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## **Synthesis and Characterization of 13X Zeolite/ Activated Carbon Composite**

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**Abstract :** In this study, composite materials consisting of Activated Charcoal (AC) and Molecular sieves (13X Zeolite) were prepared for application in carbon dioxide capture and storage. The composite, composed of AC and 13X Zeolite with weight percentage ratios 5:95 and 25:75 were synthesized using Sol-gel method. The samples were heat treated in furnace at 310 °C at two different ramping rates of 5 and 10°C/minute. The composites characterized by XRD, Scanning electron microscope, FTIR and Thermo gravimetric analysis for phase analysis, morphology, presence of functional groups and thermal stability.

**Keywords:** Zeolite 13X; Activated Carbon; Sol-gel Method; Nanocomposite.

### **Introduction**

The carbon dioxide level in the atmosphere is increasing rapidly and a large part of this is contributed by the fossil fuel based power plants<sup>1</sup>. Separation of the CO<sub>2</sub> gas from the mixture of gases emitted by the power plants is a technological challenge. The current technology used for carbon capture and storage is mainly based on alkanolamine solutions which adsorbs the carbon dioxide by the process of chemisorptions<sup>2-4</sup>. Adsorption efficiency of amine based adsorbers is very high but they are energy intensive. During regeneration they can consume 10 to 30% energy of the power plants output. Besides being expensive, Amine based adsorbers are highly corrosive and chemically unstable at higher temperatures<sup>5</sup>.

Like chemisorptions, physisorption is also a reversible process but it consumes less energy for regeneration of the adsorbed. The objective is to find a material which selectively adsorbs CO<sub>2</sub> gas from the flue gas and have very high surface area. Current research focus is on porous activated carbon, Zeolite and Metal Organic Framework (MOF)<sup>5-10</sup>. Activated carbon is highly porous material with large surface area and pore accessibility but the pore sizes are non-uniform. It is thermally and chemical very stable and are usually hydrophobic<sup>11</sup>. It has better carbon dioxide selectivity at higher pressure and temperature. On the other hand, Zeolites are aluminosilicate with a very uniform porous structure and very good CO<sub>2</sub> adsorption capacity at low temperature and at high or low pressure. Zeolites are hydrophilic, so exhibits instability in presence of water. A 13X Zeolite/AC composite posses the properties of both zeolites and activated carbon. In this study, crystallinity, thermal stability and morphology of the 13X Zeolite/AC composite is presented.

## Experimental

### Material

Commercially available purified molecular sieves (13X Zeolite) were purchased from Himedia Labs Pvt. Ltd. The molecular sieves were prepared as a powder sample by crushing and air drying. Activated Charcoal (AC) and Aluminum hydroxide was obtained from Merck specialties Pvt. Ltd., and S.D. fine chemical Ltd., respectively.

### Synthesis process

The composites were prepared by Sol-gel method using Activated Charcoal (AC) and 13X Zeolite. A colloidal solution was formed by mixing 95 wt% of 13X Zeolite and 5 wt% of Activated Charcoal in deionized water. The solution was stirred and then kept in ultrasonic bath for 10 minutes at room temperature. After ultrasonication, 1.12 wt% of  $\text{Al}(\text{OH})_3$  was mixed in the solution and left for 24 hours. The solution was washed several times with deionized water and then dried in a hot air oven at  $80^\circ\text{C}$ . The dried sample was transferred to a ceramic crucible and placed in a furnace at  $310^\circ\text{C}$  for 3 Hours at a ramp rate of  $5^\circ\text{C}/\text{m}$ . The sample was allowed to cool down to room temperature and used for characterization. The prepared composite was named as S1 (ACZB595). By Similar procedure, another sample S2 (ACZB2575) was prepared using 25 wt% of AC and 75 wt% of 13X Zeolite.

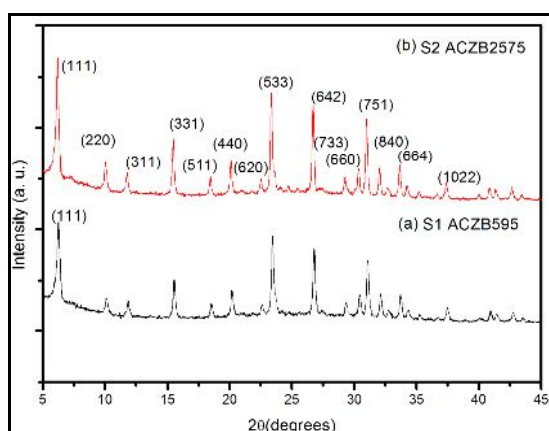
### Characterization

The crystallographic structure of the composite was determined by powder X-ray diffraction (X' port powder X ray system) using  $\text{CuK}\alpha$  radiation ( $\lambda=1.5406\text{\AA}$ ). Data collection was performed in the  $2\theta$  range  $5-100^\circ$  with a step size of  $0.017^\circ$ . SEM images were obtained with (S-3400 N Hitachi) Scanning electron microscope. FT-IR spectra were taken with Alpha -T FT-IR spectrometer in the range of  $400-4000\text{ cm}^{-1}$  using kBr pellet technique with a resolution of  $2\text{ cm}^{-1}$  and TGA/DSC analysis was performed using under  $\text{N}_2$  atmosphere.

