ISSN : 0974 - 7451 Volume 12 Issue 2

Environmental Science
An Indian Journal
Current Research Paper

ESAIJ, 12(2), 2016 [065-069]

# Carbon dioxide capture by adsorption using sulfur doped carbon material

**G.Thayanidhi, R.Palani*, N.Meyyappan, R.Parthiban**
**Department of Chemical Engineering, Sri Venkateswara College of Engineering, Tamilnadu-602117, (INDIA)**
**E-mail : rpalani@svce.ac.in**

## ABSTRACT

Porous carbon materials have many technological and industrial applications. In this study, the porous sulfur doped carbon has been prepared using activated carbon and thiourea with potassium hydroxide as the activating agent. In order to obtain a better surface area, the process was repeated for different activation time and temperature. As a result, the material synthesized at 400°C with an activation time of 1 hour showed the maximum surface area of 783.57 $m^2$/g. Maximum carbon dioxide adsorption capacity of the sorbent was found to be 43.8 mg/g at an exposure time of 30 minutes. In addition, experimental data was modelled with different kinetics and from the regression coefficient, pseudo second order model was found to be well fitted with the experimental data.


## KEYWORDS

Adsorption;
Carbon dioxide;
Sulphur doped.

## INTRODUCTION

An energy efficient as well as a low cost method for selective carbon dioxide capture has a great importance in achieving a remarkable reduction in atmospheric carbon dioxide levels[1]. Many techniques like absorption, membrane separation, cryogenic distillation and adsorption are used for carbon dioxide separation. The most common method for $CO_2$ removal from flue gases involves the application of solid adsorbents[2]. Carbon dioxide could be adsorbed on modified Mg-Al-layered double hydroxides for about 1.36 mmol/g[3]. It had been reported that sulfur or nitrogen containing carbon based material can trap $CO_2$ eight times more than aqueous amines and is beneficial than any other method[4]. The acid base interaction and polar interactions of $CO_2$ are responsible for high adsorption capacity and high degree of pore utilization[5]. Doping of polythiophene on graphene yields an adsorbent with $CO_2$ adsorption capacity of 4.5 mmol/g at 298 K and 1 atm[6]. Graphene and other materials being costlier sources of carbon, some other carbon material can be used and can be synthesized at different activation time. Activation plays an important role in adsorption and increase in activation time favors the adsorbent surface area to some extent[7-9]. This was the motivation to synthesize a sulphur doped activated carbon where thiourea is the sulfur source. Activated carbon has wide applications that it is used even in adsorption of vapors from cigarette smoke[10]. Adsorption experiments and kinetic studies were carried out in thermo gravimetric analyser[11].

## EXPERIMENTAL

### Synthesis of adsorbent

To synthesize the carbon based adsorbent, known amount of activated carbon and thiourea were taken at different ratio and a ratio of 1:9was found to be optimum[6]. It was then dispersed in chloroform using a magnetic stirrer. To this solution, a coagulant namely 10g of ferric chloride dissolved in100ml chloroform was added. Then the mixture was left undisturbed for 12 hours. After 12 hours, 300 ml methanol was added and filtered. The obtained precipitate was suspended in 150 ml of 1M HCl at room temperature. The resulting solution was filtered and washed with deionised water until a neutral pH was obtained. Then the material was dried at 60°C for 5 hrs under vacuum.

The sorbent was activated using 7M KOH solution. The resulting solution was filtered and dried at 150°C. The obtained sample was divided into four samples namely $S_1$, $S_2$, $S_3$ and $S_4$. The activation time and temperature of each sample is shown in TABLE 1. After activation the samples were washed with HCl to remove excess KOH. It was then filtered, washed with deionised water and dried under vacuum at 80°C for 24 hours.

**TABLE 1 : Activation time and temperature of the samples $S_1$, $S_2$, $S_3$ and $S_4$.**

| Sample | Time(h) | Temperature(oC) |
|---|---|---|
| S1 | 3 | 150 |
| S2 | 5 | 150 |
| S3 | 1 | 400 |
| S4 | 1 | 500 |

### Characterization

The samples at different activation time and temperature were subjected to porosimetry analysis. BET surface area and pore size distribution were calculated by $N_2$ adsorption/desorption isotherm at 77 K using micromeritics ASAP 2020.

