Article

Carbon Dioxide Capture from Flue Gas Using Tri-Sodium Phosphate as an Effective Sorbent

Tushar Sakpal 1,†, Asheesh Kumar 2,*,‡, Zachary M. Aman 2,‡ and Rajnish Kumar 3,‡

1 Catalytic Processes and Materials, Faculty of Science and Technology, MESA+ Institute for Nanotechnology, University of Twente, Drienerlolaan 5, 7522 NB Enschede, The Netherlands
2 Department of Chemical Engineering, University of Western Australia, 35 Stirling Highway, Crawley, Western Australia 6009, Australia
3 Department of Chemical Engineering, Indian Institute of Technology, Madras, Chennai 600036, India
* Correspondence: asheesh.kumar@uwa.edu.au; Tel.: +61-406-206-232
† Authors contributed equally.

Received: 18 June 2019; Accepted: 24 July 2019; Published: 26 July 2019

Abstract: Fossil fuels are dominant as an energy source, typically producing carbon dioxide (CO₂) and enhancing global climate change. The present work reports the application of low-cost tri-sodium phosphate (TSP) to capture CO₂ from model flue gas (CO₂ + N₂) mixture, in a batch mode and fixed-bed setup. It is observed that TSP has a high CO₂ capture capacity as well as high CO₂ selectivity. At ambient temperature, TSP shows a maximum CO₂ capture capacity of 198 mg CO₂/g of TSP. Furthermore, the CO₂ capture efficiency of TSP over a flue gas mixture was found to be more than 90%. Fresh and spent materials were characterized using powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), and Fourier transformed infrared spectroscopy (FTIR). Preliminary experiments were also conducted to evaluate the performance of regenerated TSP. The spent TSP was regenerated using sodium hydroxide (NaOH) and its recyclability was tested for three consecutive cycles. A conceptual prototype for post-combustion CO₂ capture based on TSP material has also been discussed.

Keywords: CO₂ capture; tri-sodium phosphate; inorganic sorbent; gas separation; flue gas mixture

1. Introduction

Coal-fired thermal power stations contribute immensely to the anthropogenic release of carbon dioxide (CO₂) in the atmosphere. CO₂ is considered to be the major greenhouse gas, potentially contributing to global climate change [1–4]. According to a report of the Intergovernmental Panel on Climate Change, the projected carbon emissions from the energy sector will be twice as high by 2050 [5]. In the year 2013, the recorded global carbon dioxide emission from burning fossil fuels was 36 billion metric tons (39.7 billion tons) [6]. Carbon dioxide capture, storage, and utilization (CCSU) is an emerging potential technology to address this issue [7]. Therefore, post-combustion CO₂ capture from the flue gas (mainly CO₂ + N₂) is a key process as it can be retrofitted to the existing fleet of coal-fired power stations [8,9]. Post-combustion capture of CO₂ from conventional power plants are quite expensive due to the low partial pressure of CO₂ (typically 10–20%) in the flue gas mixture. It is well established that in amine-based CO₂ capture processes, corrosion of process pipelines remains a genuine concern [10]. Adsorption of CO₂ using solid sorbents has proved to be efficient at lab-scale operation since they can produce high-purity CO₂ streams with low energy consumption and minimum concerns on corrosion of process pipelines [11]. As a result, a wide variety of solid adsorbents have been studied in recent past such as zeolites [12], activated carbons [13], hydrotalcite-like compounds [10], metal oxides [14], metal-organic frameworks (MOFs) [15], silica...
gel [16], amine-based adsorbents [17,18], and amine-functionalized silica gel [19]. However, many of the solid adsorbents developed so far suffer from problems such as low scalability, poor moisture tolerance, and high material cost. Some of these adsorbents are also used to capture CO$_2$ directly from the air where the concentration of CO$_2$ is comparatively low [20,21].

Trisodium phosphate (TSP) is an inorganic material that has the potential to capture CO$_2$ from the flue gas in a cost-effective way. TSP is a highly alkaline (pH of a 1% aqueous solution is 12.5, measured on pH meter from Mettler Toledo) and non-volatile compound with negligible thermal degradation (melting point of anhydrous and dodecahydrate TSP is 1856 and 346.5 K, respectively). It is frequently used as a food additive, cleaning agent, and in boilers, because phosphate in TSP buffers the water to minimize pH fluctuation, and precipitates like calcium or magnesium salts gets deposited as a soft layer rather than a hard scale [22].

Previously, Balsora and Mondal [23] have reported the solubility of CO$_2$ in aqueous TSP and blends of diethanolamine (DEA) with TSP. Authors studied the absorption of CO$_2$ at different TSP concentrations (1.0–2.0 kmol/m$^3$), temperatures (303.14–333.14 K), and inlet CO$_2$ partial pressures (10.13–20.26 kPa). It was reported [23] that CO$_2$ solubility increases with increasing TSP concentration as well as temperature. It was also reported that the CO$_2$ solubility increases with the increasing mole fraction of TSP at a fixed temperature and partial pressure of CO$_2$. Maximum CO$_2$ solubility in DEA and TSP blends was found to be lower than that of TSP alone [24].

For the first time, to the best of our knowledge, we are using TSP as a solid sorbent for the removal of CO$_2$ from flue gas mixture. The objective of the present work is to study the kinetics of CO$_2$ capture and separation efficiency of carbon dioxide from flue gas mixture using solid TSP as a sorbent. A model flue gas mixture with 16.1 mol% CO$_2$ and 83.9 mol% N$_2$ is used during experiments [25]. A gas mixture of 85 mol% CO$_2$ and 15 mol% N$_2$ is also used to elucidate the effect of CO$_2$ composition. Fresh and spent materials were characterized using SEM, PXRD, and FTIR spectroscopy to gain mechanistic insights. Finally, regeneration and reusability of spent TSP are also studied.

