiO<sub>2</sub> is added to the solution and stirred for 4 h at 500 rpm at 40 °C. The obtained product is dried for 12 h at 80 °C and then washed it with methanol through centrifuge for 3 times at 5000 rpm for 5 min. Then again, it is dried at 80 °C for 12 h<sup>[12]</sup>.



Figure 5: Synthesis of m-SiO<sub>2</sub>-PEI

#### 2.6 Synthesis of MgO@m-SiO<sub>2</sub>

MgO@m-SiO<sub>2</sub> is prepared by straightforward grinding method followed by calcination. In this process, an agate mortar is used for grinding 0.2 g of MgO and 0.1 gr of m-SiO<sub>2</sub> for 30 minutes. The obtained product is placed in the furnace and is set at 550 °C for 10



Figure 6: Synthesis of MgO@m-SiO<sub>2</sub>

#### 2.7 Synthesis of MgO@m-SiO<sub>2</sub>-PEI

Wet impregnation method is used to prepare MgO@m-SiO<sub>2</sub>-PEI. In this process, 0.1 grams of PEI-600 is added to the 3 mL of methanol in a beaker. Magnetic stirring is done for 2 h at 500 rpm at 40 °C. Afterwards, 0.2 g of MgO@m-SiO<sub>2</sub> is added to the solution and stirred for 4 hours at 500 rpm speed at 40 °C. The obtained product is dried for 12 h at 80 °C and then washed it with methanol with a centrifuge for 3 times at 5000 rpm for 5 min. Then again, it is dried at 80°C for 12 h<sup>[12]</sup>.



Figure 7: Synthesis of MgO@m-SiO<sub>2</sub>-PEI

#### **Chapter 3: Result and Discussion**

#### **3.1 Powder X-ray Diffraction Studies**

#### 3.1.1 PXRD MgO and MgO-PEI

The choice of carbonate precursor for the precipitation of MgO has significant role in the crystallinity and structure of the products. To study the effect of carbonate precursor, we used Na<sub>2</sub>CO<sub>3</sub>, LiCO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> for MgO preparation. The XRD pattern of the same as shown in *Figure 8a, 9a, and 9b*.

The MgO was synthesised by a simple precipitation-ageing-calcination method. The XRD image *Figure 8b* shows reflections at around 38°, 43°, 63°, 74° and 78° these are assigned to (111), (200), (220), (311) and (222) planes respectively<sup>[15]</sup>. The peak at 43° is attributed to characteristics peaks of MgO. Thus, PXRD confirms the presence of crystalline MgO.



Figure 8: (a) PXRD of MgO prepared from Na<sub>2</sub>CO<sub>3</sub>, (b) PXRD spectra of MgO-PEI

In *Figure 8a*, The reflections of (111), (200), (220), (311) and (222) are of the mesoporous MgO. The sharp peak (*Figure 8b*) at 30° is occurring due to an impurity or an instrumentation error. The initial curves in the graph are occurring because of the presence of PEI. It confirms the presence of MgO in MgO-PEI<sup>[15][16]</sup>.



Figure 9: (a) PXRD of MgO prepared from K<sub>2</sub>CO<sub>3</sub> and (b) Li<sub>2</sub>CO<sub>3</sub>

Moreover, MgO prepared from LiCO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> also shows the characteristics peak of MgO at 43 °, however, after proper washing of MgO precipitate shows impurity peaks of K<sup>+</sup> and Li<sup>+</sup> in the XRD spectra. These impurities predominantly affect the crystallinity of the MgO. From the XRD results, it can be concluded that the MgO prepared from Na<sub>2</sub>CO<sub>3</sub> has better crystallinity than others. Thus, the further studies are carried out using MgO prepared from Na<sub>2</sub>CO<sub>3</sub>. The XRD characterisation of these MgO gives us graphs which contain different peaks which are not of MgO but of the salts formed while preparing MgO, and these are KCl and LiCl. The peaks of LiCl are more prominent because the salt LiCl is very fine and in the process, washing the precipitate using a centrifuge, the salt did not wash off thoroughly that is why there are more peaks of LiCl in the MgO prepared from Li<sub>2</sub>CO<sub>3</sub> (*Figure 9b*).