### $CO_2$ adsorption studies

#### • Experimental study

To carry out the adsorption studies at room temperature, a column was fabricated with a total length of 20 cm which is shown in figure 1. It has an inlet and outlet for carbon dioxide at the top and bottom respectively. The outlet of a $CO_2$ cylinder was connected to a rotameter followed by the reactor inlet. The middle part of the reactor has perforated plate smaller enough to hold the adsorbent that was tightly packed in the form of pellets. The gas was passed at a flow rate of 1.5 lpm at 0.2 kg/cm$^2$ for 30 minutes. The weight change for every 5 minutes was noted to determine the adsorption capacity of the sorbent.

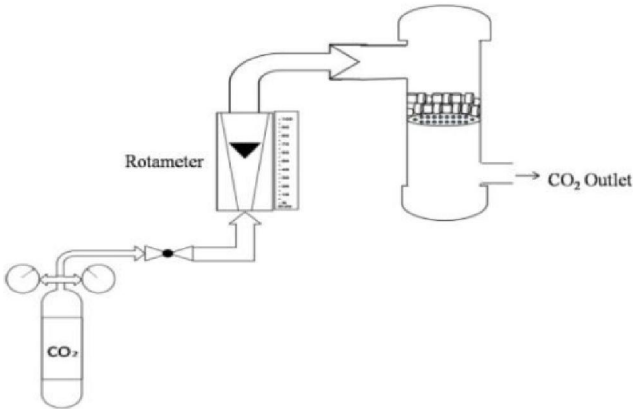


**Figure 1 : Experimental setup for $CO_2$ adsorption.**

#### • Thermo gravimetric analysis

The adsorption performance of the sulfur doped carbon material at high temperature was studied using TGA (50 Shimadzu). The sample was placed in the aluminium pan such that it was completely filled. The weight of the sample was read by the TGA itself. Isothermal studies were made at 100°C. $CO_2$ gas was passed at 50 cm$^3$/min for 1h. At time t, the adsorption capacity was calculated using the following relation in terms of mg of $CO_2$/g of adsorbent

$$\text{Adsorption capacity} = \frac{(W_t - W_0)}{W_0} \quad (1)$$

$W_t - W_0$ = change in weight, mg.
$W_0$ = initial weight of the sample, g.
After sometime, equilibrium was achieved.

## RESULTS AND DISCUSSION

### Effect of activation time

The typical isotherm of the carbon based samples $S_1$ and $S_2$ at different activation time are shown in figure 2a) and 2b). The sample $S_1$ activated for 3h was found to have a BET surface area of 651.0406 m²/gand the same for $S_2$ activated for 5h was 747.5832 m²/g. Further