2. Materials and Methods

2.1. Materials

Pure carbon dioxide gas, flue gas mixtures (16.1 mol% CO$_2$/83.9 mol% N$_2$), and a gas mixture of 85 mol% CO$_2$/15 mol% N$_2$ with a certified purity of more than 99.9% were supplied by Deluxe Industrial Gases, Pune, India. Dodecahydrate tri-sodium phosphate, Na$_3$PO$_4$$\cdot$12H$_2$O, with ≥98% purity (AR grade) was purchased from Rankem Ltd, Pune, India. Sodium hydroxide with >98% purity was purchased from Qualigens Fine Chemicals, Mumbai, India. All the materials were used without any further purification.

2.2. Characterization of Materials

FTIR spectra were recorded using GX Perking Elmer spectrometer with 4 cm$^{-1}$ resolutions, while the number of scans was 10. Prior to measurement, the sample was diluted with KBr and pressed into thin wafers. The SEM images (morphological studies) were obtained on an FEI Quanta 200 3D dual beam ESEM, operating at 20 kV. Powder X-ray diffraction spectra for fresh and spent TSP were recorded on Philips powder XRD between the 2θ of 5°–60° at room temperature.

2.3. Apparatus and Procedure

Two high-pressure stainless-steel (SS-316) reactors with different volumes were used in this study. The experiments with 4 g TSP were done in a 25 cc reactor (Figure 1), while a 250 cc reactor was used for 40 and 100 g TSP samples. The ports with Swagelok connection, on top of the cover plate of the reactor, were used for a thermocouple, gas inlet, gas outlet, and pressure transducer. The pressure of the reactor during experiments was recorded using a pressure transducer (Wika, Klingenberg, Germany), with a range of 0–16 MPa and accuracy of 0.075% of the span. Analog signals from pressure transducer and
A thermocouple were processed with the help of a data acquisition system and a dedicated computer, connected to the experimental setup. The required experimental temperature was acquired by an external temperature-controlled unit (ER, Julabo GmbH, Germany). The setup was equipped with a gas chromatograph GC-2014AT (Shimadzu corporation, Kyoto, Japan) to measure the composition of the gas phase in the reactor.

Figure 1. Schematic diagram of the experimental setup.

The reactor along with the fittings was evacuated at 0.001 MPa for 10 minutes using an external vacuum pump (KNF lab, Trenton, NJ, USA). The evacuated reactor was pressurized by supplying CO$_2$ and N$_2$ mixture to the experimental pressure at experimental temperature. Time zero of the reaction was the time at which the sorbent was exposed to the flue gas mixture and the drop in pressure inside the reactor was recorded every 5 s using a data acquisition system (DAQ). The drop in pressure and temperature with respect to time was used to get the kinetics of the reaction. The total number of moles of gas consumed was calculated by using Equation (1). The gas composition at the end of the experiment was analyzed by injecting a small quantity of gas, taken from the reactor, into gas chromatography. The GC is equipped with a thermal conductivity detector and Shin Carbon ST column. Experimental procedure for 40 g and 100 g TSP was similar to the one followed for 4 g measurements.

2.4. Regeneration Process

Some of the preliminary experiments were conducted to regenerate the spent TSP. More precisely, the spent TSP was regenerated using sodium hydroxide (NaOH), in which sodium hydroxide (NaOH) pellets were inserted inside the reactor (containing CO$_2$-loaded TSP in slurry form) and mixed at room temperature and atmospheric pressure condition for ~15 min. Reaction mechanism of spent TSP with NaOH has been discussed in Section 3.2. (Refer to results and discussion section).

2.5. The Calculation for the Amount of Gas Consumed

The reaction between TSP and CO$_2$ starts as soon as they are brought in contact with each other, and this results in a continuous drop of the reactor pressure. At a given time, the total number of moles of the gas consumed can be calculated by the following equation [25].
\[ (\Delta n_{\text{con,}t})_t = V_R \frac{P}{zRT} V_R \frac{P}{zRT} \]

where \( P \) is pressure (kPa), \( R \) is the gas constant (J·K\(^{-1}\)·mol\(^{-1}\)), \( T \) is temperature (K), \( V \) is the volume of the reactor (cm\(^3\)), and \( n \) is the number of moles of gas present in the system. \( z \) is the compressibility factor calculated by the following equation [26].

\[ Z = 1 + \beta^0 \frac{P_r}{T_r} + \alpha \beta^1 \frac{P_r}{T_r} \]

where \( \beta^0 = 0.083 - 0.422 \frac{T_{\text{crit}}}{T_r} \), \( \beta^1 = 0.139 - 0.172 \frac{T_{\text{crit}}}{T_r} \), \( T_r = T \exp \frac{T_{\text{critical}}}{T_r} \), \( P_r = P \exp \frac{P_{\text{critical}}}{T_r} \), and \( \omega \) = Acentric factor.

2.6. Calculation of Rate of Gas Consumption

The rate of gas consumption is calculated using the forward difference method given below [25].

\[ \frac{d(\Delta n_{\text{con}})}{dt} = \frac{\Delta n_{\text{con}}(t+\Delta t) - \Delta n_{\text{con}}(t)}{\Delta t} \]

where \( \Delta n_{\text{con}} \) is the number of moles of gas consumed at the end of the experiment. Here, \( \Delta n_{\text{con}} \) is the number of moles of gas consumed at the end of the experiment.