#### 3.1.2 PXRD of m-SiO<sub>2</sub>

*Figure 10a* shows the PXRD spectra of mesoporous  $SiO_2$ . The steep and low-angle (100) reflection peak show the characteristic of typical mesoporous structures. The relatively weak peaks at the (110) and (200) confirm the highly ordered mesostructures of the silica host<sup>[17][18]</sup>.



Figure 10: PXRD of mesoporous Silica (m-SiO<sub>2</sub>)

#### 3.1.5 PXRD of MgO@m-SiO2 and MgO@m-SiO2-PEI

In *Figure 11a*, the initial curve in the XRD is the characteristic peak of amorphous  $SiO_2^{[19]}$ , the sharp peak at 30° is occulting due to unknown impurity or the instrumentation error and the subsequent peaks of (111), (200), (220), (311) and (222) are of crystalline MgO peaks. Thus, it confirms the formation of MgO@SiO<sub>2</sub>.

The high intense peaks (111), (200), (220), (311) and (222) in the *Figure 11b* are of crystalline MgO and the initial broad curve is of amorphous PEI and  $SiO_2^{[16]}$ . So, We can say that the material is MgO@m-SiO<sub>2</sub>-PEI.



Figure 11: (a) PXRD characterization of MgO@m-SiO2, and (b) MgO@m-SiO2-PEI

#### **3.2 Fourier-Transform Infrared Spectroscopy**

#### 3.2.1 FTIR of MgO and MgO-PEI

A band at around 433 cm<sup>-1</sup> is assigned to the Magnesium-Oxygen bending vibration. Near 1381 cm<sup>-1</sup> are due to C=O stretching frequency shows the presence of the aromatic ring. These peaks indicate us that this material is MgO (*Figure 12a*). A large, broad band at around 3293 cm<sup>-1</sup> is assigned to the Nitrogen-Oxygen bending vibration. Another one at around 2829 cm<sup>-1</sup> is attributed to stretching frequency of C-H stretch, a small band near 1111 cm<sup>-1</sup> are due to C-N, and another sharp band near 1460 cm<sup>-1</sup> are due to C-H bending frequency. Finally at 433 cm<sup>-1</sup> is due to Mg-O. These peaks indicate us that this material is MgO-PEI (*Figure12b*).



Figure 12: (a) FTIR spectra of MgO, and (b) MgO-PEI

#### 3.2.2 FTIR of m-SiO<sub>2</sub> and m-SiO<sub>2</sub>-PEI

A peak band at around 1052 cm<sup>-1</sup> is attributed to the Si-O-Si bond frequency. Another one at around 447 cm<sup>-1</sup> is due to Si-O bond vibrations. These peaks indicate us that this material is SiO<sub>2</sub> (*Figure 13a*). A large, broad band at around 3285 cm<sup>-1</sup> is assigned to the N-H bending vibration. Another one at around 2833 cm<sup>-1</sup> is attributed to stretching frequency of C-H stretch, and another sharp band near 1460 cm<sup>-1</sup> are due to C-H bending frequency. At 447 cm<sup>-1</sup> is due to Si-O and a high steep peak at 1039 cm-1 is of Si-O-Si. These peaks indicate us that this material is m-SiO<sub>2</sub>-PEI (*Figure 13b*).



Figure 13: (a) FTIR spectra of SiO<sub>2</sub>, and (b) SiO<sub>2</sub>-PEI

#### 3.2.3 FTIR of MgO@m-SiO<sub>2</sub>

A peak band at around 1052 cm<sup>-1</sup> is attributed to the Si-O-Si bond frequency. Another one at around 463 cm<sup>-1</sup> is due to Mg-O bond vibrations. These peaks indicate us that this material is MgO@m-SiO<sub>2</sub> (*Figure 14a*). A large, broad band at around 3288 cm<sup>-1</sup> is assigned to the N-H bending vibration. Another one at around 2833 cm<sup>-1</sup> is attributed to stretching frequency of C-H stretch. A band at 1584 cm<sup>-1</sup> is due to C-H bending frequency. A long and sharp peak at 1047 cm<sup>-1</sup> is due to O-Si-O and a peak at 451 cm<sup>-1</sup> is of Mg-O. These peaks indicate us that this material is MgO@m-SiO<sub>2</sub>-PEI (*Figure 14b*).