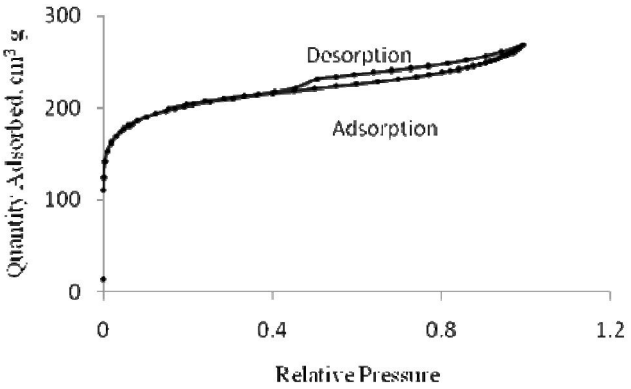


**Figure 2(a) : Isotherm of sample 1(3 h and 150 °C)**

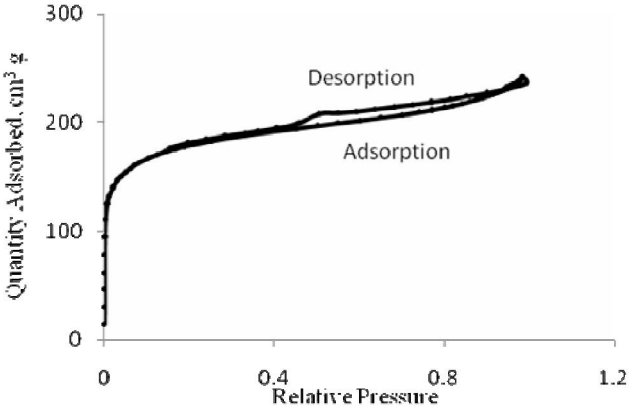


**Figure 2(b) : Isotherm of sample 2(5 h and 150 °C)**

increase in time had no effect on surface area. The samples were found to be mesoporous.

## Effect of activation temperature

The isotherm of $S_3$ and $S_4$ are shown in figure 3a) and 3b) respectively. $S_3$ and $S_4$ activated at 400°C and 500°C for 1h had a surface area of 783.57 $m^2/g$ and 90.56 $m^2/g$ respectively. An increase in temperature beyond 500°C resulted in the degradation of the material. The samples were reported to be mesoporous.

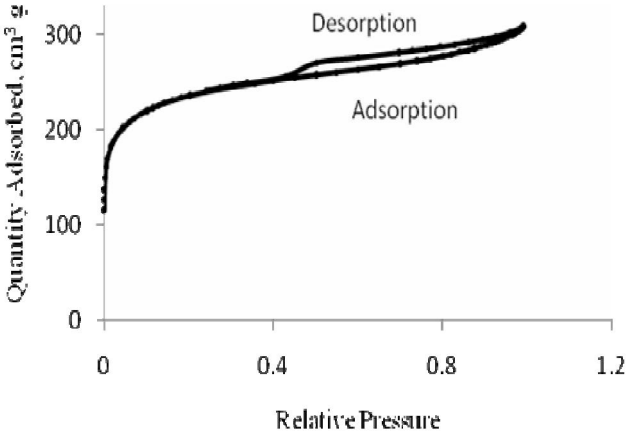


**Figure 3(a) : Isotherm of sample 3 (1 h and 400 °C)**

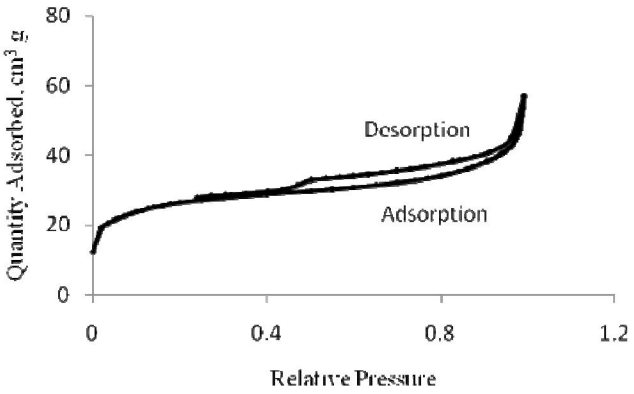


**Figure 3(b) : Isotherm of sample 4 (1 h and 500 °C)**

## Carbon dioxide adsorption

At room temperature, the adsorption capacity was 43.8 mg of carbon dioxide per gram of the adsorbent. This was carried out in a column packed with the sorbent that was exposed to carbon dioxide for 1hour to determine the adsorption capacity. In order to carry out the experiments at higher temperature TGA was used. At 100 °C, the adsorption capacity of the sample was found to be 6.4 mg/g. This shows that an increase in temperature does not favour adsorption. The quantity adsorbed is shown in TABLE 2

**TABLE 2 : Carbon dioxide adsorption capacity at different temperatures for 30 minutes**

| Time (min) | Weight of the Adsorbent at 30 °C (g) | Weight of the adsorbent at 100 °C (mg) |
|---|---|---|
| 0 | 5.206 | 7.185 |
| 5 | 5.315 | 7.200 |
| 10 | 5.364 | 7.213 |
| 15 | 5.428 | 7.224 |
| 20 | 5.434 | 7.231 |
| 25 | 5.434 | 7.231 |
| 30 | 5.434 | 7.231 |