2.7. The Calculation for CO\(_2\) Capture Efficiency (\( \eta \))

CO\(_2\) capture efficiency of the material over a gas mixture (flue gas mixture) was calculated by using Equation (4), which was adopted from our previous work [25] and modified.

\[ \eta = \frac{x_{\text{CO}_2}^{\text{feed}} - x_{\text{CO}_2}^{\text{end}}}{x_{\text{CO}_2}^{\text{feed}}} \times 100 \]

where \( x_{\text{CO}_2}^{\text{feed}} \) is the mole fraction of CO\(_2\) in the feed gas mixture and \( x_{\text{CO}_2}^{\text{end}} \) the mole fraction of CO\(_2\) at the end of the experiment determined by gas chromatography.

3. Results and Discussion

3.1. Material Characterization Analysis

TSP, before and after the gas uptake measurements, were analyzed using FTIR spectroscopy for identification of the functional groups. Figure 2a shows the FTIR spectra of pure TSP and regenerated TSP while Figure 2b shows the CO\(_2\)-loaded pure TSP and CO\(_2\)-loaded regenerated TSP. Several distinct peaks can be seen for fresh TSP at 3200, 1660, 1450, 1000, and 694 cm\(^{-1}\). The strong downward peak at 1000 cm\(^{-1}\) corresponds to the O–P–O asymmetric stretching present in PO\(_3\) group of TSP [27]. Regenerated-TSP also shows a similar spectrum as fresh TSP, with one additional peak at 866 cm\(^{-1}\), which is a characteristic band for C–O stretching in the carbonate ions (CO\(_3^{2-}\)). This implies the formation of sodium carbonate as a side product during regeneration by NaOH [27]. Figure 2b shows the characteristic peaks resulting from the reaction of CO\(_2\) with TSP. Peaks at 970, 1066, and 1470 cm\(^{-1}\) show the presence of disodium hydrogen phosphate and peaks at 696, 837, 1300, 1401, 1625, 1910, and 2500 cm\(^{-1}\) represents sodium bicarbonate, the two major products formed by the reaction of CO\(_2\) with TSP [27,28]. A broad peak at 3500–3200 cm\(^{-1}\), which can be attributed to –OH stretch, confirms the presence of water.

Further, to confirm the products formed by the reaction of TSP and CO\(_2\), samples were analyzed using powder X-ray diffraction. Figure 3a shows the XRD patterns of pure TSP and regenerated TSP. Peaks at 9, 15, 21, 24, 29, 31, 33, and 46 were obtained in both TSP and regenerated-TSP (JCPDS...
PDF No: 01-0957). The qualitative comparison of intensities shows that the regenerated TSP is less intense compared to fresh TSP, implying the partial regeneration of TSP and the possible formation of sodium carbonate in the presence of NaOH. Moreover, the XRD patterns for CO$_2$-loaded TSP and CO$_2$-loaded regenerated TSP (Figure 3b) confirms the presence of NaHCO$_3$ (JCPDS PDF No: 01-0909) and Na$_2$HPO$_4$ (JCPDS PDF No: 01-0997).

**Figure 2.** (a) FTIR spectra of pure TSP and regenerated trisodium phosphate (TSP); (b) FTIR spectra of CO$_2$-loaded pure TSP and CO$_2$-loaded regenerated TSP.

**Figure 3.** XRD spectrum of (a) pure TSP and regenerated TSP; (b) CO$_2$-loaded pure TSP and CO$_2$-loaded regenerated TSP.
3.2. Sorption Reaction Mechanism

Material characterization supports the formation of sodium bicarbonate and disodium hydrogen phosphate during CO$_2$ capture cycle (Equation (5)) and partial regeneration of TSP by the treatment of NaOH (Equation (6)) (discussed in Section 3.3). During regeneration of TSP, NaOH also reacts with the sodium bicarbonate which has formed earlier in the reactor (Equation (5)) resulting in the formation of sodium carbonate (Equation (7)) (confirmed by IR). Residual sodium carbonate thus reacts with CO$_2$ in the next CO$_2$ capture cycle to give sodium bicarbonate (Equation (8)).

\[
\text{CO}_2(g) + \text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}(s) \rightarrow \text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}(s) + 4\text{H}_2\text{O} \quad (5)
\]

\[
\text{Na}_2\text{HPO}_4 + \text{NaOH} \rightarrow \text{Na}_3\text{PO}_4 + \text{H}_2\text{O} \quad (6)
\]

\[
\text{NaHCO}_3 + \text{NaOH} \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \quad (7)
\]

\[
\text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2(g) \rightarrow \text{NaHCO}_3 \quad (8)
\]

The sorption mechanism of acidic carbon dioxide gas in basic tri-sodium phosphate is quite complicated, which start at a solid-gas interface. However, as reaction proceeds, liquid phase (water) appears, which negatively affects the reaction kinetics (Equation (5)). Thus, it is important to understand the CO$_2$ capture kinetics using TSP as a sorbent. Keeping it in mind, the effect of various experimental parameters on the kinetics were studied and is discussed below.