Figure 14: (a) FTIR of MgO@m-SiO<sub>2</sub>, and (b) MgO@m-SiO<sub>2</sub>-PEI

## **3.3 Scanning Electron Microscopy**

#### 3.3.1 SEM of MgO

The SEM images of MgO show us a porous and uniform micro spherical morphology with the sphere diameter of around  $8.1 - 26.8 \mu m$ . A large number of nanosheets are observed in each MgO microsphere, implying each microsphere is made up of a vast number of nanosheets (*Figure 15*). Mesopores with a small size of about 163.3  $\mu m$  can be observed. From the data collected from EDX (*Figure 16*), we can see that the material contains Magnesium, Oxygen and few traces of Gold. We are detecting gold because we have coated the sample with gold before putting it in the SEM machine. Therefore, we can say that this material is MgO.



Figure 15: [a,b,c] SEM images of MgO microspheres prepared from Na<sub>2</sub>CO<sub>3</sub> [c] is the magnified image of [b]



Figure 16: EDX graph of MgO

#### 3.3.2 SEM of MgO-PEI

The SEM images of MgO-PEI (*Figure 17*) shows us a group of clustered particles of MgO-PEI, these clusters have a size approximately 51.9  $\mu$ m, and the pore gaps in these clusters have approximately 1.22  $\mu$ m(*Figure 17*). The particles got agglomerated because of PEI added in. From the data collected from EDX (*Figure 18*), we can see that the material contains Magnesium, Oxygen, Carbon, Nitrogen and few traces of Gold. We are detecting gold because we have coated the sample with gold before putting it in the SEM machine. The traces of Carbon and Nitrogen can prove that the material has some organic substance in it. Therefore, we can say that this material is MgO-PEI.



Figure 17: [a,b,c] SEM images of MgO-PEI [c] is the magnified image of [b]



Figure 18: EDX graph of MgO-PEI

#### 3.3.3 SEM of m-SiO<sub>2</sub>

The SEM image of mesoporous  $SiO_2$  show us an agglomerated mesoporous spheres like particles sitting on top of each other and each sphere having a diameter of around 0.4 - 0.7  $\mu$ m (*Figure 19*). From the data collected from EDX (*Figure 20*), we can see that the material contains Magnesium, Oxygen and few traces of Gold. We are detecting gold because we have coated the sample with gold before putting it in the SEM machine. Therefore, we can say that this material is m-SiO<sub>2</sub>.



Figure 19: [a,b,c] SEM images of m-SiO<sub>2</sub> [c] is the magnified image of [b]



Figure 20: EDX graph of m-SiO<sub>2</sub>

#### 3.3.4 SEM of m-SiO<sub>2</sub>-PEI

The SEM image of mesoporous SiO<sub>2</sub>-PEI show an agglomerated mesoporous spheres like structures sitting on top of each other just like SEM images of m-SiO<sub>2</sub> and all these are connected thought extended bridges and individual particle having a diameter of approximately  $0.52 - 1.36 \mu m$  (*Figure 21*). From the data collected from EDX (*Figure 22*), we can see that the material contains Silicon, Oxygen, Carbon, Nitrogen and few traces of Gold. We are detecting gold because we have coated the sample with gold before putting it in the SEM machine. The traces of Carbon and Nitrogen can prove that the material has some organic substance in it. Therefore, we can say that this material is m-SiO<sub>2</sub>-PEI.