## Kinetic studies

Lagergren pseudo first order model and pseudo second order model were performed in this work. The Lagergren pseudo first order model is expressed by,

$$\log(q_e - q_t) = \log(q_e) - \left(\frac{k_1}{2}.303\right)t \qquad (2)$$

Current Research Paper

Pseudo second order model is expressed by,

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{t}{q_t}\right)t \qquad (3)$$

where $q_e$ and $q_t$ are the quantity adsorbed per gram of the adsorbent (mg/g) at equilibrium and time t respectively. The pseudo first order model, pseudo second order model and the parameters estimated from them were shown in figure 4a, figure 4b and TABLE 3 respectively. A plot was made between t and log ($q_e$ – $q_t$) for pseudo first order and another plot was made between t and $t/q_t$.

The regression value states that the experimental data fits with the pseudo second order model

**Activation energy**

Since the physisorption involves the weak van derWaals forces, the activation energy is usually around 5 to 40 kJ/mol. Arrhenius equation is used to calculate

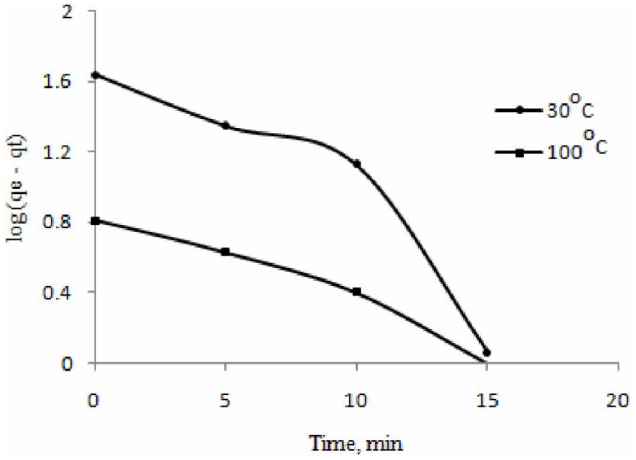


**Figure 4(a) : Pseudo first order model**

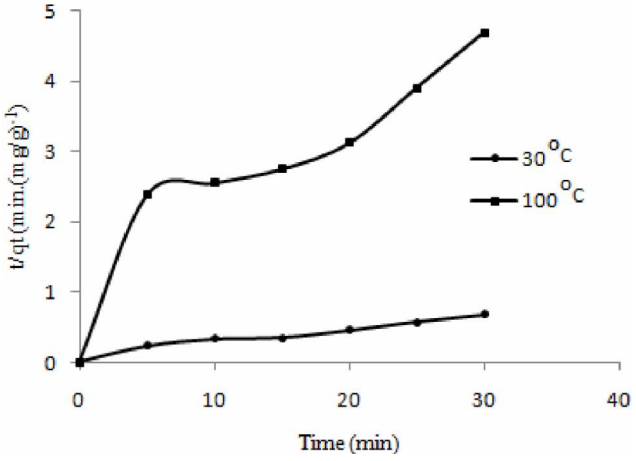


**Figure 4(b) : Pseudo second order model**

**TABLE 3 : Kinetic analysis at 30 and 100 degree Celsius**

| Kinetic model | Parameter | Temperature | |
|---|---|---|---|
| | | 30 °C | 100°C |
| Pseudo first order | $k_1$(1/min) | 2.289 | 0.113 |
| | $q_e$(mg/g) | 62.08 | 7.630 |
| | $R^2$ | 0.8633 | 0.7885 |
| Pseudo second order | $k_2$(g/mg min) | 0.0056 | 0.0182 |
| | $q_e$(mg/g) | 49.50 | 7.911 |
| | $R^2$ | 0.9542 | 0.8612 |

the activation energy. It is given by,

$$\ln k = \left(-E_a/RT\right) + \ln k_0 \qquad (4)$$

k is the rate constant of pseudo-second-order kinetic model (g/mg·min), $E_a$ is the adsorption activation energy (J/mol), R is the gas constant (8.314 J/mol·K), T is the adsorption temperature in Kelvin, and $k_o$ is the temperature independent factor (g/mg·min). A plot is made between lnk and 1/T, where the activation energy is given by the slope which is found to be 16kJ/mol.