3.3. Gas Uptake Kinetics

3.3.1. Effect of Temperature on the Gas Uptake Kinetics

The performance of TSP for maximum CO$_2$ uptake was studied at the temperature ranges from 15 to 50 °C and pressure 3.5 MPa of pure CO$_2$. The gas uptake profile along with the rate of gas consumption calculated using forward difference method is represented in Figure 4. CO$_2$ consumption during a gas uptake measurement was calculated by using Equation (1). Table 1 summarizes the CO$_2$ uptake data, operating temperature and pressure, CO$_2$ composition, and amount of solid adsorbent used in each case. All the experiments were repeated three times (except for some measurements, which were repeated twice) and data are shown with its standard deviation. Among all, 4 g TSP shows the best result of 198 mg/g (standard deviation: 4.72) at 30 °C with 3.5 MPa pressure and 100% CO$_2$ concentration. Using these optimized conditions, the process was studied with a larger sample size of 40 g and 100 g of TSP.

As shown in Figure 4a, the effect of temperature on the gas uptake kinetics of TSP was studied at 15, 30, and 50 °C. It was found that 30 °C is an optimum temperature at which maximum CO$_2$ was consumed. Figure 4b shows the rate of gas uptake (mg CO$_2$/g adsorbent/min) calculated by the forward difference method for the above three experiments. The magnitude of gas uptake was found to be approximately three times higher at 30 °C compared to 15 °C, the initial rate of gas uptake was approximately two times higher at 30 °C compared to 15 and 50 °C. At low temperature (15 °C), there is insufficient energy to drive the reaction forward, which results in low CO$_2$ capture capacity. On the other hand, at a higher temperature (50 °C), the TSP shows poor stability due to the fact that it has a low melting point of 73.5 °C. However, at 30 °C, the activation energy is sufficient enough to achieve maximum CO$_2$ conversion without losing its structure.

The reaction of TSP with CO$_2$ is exothermic in nature, and in the fixed-bed setup, heat dissipation is limited, thus resulting in a localized temperature rise at the reaction site. Figure 4c represents the temperature profile along with the pressure drop data at 30 °C. From Figure 4c, it can be seen that a sudden rise in temperature occurs during the reaction of TSP with CO$_2$. It proves the exothermic nature of the reaction. As the reactor was kept in a temperature-controlled water bath, the temperature is brought back to the experimental temperature (30 °C). We believe lower CO$_2$ capture at 50 °C is the result of this exothermic nature of the reaction [29–31]. TSP starts melting at 73.5 °C and an exothermic
reaction leads to the formation of liquid TSP. In a fixed-bed configuration, liquid TSP would create a mass transfer resistance for CO$_2$ to come in contact with fresh TSP molecule, thus reducing the reaction kinetics. In a similar chemical sorption process, Kamarudin [29] showed maximum CO$_2$ capture at an optimum temperature of 25 °C for CO$_2$ capture in monoethanolamine (MEA)-loaded MCM-41.

**Figure 4.** (a) Comparison of CO$_2$ uptake capacity (mg of CO$_2$/g of sorbent) at 3.5 MPa pressure and three different temperatures (15, 30, and 50 °C); (b) Rate of gas uptake (mg of CO$_2$/g of sorbent/min) for the same system; (c) pressure and temperature data with respect to time at 30 °C (Curves provided to guide the eye).

### 3.3.2. Effect of Gas Pressure on the CO$_2$ Uptake Kinetics

The total CO$_2$ uptake (Figure 5a) and rate of CO$_2$ uptake (Figure 5b) at 2, 3.5, and 5 MPa CO$_2$ pressure indicate that the initial rate of gas uptake was higher at higher pressure. The experiment conducted at 2 MPa pressure was re-pressurized to initial pressure once most of the CO$_2$ in the gas phase reacted with TSP. In this experiment, about 62% of TSP saturation was achieved during the first stage and the remaining TSP gets saturated in the second stage after re-pressurization. As shown in Figure 5b, the rate of CO$_2$ uptake is independent of the experimental pressure making it suitable for continuous operation.
Table 1. Summary of the experimental conditions, gas composition, and CO$_2$ uptake data along with standard deviation for all the kinetic experiments carried out at small (4 g), medium (40 g), and large scale (100 g).