Figure 21: [a,b,c] SEM images of m-SiO<sub>2</sub>-PEI [c] is the magnified image of [b]



Figure 22: EDX graph of m-SiO<sub>2</sub>-PEI

#### 3.3.5 SEM of MgO@m-SiO<sub>2</sub>

The pure SiO<sub>2</sub> sample shows the irregularly sphere-like morphology with surfaces of a uniform roughness. By putting MgO into the synthesis solution, the morphology of the resulting MgO@SiO<sub>2</sub> changed. The accumulation of particles with different sizes could be seen for all the MgO containing sample (*Figure 23*), s. These rough surfaces having a diameter of around 1.51 - 0.97  $\mu$ m. From the data collected from EDX (*Figure 24*), we can see that the material contains Magnesium, Silicon, Carbon, Oxygen and few traces of Gold. We are detecting gold because we have coated the sample with gold before putting it in the SEM machine. Therefore, we can say that this material is MgO@m-SiO<sub>2</sub>.



Figure 23: [a,b,c] SEM images of MgO@m-SiO<sub>2</sub> [c] is the magnified image of [b]



Figure 24: EDX graph of MgO@m-SiO<sub>2</sub>

#### 3.3.6 SEM of MgO@m-SiO<sub>2</sub>-PEI

The SEM image of MgO@m-SiO<sub>2</sub>-PEI show us spheres and rocky type structures with rough surface scattered around and each particle having a diameter of around  $0.67 - 1.5 \mu m$  (*Figure 25*). From the data collected from EDX (*Figure 26*), we can see that the material contains Silicon, Oxygen, Magnesium, Carbon, Nitrogen and few traces of Gold. We are detecting gold because we have coated the sample with gold before putting it in the SEM machine. The traces of Carbon and Nitrogen can prove that the material has some organic substance in it. Therefore, we can say that this material is MgO@m-SiO<sub>2</sub>-PEI.



Figure 25: [a,b,c] SEM images of MgO@m-SiO<sub>2</sub>-PEI [c] is the magnified image of [b]



Figure 26: EDX graph or MgO@m-SiO<sub>2</sub>-PEI

#### 3.4 N<sub>2</sub> Adsorption/Desorption Isotherm

#### 3.4.1 N<sub>2</sub> Isotherm of MgO

The Brunauer–Emmet–Teller (BET) method was used to calculate the specific surface area of MgO. The pore distribution was calculated from the desorption branch of the isotherms using the Barret–Joyner–Halanda (BJH) method. The Nitrogen adsorption/desorption isotherm graph of MgO is of type 4 isotherm curve<sup>[20]</sup> and it will occur when capillary condensation occurs (*Figure 27a*). Gases condense in the tiny capillary pores of the solid at pressures below the saturation pressure of the gas. At the lower pressure regions, it shows the formation of a monolayer followed by a formation of multilayers. This isotherm is most suitable for mesoporous materials. The textural properties were shown in *Table 1*. The as-prepared MgO contains many pores, thus giving us this high surface area of 119.5 m<sup>2</sup>/g and the calculated pore diameter is also significant. BJH pore size distribution shows two ranges between 0-10 nm and between 20-30 nanometres which confirm the mesoporous nature of the adsorbent (*Figure 26b*).



Table 1: Textural properties of MgO microsphere

Figure 27: (a) N<sub>2</sub> Adsorption/Desorption Isotherm of MgO, (b) Pore size distribution of MgO

#### 3.4.2 N<sub>2</sub> Isotherm of MgO-PEI

The Nitrogen adsorption/desorption isotherm graph of MgO-PEI is of type 4 isotherm curve (*Figure 28a*)<sup>[20]</sup>. Therefore, confirms the mesoporous nature of the material. The textural properties were shown in *Table 2*. The as-prepared MgO-PEI contains fewer pores because polyethyleneimine is accumulating at the pores, thus giving us a smaller surface area of 1.3  $m^2/g$  and the calculated pore diameter is small compared to MgO. The MgO surface area is 85.7 times larger than MgO-PEI surface area.