## Results and Discussion

### XRD Results

Figure 1 shows the XRD pattern of the synthesized 13X Zeolite and Activated Charcoal composite for sample S1 (ACZB595) and S2 (ACZB2575). The diffraction maxima of the samples are typical of faujasite type 13X Zeolite (JCPDS No: 12-0228). The XRD peak indexed at  $2\theta = 6.26^\circ$  in Fig. 1(a) and at  $2\theta = 6.18^\circ$  in Fig. 1(b) corresponds to (111) plane of the 13X Zeolite<sup>12</sup>.

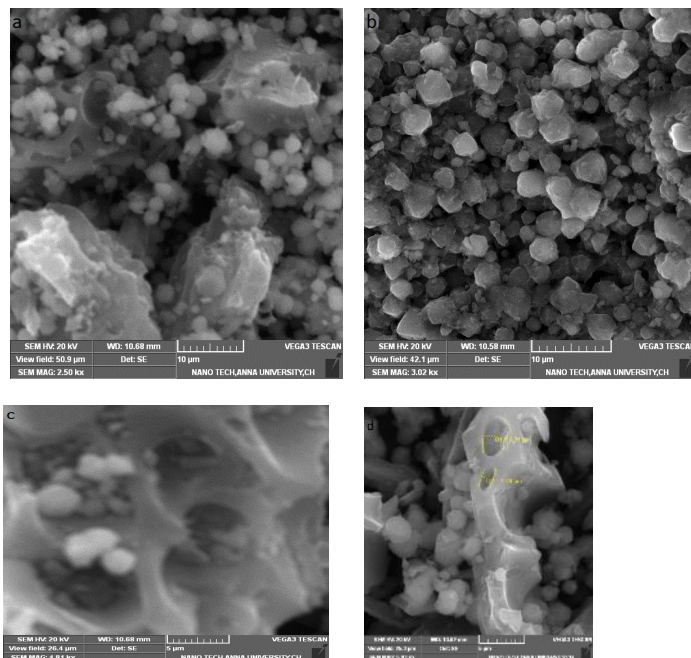


**Fig. 1: XRD patterns of (a) S1 (ACZB595) and (b) S2 (ACZB2575) composites**

The XRD pattern confirms the crystalline structure of the composites S1 and S2, consisting of 5 wt% and 25 wt% of amorphous activated charcoal respectively<sup>12-13</sup>.

## SEM Analysis

Fig. 2 shows the morphology of the 13X Zeolite/AC composite, investigated by Field emission – Scanning Electron Microscope. Fig. 2 (a) and (b) displays the wide range of crystal sizes which consist of non uniform particles and irregular surfaces. The particle morphology of the composite having 95 wt% 13X Zeolite is octahedral, which is the case for FAU type framework structures<sup>12</sup>.

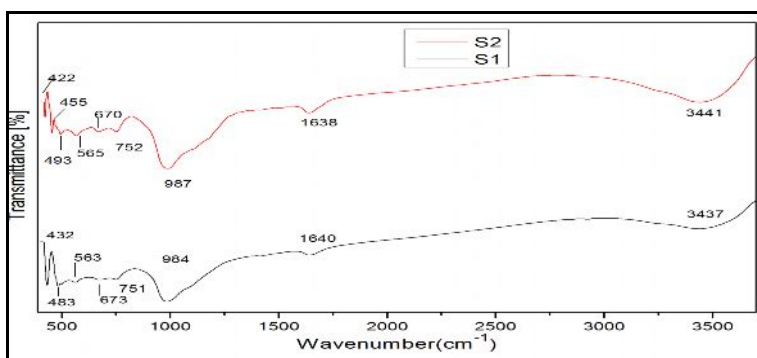


**Fig. 2:** FE-SEM images of 13X Zeolite/AC composite, S1 ACZB595 (a), (b), (c), (d).

Fig. 2 shows the porous structure of the composite; pores of 1 to 5  $\mu\text{m}$  are shown in fig. (c) and (d). Some of the particles seen in fig. 2 are of irregular shape and non-uniform sizes may be attributed to the presence of Activated charcoal<sup>14</sup>.