<table>
<thead>
<tr>
<th>Exp. No.</th>
<th>Experimental Pressure, $P_{exp}$ (MPa)</th>
<th>Composition (%)</th>
<th>Experimental Temperature ($T_{exp}$)</th>
<th>Gas Uptake (mg of CO$_2$/g of Sorbent)</th>
<th>Std. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>3.5</td>
<td>100 0</td>
<td>15</td>
<td>68</td>
<td></td>
</tr>
<tr>
<td>1b</td>
<td>3.5</td>
<td>100 0</td>
<td>15</td>
<td>64</td>
<td>2.64</td>
</tr>
<tr>
<td>1c</td>
<td>3.5</td>
<td>100 0</td>
<td>15</td>
<td>63</td>
<td></td>
</tr>
<tr>
<td>2a</td>
<td>3.5</td>
<td>100 0</td>
<td>30</td>
<td>198</td>
<td></td>
</tr>
<tr>
<td>2b</td>
<td>3.5</td>
<td>100 0</td>
<td>30</td>
<td>189</td>
<td></td>
</tr>
<tr>
<td>2c</td>
<td>3.5</td>
<td>100 0</td>
<td>30</td>
<td>191</td>
<td></td>
</tr>
<tr>
<td>3a</td>
<td>3.5</td>
<td>100 0</td>
<td>50</td>
<td>120</td>
<td></td>
</tr>
<tr>
<td>3b</td>
<td>3.5</td>
<td>100 0</td>
<td>50</td>
<td>117</td>
<td>2.08</td>
</tr>
<tr>
<td>3c</td>
<td>3.5</td>
<td>100 0</td>
<td>50</td>
<td>116</td>
<td></td>
</tr>
<tr>
<td>4a</td>
<td>2.0</td>
<td>100 0</td>
<td>30</td>
<td>189</td>
<td></td>
</tr>
<tr>
<td>4b</td>
<td>2.0</td>
<td>100 0</td>
<td>30</td>
<td>192</td>
<td></td>
</tr>
<tr>
<td>4c</td>
<td>2.0</td>
<td>100 0</td>
<td>30</td>
<td>191</td>
<td></td>
</tr>
<tr>
<td>5a</td>
<td>5.0</td>
<td>100 0</td>
<td>30</td>
<td>196</td>
<td></td>
</tr>
<tr>
<td>5b</td>
<td>5.0</td>
<td>100 0</td>
<td>30</td>
<td>193</td>
<td>4.04</td>
</tr>
<tr>
<td>5c</td>
<td>5.0</td>
<td>100 0</td>
<td>30</td>
<td>188</td>
<td></td>
</tr>
<tr>
<td>6a</td>
<td>3.5</td>
<td>85 15</td>
<td>30</td>
<td>181</td>
<td></td>
</tr>
<tr>
<td>6b</td>
<td>3.5</td>
<td>85 15</td>
<td>30</td>
<td>177</td>
<td></td>
</tr>
<tr>
<td>6c</td>
<td>3.5</td>
<td>85 15</td>
<td>30</td>
<td>179</td>
<td></td>
</tr>
<tr>
<td>7a</td>
<td>3.5</td>
<td>16.1 83.9</td>
<td>30</td>
<td>140</td>
<td>2.88</td>
</tr>
<tr>
<td>7b</td>
<td>3.5</td>
<td>16.1 83.9</td>
<td>30</td>
<td>140</td>
<td></td>
</tr>
<tr>
<td>7c</td>
<td>3.5</td>
<td>16.1 83.9</td>
<td>30</td>
<td>135</td>
<td></td>
</tr>
<tr>
<td>8a</td>
<td>3.5</td>
<td>100 0</td>
<td>30</td>
<td>169</td>
<td></td>
</tr>
<tr>
<td>8b</td>
<td>3.5</td>
<td>100 0</td>
<td>30</td>
<td>162</td>
<td></td>
</tr>
<tr>
<td>9a</td>
<td>3.5</td>
<td>100 0</td>
<td>30</td>
<td>145</td>
<td>4.04</td>
</tr>
<tr>
<td>9b</td>
<td>3.5</td>
<td>100 0</td>
<td>30</td>
<td>139</td>
<td></td>
</tr>
</tbody>
</table>

* 40 g of TSP was used. # 100 g of TSP was used (In rest of the experiments 4 g TSP was used).

Figure 5. (a) Comparison of CO$_2$ uptake capacity (mg of CO$_2$/g of sorbent) at different pressure (2.0, 3.0, and 5.0 MPa) and 30 °C temperature; (b) rate of gas uptake (mg of CO$_2$/g of sorbent/min) for the same system (Curves provided to guide the eye).
3.4. Gas Phase Analysis

$\text{CO}_2$ capture efficiency ($\eta$) of the material in the flue gas mixture was calculated by using Equation (4). Mole fraction of gaseous components at the start and end of the gas uptake measurement were the major parameters for this calculation. To probe the mole fraction of gaseous components at the end of the experiment, a small sample of the gaseous phase is analyzed using gas chromatography (Table 2). For $\text{CO}_2$ capture efficiency measurement of TSP, experiments were conducted at the optimum temperature of 30 °C using a mixture of $\text{CO}_2$ and $\text{N}_2$ gas with initial mol% of 16.1 and 83.9, respectively. The system was pressurized (at 3.5 MPa) repeatedly with $\text{CO}_2$/N$_2$ mixture until no gas uptake was observed (4 g TSP was used in the 25 cm$^{-3}$ reactor) (Figure 6a). Since flue gas used in this study contains only 15% of $\text{CO}_2$ (rest $\text{N}_2$), TSP was not saturated in the first stage of pressurization. Every stage of pressurization contained only 0.56 MPa of $\text{CO}_2$ (16.1% of 3.5 MPa). Therefore the system has to pressurize repeatedly so as to ensure the complete saturation of TSP taken in the reactor. Five pressurization stages were required to attain the level of saturation (Figure 6a). A flat gas uptake curve signifies that all the TSP in the reactor has been saturated and thus no further drop in reactor pressure is observed. Figure 6a represents the gas uptake for all the five stages. As seen in Figure 6a, in the first two stages, $\text{CO}_2$ sorption comes out to be the same and equal to ~43 mg/g. However, it was found that in all the subsequent stages (III, IV, and V), the gas uptake starts to decrease. In the fifth stage, the $\text{CO}_2$ capture capacity of the material was found to have significantly decreased, confirming complete saturation of TSP in the reactor. At each stage, $\text{CO}_2$ capture efficiency was calculated and reported in Table 2. As shown in the table, separation efficiency drops as TSP is getting saturated with $\text{CO}_2$ gas and in this work, only five recycles were done. During the first three stages, the $\text{CO}_2$ molecule found a number of active sites for reaction and hence ~92% of $\text{CO}_2$ capture efficiency over a gas mixture of $\text{CO}_2$/N$_2$ was achieved. In the last two stages, active sites for the reaction were reduced rapidly as TSP was saturated and $\eta$ value dropped to the value of ~52% and 3% at the end of fourth and fifth stages, respectively.