Table 2: Textural	l properties	of MgO-PEI
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BET surface area of MgO-PEI	$1.3 \ m^2/g$
Pore diameter of MgO-PEI	3.3 nm
Pore volume of MgO-PEI	0.012 cc/g



**Figure 28**: (a) N<sub>2</sub> Adsorption/Desorption Isotherm of MgO, (b) Pore size distribution of MgO-PEI

#### 3.4.3 N<sub>2</sub> Isotherm of m-SiO<sub>2</sub>

The Nitrogen adsorption/desorption isotherm graph of m-SiO<sub>2</sub> is of type 5 isotherm curve (*Figure 29a*)<sup>[20]</sup>. Type 5 isotherm is not common, has weak adsorbent-adsorbate interactions and these materials are porous adsorbent. The textural properties were shown in *Table 3*. The as-prepared mesoporous SiO<sub>2</sub> has a very large surface area of 1152.9 m<sup>2</sup>/g due

to its high porosity. The m-SiO<sub>2</sub> surface area is 9.6 times larger than MgO surface area. According to the pose distribution obtained by BJH method, it is observed that the predominance of pores with a diameter of 3.06 nm causing it to have very high surface area, thus suggesting that the concave isotherm behaviour is attributed to the narrow mesopores that can allow CO<sub>2</sub> to pass through the material (*Figure 28b*).

BET surface area of m-SiO <sub>2</sub>	$1152.9 \ m^2/g$
Pore diameter of m-SiO <sub>2</sub>	3.06 nm
Pore volume of m-SiO <sub>2</sub>	0.22 cc/g

Table 3: Textural properties of m-SiO<sub>2</sub>



Figure 29: (a)  $N_2$  Adsorption/Desorption Isotherm of m-SiO<sub>2</sub>, (b) Pore size distribution of m-SiO<sub>2</sub>

#### 3.4.4 N<sub>2</sub> Isotherm of m-SiO<sub>2</sub>-PEI

The Nitrogen adsorption/desorption isotherm graph of m-*SiO*<sub>2</sub>-*PEI* is of type 4 isotherm curve (*Figure 30a*)<sup>[20]</sup>. Therefore, confirms the mesoporous nature of the material. The textural properties were shown in *Table 4*. The as-prepared m-*SiO*<sub>2</sub>-*PEI* has fewer pores because polyethyleneimine is getting heavily accumulated at the pores, so the surface area of 342.7 m<sup>2</sup>/g which is 3.3 times less than m-SiO<sub>2</sub> surface area. BJH pore size distribution shows 3 peaks forming in the range of 0-15 nm which confirms the mesoporous nature of the adsorbent (*Figure 29b*).

BET surface area of m-SiO2-PEI	$324.7 \ m^2/g$
Pore diameter of m-SiO <sub>2</sub> -PEI	2.8 nm
Pore volume of m-SiO <sub>2</sub> -PEI	0.13 cc/g

Table 4: Textural properties of m-SiO<sub>2</sub>-PEI



**Figure 30**: (a) N<sub>2</sub> Adsorption/Desorption Isotherm of m-SiO<sub>2</sub>-PEI, (b) Pore size distribution of m-SiO<sub>2</sub>-PEI

#### 3.4.5 N<sub>2</sub> Isotherm of MgO@m-SiO<sub>2</sub>

The Nitrogen adsorption/desorption isotherm graph of MgO@m-SiO<sub>2</sub> is of type 4 isotherm curve (*Figure 31a*)<sup>[20]</sup>. Therefore, confirms the mesoporous nature of the material. The textural properties were shown in *Table 5*. The as-prepared MgO@m-SiO<sub>2</sub> has a smaller surface area of 96.1 m<sup>2</sup>/g.

Table 5: Textural properties of  $MgO@m-SiO_2$ 

BET surface area of MgO@m-SiO <sub>2</sub>	96.1 $m^2/g$
Pore diameter of MgO@m-SiO2	3.06 nm
Pore volume of MgO@m-SiO <sub>2</sub>	0.89 cc/g



Figure 31: (a) N<sub>2</sub> Adsorption/Desorption Isotherm of MgO@m-SiO<sub>2</sub>, (b) Pore size distribution of MgO@m-SiO<sub>2</sub>

#### 3.4.6 N<sub>2</sub> Isotherm of MgO@m-SiO<sub>2</sub>-PEI

The Nitrogen adsorption/desorption isotherm graph of MgO@m-SiO<sub>2</sub>-PEI is of type 4 isotherm curve (*Figure 32a*)<sup>[20]</sup>. Therefore, confirms the mesoporous nature of the material. The textural properties were shown in *Table 6*. The as-prepared of MgO@m-SiO<sub>2</sub>-PEI contains fewer pores because polyethyleneimine is accumulating at the pores, thus giving us a smaller surface area of 33.3 m<sup>2</sup>/g. The pore volume is decreasing because of the PEI accumulating at the free pores of material.