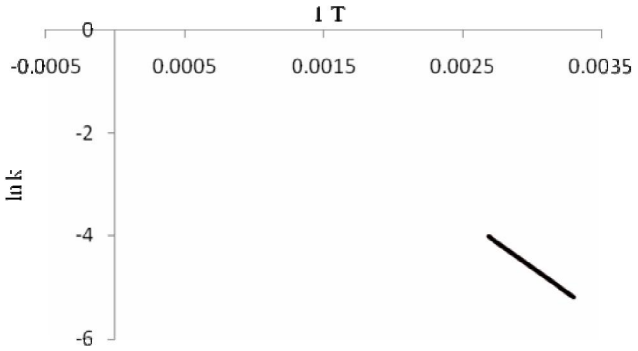


**Figure 5 : Arrhenius plot for activation energy**

## CONCLUSION

From the experimental work, it is concluded that an increase in activation time improves the adsorbent surface area while increasing the temperature beyond 400 °C results in degradation of the adsorbent. The prepared sulphur doped carbon material reported an adsorption capacity of 43.8 mg/g at room temperature and 6.4 mg/g at 100 °C which shows that low temperature favours adsorption. The kinetic studies

shows that the experimental data fits with pseudo second order model and the process is found to be physisorption as the activation energy is 16 kJ/mol

## ACKNOWLEDGEMENT

This work was supported by Sri Venkateswara College of Engineering, Department of Chemistry-IIT Madras and National Metallurgical Laboratory, Taramani.

## REFERENCES

**[1]** J.F.M.Orr; $CO_2$ capture and storage: are we ready? Energy Environ Sci., **2(5)**, 449–58 **(2009)**.

**[2]** R.V.Siriwardane, M.Shen, E.P.Fisher, J.A.Poston; Adsorption of $CO_2$ on molecular sieves and activated carbon. Energy Fuels 2001;15(2):279–84

**[3]** T.Dantas, V.Fernandes, A.Dos Santos, F.Bezerra, A.Arujo, A.Alves; $CO_2$ adsorption on modified Mg-Al layered double hydroxides. Adsorption Science & Technology, **33(2)**, 165-174 **(2015)**.

**[4]** Joseph Bennington, James Tour; New material could improve carbon capture of natural gas. Nat. Communications, **(2014)**.

**[5]** Mykola Seredych, Jacek Jagiello, Teresa J.Bandosz; Complexity of $CO_2$ adsorption on nanoporous sulfur-doped carbons – Is surface chemistry an important factor? Carbon, **74**, 207-217 **(2014)**.

**[6]** Humaira Seema, K.Christian Kemp, Nhien H.Le, Sung-Woo Park, Vimlesh Chandra, Jung Woo Lee, Kwang S.Kim; Highly selective $CO_2$ capture by S-doped microporous carbon materials. Carbon, **66**, 320-6 **(2014)**.

**[7]** Zhong Tang, M. Mercedes Maroto-Valer, Yinzhi Zhang; $CO_2$ capture using anthracite based sorbents. Fuel Chem., **49(1)**, 298-9 **(2004)**.

**[8]** Y.Zhu, S.Murali, M.D.Stoller, K.J.Ganesh, W.Cai, P.J.Ferreira et al.; Carbon-based supercapacitors produced by activation of graphene. Science, **332(6037)**, 1537–41 **(2011)**.

**[9]** E.Raymundo-Pin ero, P.Azis, T.Cacciaguerra, D.Cazorla-Amoro, A.Linares-Solano, F.Beguin; KOH and NaOH activation mechanisms of multiwalled carbon nanotubes with different structural organization. Carbon, **43(4)**, 786–95 **(2005)**.

**[10]** Peter Branton, Robert Bradley; Activated Carbon for the adsorption of vapour from cigarette smoke. Adsorption Science & Technology 2010; 28(1): 3-21.

**[11]** Nor Adilla Rashidi, Suzana Yusup, Lam Hon Loong; Kinetic Studies on Carbon Dioxide Capture using Activated Carbon. Chemical Engineering Transactions, **35**, 361-366 **(2013)**.