Table 2. CO$_2$ composition at the start of the experiment (feed gas) and at the end of the experiment analyzed by gas chromatography from a gas mixture of 16% CO$_2$ and rest N$_2$ along with calculated CO$_2$ capture efficiency ($\eta$)%.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>1st Stage</th>
<th>2nd Stage</th>
<th>3rd Stage</th>
<th>4th Stage</th>
<th>5th Stage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed gas ($\text{CO}_2$) composition mol fraction</td>
<td>0.161</td>
<td>0.161</td>
<td>0.161</td>
<td>0.161</td>
<td>0.161</td>
</tr>
<tr>
<td>Gas phase composition ($\text{CO}_2$) at the end of the experiment mol fraction</td>
<td>0.0116</td>
<td>0.0116</td>
<td>0.0117</td>
<td>0.077</td>
<td>0.156</td>
</tr>
<tr>
<td>$\text{CO}_2$ capture efficiency ($\eta$) %</td>
<td>92.79</td>
<td>92.79</td>
<td>92.73</td>
<td>52.17</td>
<td>3.10</td>
</tr>
</tbody>
</table>

The separation efficiency of TSP for $\text{CO}_2$ in the flue gas was found to be over 90%. The selectivity of $\text{CO}_2$ over N$_2$ (Figure 6b) shows that the N$_2$ (being an inert gas) did not take part in the reaction with TSP and the gas uptake we got was purely due to reaction of $\text{CO}_2$.

3.5. Effect of CO$_2$ Concentration on Gas Uptake

To evaluate the influence of CO$_2$ concentration on the CO$_2$ capture efficiency of TSP, gas mixtures with different composition of CO$_2$ (16%, 85%, and 100% CO$_2$ balance with N$_2$) were used in the present work. Figure 7 represents the gas consumption along with the rate of gas uptake for the experiments carried out at three different CO$_2$ compositions. As we have seen from gas phase analysis and reaction mechanism; since nitrogen did not react with TSP, the gas consumption measured for the CO$_2$/N$_2$ mixture can be considered as the CO$_2$ capture capacity only. As seen in Figure 7a, CO$_2$ concentration significantly influences the gas uptake capacity of the material. It was found that with an increase in CO$_2$ concentration, gas consumption increases. The gas consumption capacity for 100% of CO$_2$ was found to be almost 1.5 times greater compared to gas consumption for 16% of CO$_2$. All three experiments with their gas capture capacity are listed in Table 1. Figure 7b represents the rate of
gas uptake for the experiments conducted with different gas composition. As seen in the figure, the rate of gas uptake also follows the same trend as discussed with Figure 7a. The initial rate of gas uptake was found almost similar for 100% and 85% CO$_2$ while the rate for 16% CO$_2$ mixture reduced to half compared to higher concentrations of CO$_2$. Xu et al. have also reported similar results for MCM-41-PEI-75 sorbent at different CO$_2$ concentrations [32], where the capture capacity of the material decreases with the lowering in the concentration of CO$_2$. CO$_2$ capture in aqueous amines has been evaluated at different CO$_2$ concentrations; Masih Hosseini Jenab et al. [33] have found that CO$_2$ absorption increases with the concentration of CO$_2$ in the gas mixture; this work was performed at 30 to 5000 kPa. Singh et al. [34] and Tontiwachwuthikul et al. [35] have also observed similar results for the absorption of CO$_2$ in aqueous amines.

3.6. Comparison of CO$_2$ Uptake with the Solid Adsorbent Available in the Literature

Table 3 compares the CO$_2$ uptake results obtain in this work with the available literature [36–47] along with experimental conditions. As seen in Table 3, MBS-2 (molecular basket sorbents loaded with PEI) and PEI–CNT present a maximum gas uptake of 140 and 170 mg of CO$_2$/g of sorbent at an optimum temperature of 75 and 50 °C, respectively [39,44].

In the current work, we also have achieved a similar gas uptake at ambient temperature (30 °C) for 16.1 and 85 mol% CO$_2$. Moreover, Sanza et al. [38] have also reported a loading of 80 mg of CO$_2$/g of adsorbent at 45 °C in SBA-15, which is less compared to the result reported in our work. The maximum absorption capacity of 198 and 140 mg CO$_2$/g of TSP obtained in the current work is quite high compared to the results reported in the literature for pure CO$_2$ and fuel gas mixture, respectively.

![Figure 6](image-url)

**Figure 6.** (a) CO$_2$ uptake capacity for flue gas mixture contains 16.1% CO$_2$ at 30 °C temperature and 3.5 MPa pressure in five different stages; (b) the selectivity of pure CO$_2$ over pure N$_2$ gas at 30 °C temperature and 3.5 MPa pressure (Curves provided to guide the eye).
MOFs have relatively high CO$_2$ uptake capacity (238 mg/g) [46]; nevertheless, rigorous synthesis pathway, cost, and safety aspects have to be considered to establish an effective CO$_2$ capture process.

![Graph](image_url)

**Figure 7.** (a) Comparison of CO$_2$ uptake capacity (mg of CO$_2$/g of sorbent) at different CO$_2$ composition (16%, 85%, and 100% CO$_2$) at 3.5 MPa pressure and 30 °C temperature; (b) rate of gas uptake (mg of CO$_2$/g of sorbent/min) for the same system (Curves provided to guide the eye).