BET surface area of MgO@m-SiO2-PEI	$33.3 m^2/g$
Pore diameter of MgO@m-SiO2-PEI	3.05 nm
Pore volume of MgO@m-SiO2-PEI	0.32 cc/g



Figure 32: (a) N<sub>2</sub> Isotherm of MgO@m-SiO<sub>2</sub>-PEI, (b) Pore size distribution of MgO@m-SiO<sub>2</sub>-PEI

#### 3.5 CO<sub>2</sub> Adsorption Studies

#### 3.5.1 MgO and MgO-PEI

 $CO_2$  adsorption-desorption measurements over mesoporous MgO was performed by BET analysis (*Figure 36a*). The isotherm was carried out using high purity  $CO_2$  gas at 25 °C, under atmospheric pressure while the regeneration was carried out under N<sub>2</sub> flow at 25 °C in vacuum. Before the analysis the sample were pre-treated for 8 h at 200 °C. The  $CO_2$  adsorption of MgO hierarchal microspheres at 25 °C is occurring due to cooperative chemisorptioninduced physisorption nature of material with  $CO_2$  which is why the graph is not starting from origin.

CO<sub>2</sub> adsorption-desorption measurements over mesoporous MgO-PEI was performed by BET analysis (*Figure 36b*). The isotherm was carried out using the same conditions as before. The CO<sub>2</sub> adsorption of MgO-PEI at 25 °C is occurring for the same reason as MgO material *i.e.* cooperative chemisorption-induced physisorption. The CO<sub>2</sub> adsorption capacity at 25°C K for MgO-PEI is 2.15 times higher than the MgO (*Table 7*).

Table 7	7: CO <sub>2</sub>	adsorption	of MgO	and MgO-PEI
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Figure 36: CO<sub>2</sub> Adsorption/Desorption Isotherm of (a) MgO and (b) MgO-PEI

#### 3.5.2 m-SiO<sub>2</sub> and m-SiO<sub>2</sub>-PEI

 $CO_2$  adsorption-desorption measurements over mesoporous SiO<sub>2</sub> was performed by BET analysis (*Figure 37a*). The isotherm was carried out using the same conditions as before. The CO<sub>2</sub> adsorption of SiO<sub>2</sub> at 25 °C is pure physisorption that is why it is starting from origin and has very high CO<sub>2</sub> adsorption capacity (*Table 8*).

 $CO_2$  adsorption-desorption measurements over mesoporous SiO<sub>2</sub>-PEI was performed by BET analysis (*Figure 37b*). The isotherm was carried out using the same conditions as before. The CO<sub>2</sub> adsorption of SiO<sub>2</sub>-PEI at 25 °C is occurring due to cooperative chemisorptioninduced physisorption nature of material with  $CO_2$  why the graph is not starting from origin. It does not have high  $CO_2$  adsorption because of the reverse effect of PEI i.e., instead of increasing the  $CO_2$  selectivity it is clogging the pores of SiO<sub>2</sub> so adsorb less.

CO <sub>2</sub> adsorption of m-SiO <sub>2</sub> at 25 °C	1.354 mmol/g
CO <sub>2</sub> adsorption of m-SiO <sub>2</sub> -PEI at 25 °C	0.872 mmol/g



Figure 37: CO<sub>2</sub> Adsorption/Desorption Isotherm of (a) m-SiO<sub>2</sub>, and (b) m-SiO<sub>2</sub>-PEI

Table 8: CO<sub>2</sub> adsorption of SiO<sub>2</sub> and SiO<sub>2</sub>-PEI

#### 3.5.3 MgO@m-SiO2 and MgO@m-SiO2-PEI

 $CO_2$  adsorption-desorption measurements over MgO@m-SiO<sub>2</sub> was performed by BET analysis (*Figure 38a*). The isotherm was carried out using the same conditions as before. The  $CO_2$  adsorption of MgO@m-SiO<sub>2</sub> at 25 °C is occurring due to cooperative chemisorption-induced physisorption nature of material with  $CO_2$  which is why the graph is not starting from origin.