## FT-IR

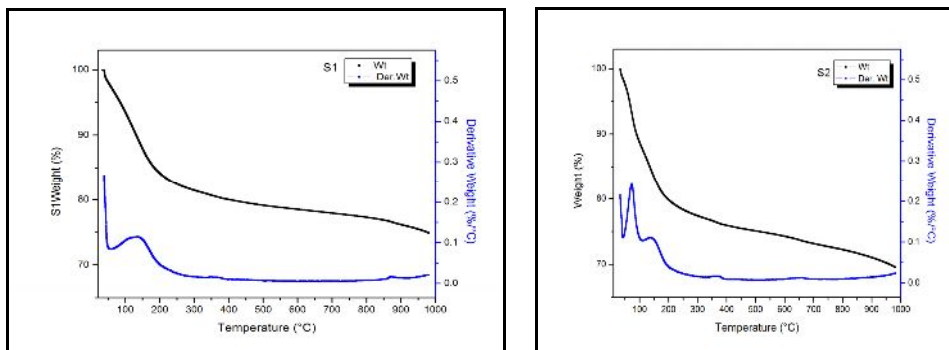
Fourier transforms infrared spectroscopy of the 13X Zeolite/Activated Charcoal composites are shown in Fig. 3. The observed bands at S1 (673, 751  $\text{cm}^{-1}$ ) and S2 (670, 752  $\text{cm}^{-1}$ ) corresponds to symmetric stretching mode ( $\leftarrow\text{O T O}\rightarrow$ ) of typical band of 13X Zeolite (where T = Si or Al). In symmetric stretching mode, peaks 673  $\text{cm}^{-1}$  and 670  $\text{cm}^{-1}$  are attributed to internal tetrahedral stretch and 751  $\text{cm}^{-1}$ , 752  $\text{cm}^{-1}$  are attributed to external linkage symmetric stretch. Peaks at S1 (984  $\text{cm}^{-1}$ ) and S2 (987  $\text{cm}^{-1}$ ) corresponds to asymmetric stretch. The bands around 483 and 493  $\text{cm}^{-1}$  may be attributed to  $\text{TO}_4$  bending or vibration of the external linkage to  $\text{TO}_4$  tetrahedral<sup>15</sup>. Transmission Peaks at 563  $\text{cm}^{-1}$  and 565  $\text{cm}^{-1}$  are attributed to the double six member rings (D6R) and peaks at 432  $\text{cm}^{-1}$  and 455  $\text{cm}^{-1}$  are attributed to T-O bend<sup>16-17</sup>. The bands observed at 1638  $\text{cm}^{-1}$  and 1640  $\text{cm}^{-1}$  are attributed to the H-O-H bending mode of water molecule. The strong bands at 3437  $\text{cm}^{-1}$  and 3441  $\text{cm}^{-1}$  are due to O-H stretching mode of the water molecules present in the composite<sup>18</sup>.



**Fig. 3:** FT-IR spectra of (a) S1 (ACZB595) and (b) S2 (ACZB2575) composites.

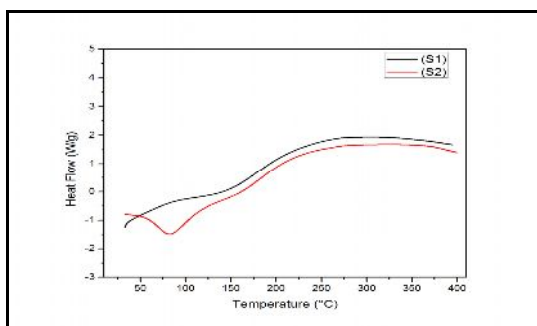
## TGA/DSC Analysis

Thermo gravimetric analyzer was used to investigate the thermal properties of the composite. Fig. 4 (a) and (b) shows the weight loss and derivative weight loss percentage of the composite vs. temperature. The composites weighting 8.6mg (S1) and 9.571 mg (S2) were heated up to 1000 °C under N<sub>2</sub> environment to dehydrate and analyze the thermal stability. As shown in the fig. 4 (a) and (b), a sharp weight loss of 17% occurs for sample S1 and 20% weight loss for sample S2 up to a temperature of 200 °C; this weight loss can be attributed to desorbing free mobile water molecules in the pores of the composites. Between 300 to 400°C the weight loss for both the samples is 1.4 %, which can be attributed to desorption of water from the hydrated cation complexes. Inside the Zeolite pores, water molecules get bounded to the framework of oxygen<sup>19</sup>. The total weight loss for samples, S1 and S2, up to 1000°C is 25 and 30 wt% respectively.



**Fig. 4: TGA curves for (a) S1 (ACZB595) and (b) S2 (ACZB2575) composites.**

Fig. 5 (a) and (b) shows the differential scanning calorimetry curve for both the samples. The DSC curves show the endothermic peaks due to desorption of water from the micro pores of the composites. The total change in enthalpy for sample S1 is 92.66J/g and for S2 is 113.47 J/g<sup>17</sup>.



**Fig. 5: DSC curves for (a) S1 (ACZB595) and (b) S2 (ACZB2575) composites.**

## Conclusion

13X Zeolite/AC composite were successfully prepared by Sol-gel method. The powder XRD analysis confirms the crystalline structure of the composite having a sharp peak corresponding to (111) plane, which is also the characteristic peak of 13X Zeolite. FESEM images show the porous structure of the composite having micro pores and particles of various sizes. FESEM observations also revealed particle morphology as octahedral. FT-IR results show the characteristic peaks of FAU type 13X Zeolite for symmetric and asymmetric modes. TGA/DSC indicates the thermal stability of the composites up to a very high temperature. Thus, the present study concludes that addition of amorphous activated charcoal up to 25 wt% in to the 13X Zeolite/AC composite does not affect the crystallinity of the composite significantly.

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