3.7. Gas Uptake Kinetics in The Regenerated TSP

In this work, regeneration of TSP was carried out by sodium hydroxide (NaOH) pellets, and the reaction took place at room temperature and atmospheric pressure condition for 15 min where regenerated TSP and sodium carbonate as a by-product was obtained (Equations (6) and (7)). The presence of sodium carbonate was also confirmed by FTIR studies (Section 3.1.). Figure 8a represents the CO$_2$ uptake for pure and regenerated TSP (three regeneration cycles). The CO$_2$ capture capacity in pure TSP was found to be 198 mg/g while after first regeneration of TSP, it was ~180 mg/g (Figure 8a). This decreasing trend of CO$_2$ capture capacity continued after the second and third regenerations of the material. Kinetics of CO$_2$ capture after regeneration cycles remained more or less same. This suggests that the regeneration of TSP does not affect the kinetics of the reaction. Reduction in CO$_2$ uptake for each regeneration cycle is mainly due to the inefficient reaction of NaOH with CO$_2$-loaded TSP. It was observed that upon reaction with NaOH, the CO$_2$-loaded TSP slurry solidifies due to the formation of hydrated TSP and sodium carbonate. However, advanced reactor design and complete downstream processing of the degenerated TSP is expected to improve the regeneration efficiency.
Table 3. Comparison of results obtained in this study and those reported earlier in the literature, along with experimental conditions.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Experimental Conditions</th>
<th>Gas Uptake (mg of CO₂/g of Sorbent)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xerogel</td>
<td>100</td>
<td>25</td>
<td>49.3 Huang et al., 2003 [36]</td>
</tr>
<tr>
<td>MCM-48</td>
<td>5</td>
<td>25</td>
<td>50.2 Huang et al., 2003 [36]</td>
</tr>
<tr>
<td>Fly ash-derived carbon materials</td>
<td>15</td>
<td>75</td>
<td>45 Amorillas et al., 2005 [37]</td>
</tr>
<tr>
<td>MCM-41</td>
<td>5</td>
<td>25</td>
<td>42.7 Harlick et al., 2006 [38]</td>
</tr>
<tr>
<td>MCM-41x</td>
<td>5</td>
<td>25</td>
<td>47.5 Harlick et al., 2006 [38]</td>
</tr>
<tr>
<td>PE-MCM-41 d</td>
<td>5</td>
<td>25</td>
<td>68.2 Harlick et al., 2006 [38]</td>
</tr>
<tr>
<td>MBS-1 a</td>
<td>14.9</td>
<td>75</td>
<td>89.2 Ma et al., 2009 [39]</td>
</tr>
<tr>
<td>MBS-2</td>
<td>14.9</td>
<td>75</td>
<td>140.0 Ma et al., 2009 [39]</td>
</tr>
<tr>
<td>MCM-41 c</td>
<td>100</td>
<td>25</td>
<td>82.3 Kamarudin, 2009 [29]</td>
</tr>
<tr>
<td>MCM-41</td>
<td>100</td>
<td>50</td>
<td>22.5 Kamarudin, 2009 [29]</td>
</tr>
<tr>
<td>SBA-15</td>
<td>100</td>
<td>50</td>
<td>33.8 Kamarudin, 2009 [29]</td>
</tr>
<tr>
<td>MCM-48</td>
<td>100</td>
<td>25</td>
<td>35.2 Kim et al., 2009 [40]</td>
</tr>
<tr>
<td>MCM-48</td>
<td>100</td>
<td>25</td>
<td>17.6 Kim et al., 2009 [40]</td>
</tr>
<tr>
<td>Silica Gel</td>
<td>15.1</td>
<td>75</td>
<td>138.0 Zhang et al., 2012 [41]</td>
</tr>
<tr>
<td>SBA-15 b</td>
<td>23</td>
<td>45</td>
<td>78.5 Sanz et al., 2012 [42]</td>
</tr>
<tr>
<td>SBA-15</td>
<td>18</td>
<td>45</td>
<td>80.3 Sanz et al., 2012 [42]</td>
</tr>
<tr>
<td>M2(dobpdc)-Modified MOF-74</td>
<td>15</td>
<td>40</td>
<td>138.2 McDonald et al., 2012 [43]</td>
</tr>
<tr>
<td>Activated carbon</td>
<td>17</td>
<td>15-25</td>
<td>107-142 Samanta et al., 2012 [8]</td>
</tr>
<tr>
<td>Purified SWNT</td>
<td>17</td>
<td>35</td>
<td>190 Samanta et al., 2012 [8]</td>
</tr>
<tr>
<td>Molecular sieve 1X</td>
<td>17</td>
<td>20-25</td>
<td>115.7-205 Samanta et al., 2012 [8]</td>
</tr>
<tr>
<td>K₂CO₃ e</td>
<td>15</td>
<td>100</td>
<td>92.4 Samanta et al., 2012 [8]</td>
</tr>
<tr>
<td>Na₂CO₃ f</td>
<td>10</td>
<td>50-70</td>
<td>114 Samanta et al., 2012 [8]</td>
</tr>
<tr>
<td>MOC Composites g</td>
<td>100</td>
<td>25</td>
<td>174 Creamer and Gao, 2016 [44]</td>
</tr>
<tr>
<td>Hollow fibres i</td>
<td>10</td>
<td>35</td>
<td>238 Patel et al., 2017 [45]</td>
</tr>
<tr>
<td>SIFSIX-2-Cu-I j</td>
<td>90</td>
<td>25</td>
<td>238 Oschatz and Antonietti, 2018 [46]</td>
</tr>
<tr>
<td>PEI-purine-CNT</td>
<td>100</td>
<td>50</td>
<td>170.0 Deng et al., 2019 [47]</td>
</tr>
<tr>
<td>PEI-CNT</td>
<td>100</td>
<td>50</td>
<td>170.0 Deng et al., 2019 [47]</td>
</tr>
<tr>
<td>TSP</td>
<td>16.1</td>
<td>30</td>
<td>140.0 Present study</td>
</tr>
<tr>
<td>TSP</td>
<td>85</td>
<td>30</td>
<td>181.0 Present study</td>
</tr>
<tr>
<td>TSP</td>
<td>100</td>
<td>30</td>
<td>198.0 Present study</td>
</tr>
</tbody>
</table>