CO<sub>2</sub> adsorption-desorption measurements over MgO@m-SiO<sub>2</sub>-PEI was performed by BET analysis (*Figure 38b*). The isotherm was carried out using the same conditions as before. The CO<sub>2</sub> adsorption (*Table 9*) of MgO@m-SiO<sub>2</sub>-PEI at 25°C is occurring due to cooperative chemisorption-induced physisorption nature of material with CO<sub>2</sub> why the graph is not starting from origin. The same thing is happening here as SiO<sub>2</sub>. Since SiO<sub>2</sub> is the shell past of the coreshell structure of MgO and SiO<sub>2</sub>, the PEI has to interact with SiO<sub>2</sub> and form a bond, but because of that PEI is clogging the pores of SiO<sub>2</sub>.

<b>Table 9</b> : CO <sub>2</sub> adsorption	of MgO(a)m-S	$SiO_2$ and MgO(	<i>a</i> )m-SiO <sub>2</sub> -PEI
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CO <sub>2</sub> adsorption of MgO@m-SiO <sub>2</sub> at 25 °C	0.317 mmol/g
CO <sub>2</sub> adsorption of MgO@m-SiO <sub>2</sub> -PEI at 25 °C	0.349 mmol/g



Figure 38: CO<sub>2</sub> Adsorption/Desorption Isotherm of (a) MgO@m-SiO<sub>2</sub>, and (b) MgO@m-SiO<sub>2</sub>-PEI

#### **Chapter 4: Conclusion**

Hierarchical porous microspheres of MgO are prepared by a straightforward precipitation-ageing-calcination method. The high adsorption capacity of porous hierarchical MgO structures assigned to its unique structure, high isoelectric point and strong surface complexation. This MgO can be used for various applications like dye adsorption capacity and CO<sub>2</sub> adsorption capacity because of its simple, cost-effective, scaled-up preparation process. Further, MgO microspheres have been functionalized using mesoporous SiO<sub>2</sub> to obtain MgO@m-SiO<sub>2</sub>, which are synthesised by grinding followed by calcination method. A significant advantage of these materials is that we can integrate them into hybrid systems, or of modifying their surfaces with selected compounds that increase their adhesion to a specific group of pollutants. By impregnating PEI with MgO helps in minimizing the effects of pollution and helps in producing large scale adsorbents as well. The PEI impregnated MgO, m-SiO<sub>2</sub> and MgO@m-SiO<sub>2</sub> samples are synthesised and tested to adsorption.

Through the characterization tests like PXRD, FTIR and SEM, we can prove that the materials are indeed impregnated by PEI. The CO<sub>2</sub> molecules and PEI modified materials interact mainly through chemical interaction which is responsible for the low regeneration ability of the synthesised materials. The surface area of MgO, m-SiO<sub>2</sub>, MgO@m-SiO<sub>2</sub> are 85.71, 3.5035, 2.884 times larger than MgO-PEI, m-SiO<sub>2</sub>-PEI, MgO@m-SiO<sub>2</sub>-PEI surface area. The outcome shows that the presence of the amine functional group in PEI helps MgO to have enhanced the CO<sub>2</sub> adsorption capacity. However, in the case of m-SiO<sub>2</sub> and MgO@m-SiO<sub>2</sub>-PEI, the accumulation of PEI in SiO<sub>2</sub> is clogging the pores causing it to lose its mesoporosity and in turn decreasing the CO<sub>2</sub> adsorption capacity. The enhance CO<sub>2</sub> adsorption due to PEI is only happening in MgO. It is concluded that adsorption of CO<sub>2</sub> is more in case of m-SiO<sub>2</sub> because of its high surface area causing the CO<sub>2</sub> molecules to pass though the pores easily and performing pure physisorption.

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