a MBS = Molecular Basket Sorbent. b SBA = Santa Barbara Amorphous. c MCM-41 = Mobil Composition of Matter No. 41. d PE-MCM-41 = Pore-Expanded Mesoporous Silica. e Active phase of K₂CO₃ (35 wt%) supported by AC, activated coke, and silica (fixed bed). f Ceramic supported sorbents (35 wt% Na₂CO₃). g Metal oxhydroxide Carbon (biochar). h Chitosan graphene oxide composite. i Amine impregnated porous material. j Metal–organic materials with coordinative saturated metal centers and periodically arrayed hexafluorosilicate (SiF₆²⁻) anions.

Figure 8. (a) CO₂ capture capacity of TSP at different regeneration levels at 30 °C and 3.5 MPa pressure (Curves provided to guide the eye) SEM images of (b) CO₂-loaded pure TSP and (c) CO₂-loaded regenerated TSP.

Furthermore, topographical (morphological) information of CO₂-loaded pure TSP and CO₂-loaded regenerated TSP was obtained by SEM images and presented in Figure 8b,c, respectively. No significant change in the morphology of TSP was observed after CO₂ uptake as well as after regeneration (Figure 8b,c).
3.8. Scalability and Conceptual Prototype

In order to evaluate the scalability of the sorption process, the CO$_2$ capture capacity was also measured using 40 and 100 g of TSP. These experiments were carried out in a 250 cm$^3$ reactor at optimum experimental conditions (3.5 MPa pressure and 30 °C temperature) as obtained from a small-scale experiment. Figure 9a represents a comparison of the gas uptake capacity at three different scales of 4, 40, and 100 g TSP. It can be seen that the initial rate of gas capture is similar for all three experiments; however, the final CO$_2$ loading decreased with an increasing amount of TSP. An efficient design of a large-scale reactor should enhance the mass transfer and better CO$_2$ loading.

![Figure 9](image_url)

**Figure 9.** (a) Comparison of CO$_2$ capture capacity measured at small and larger scales in which 40 g and 100 g of TSP was used for large scale and 4 g for a small scale; (b) rate of gas uptake (mg of CO$_2$/g of sorbent/min) for the same system (Curves provided to guide the eye).

A conceptual flow diagram for post-combustion CO$_2$ capture at an industrial level using TSP as a solid sorbent has been shown in Figure 10. The system is composed of three fixed bed columns charged with TSP as a packing material. Flue gas coming from power plants are passed through the first column (using valve V-1) such that CO$_2$ preferentially gets captured by the packing material (online confirmation by gas chromatography). Nitrogen from the flue gas coming out from the first column is collected in a separate reservoir by opening valve 4 (V-4). After certain residence time in the first TSP column, the flue gas is allowed to go through the second column of TSP (using valve V-2). Simultaneously, NaOH solution is fed from the feeder to regenerate CO$_2$-loaded TSP in column 1 (using valve V-9). CO$_2$ emitted during the regeneration step is stored in a separate reservoir. Likewise, all three columns are used in a cyclic manner to capture CO$_2$ from the flue gas stream.
4. Conclusions

The kinetics of CO$_2$ capture using an inorganic sorbent (TSP) was studied in a fixed-bed configuration. Employing a flue gas mixture, it was observed that CO$_2$ capture capacity of TSP reached a local maximum at room temperature (~30 °C) across the range of temperatures studied. However, total pressure of a flue gas showed a negligible effect for gas uptake. TSP was found to be highly selective for CO$_2$ in a mixture of CO$_2$ and N$_2$. The selective capture of CO$_2$ over N$_2$ was found to be ~93%. Unlike other chemical sorbents, TSP is an inexpensive solid material. Some of the preliminary work reported in this study demonstrates that TSP can be regenerated, making it an ideal solid sorbent for CO$_2$ capture from a flue gas mixture.

Author Contributions: R.K. and A.K. designed the experimental work plan. T.S. performed all the experiments and helped in writing the manuscript. R.K. is an expert in carbon capture and gas separation research and reviewed the discussion. R.K. and Z.M.A. reviewed and revised the manuscript. All authors read and approved the manuscript before submission.

Funding: This research was funded by Science and Engineering Research Board, Department of Science and Technology, Government of India, grant number “EMR/2017/000810” and the Council of Scientific and Industrial Research (CSIR), India, grant number “CSC 0123”.

Acknowledgments: The authors gratefully acknowledge CSIR-National Chemical Laboratory (NCL), Pune, India (a part of this work was performed here). A. Kumar and T. Sakpal would like to acknowledge the financial support for this work from the Council of Scientific and Industrial Research (CSIR), India (CSC 0123). R. Kumar appreciates the financial support from the Science and Engineering Research Board, Department of Science and Technology, Government of India (EMR/2017/000810). Z.M. Aman acknowledges Chevron and Woodside for their support of the Professorial Chair in Long Subsea Tiebacks.

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

References


42. Sanz, R.; Calleja, G.; Arencibia, A.; Sanz-Pérez, E.S. Amino functionalized mesostructured SBA-15 silica for CO₂ capture: Exploring the relation between the adsorption capacity and the distribution of amino groups by TEM. *Microporous Mesoporous Mater.* 2012, 158, 309–317. [CrossRef]


© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).