

## CO<sub>2</sub> emission and its mitigation by adsorption on zeolites and activated carbon

Climate change due to increased atmospheric concentration of greenhouse gases (GHGs) is a cause for concern worldwide<sup>1</sup>. The major contributor to enhanced greenhouse effect is CO<sub>2</sub>. By ratification of the Kyoto protocol (KP), developed countries have agreed to reduce their GHG emissions by 5.2% below the 1990 levels by 2012. Power plants are major sources of CO<sub>2</sub>, emitting about 63% of the global industrial emissions<sup>2</sup>. Currently the world's primary energy need is met mostly by fossil fuels. In addition, coal is projected to be a dominant fuel<sup>3</sup>. CO<sub>2</sub> capture from large point sources (LPS) such as power plants is a potential emission mitigation option. A 500 MW coal-fired power plant with 40% efficiency emits about 2.5–3.5 million tons (mt) CO<sub>2</sub> per year<sup>4</sup>. Thus, even a few CO<sub>2</sub> capture plants of such capacity can lead to significant reduction in country-level total emissions.

The power and industry sectors jointly dominate global CO<sub>2</sub> emissions, with 60% share in total emissions. CO<sub>2</sub> from these sectors is generated by boilers and furnaces, and is emitted from large exhaust stacks. According to a study, LPS in India largely contribute to CO<sub>2</sub> and SO<sub>2</sub> emissions (above 65%)<sup>5</sup>. These emissions come primarily from fossil-fuel combustion. Sector-wise contribution to Indian LPS CO<sub>2</sub> emission in 1995 was power plants (47%), followed by cement (9%) and steel plants (6%). Earlier<sup>6,7</sup>, Indian emissions were reported as 778 Tg CO<sub>2</sub>.

CO<sub>2</sub> mitigation can be achieved by three means: improving energy efficiency, use of alternative clean fuels (hydrogen, biodiesel, etc.) and by CO<sub>2</sub> capture and sequestration. Though CO<sub>2</sub> capture is considered a short-term option, it seems to be the only feasible solution from the sustainable development point of view. This is because, coal, being projected as the dominant fuel in the near future, existing emission sources can be coupled with CO<sub>2</sub> capture plants as the technology becomes available.

From the post combustion flue gases, CO<sub>2</sub> can be captured by a variety of techniques like chemical absorption, physical absorption, membrane separation and cryogenic separation. Amine scrubbing technology has been in vogue for over 60 years in chemical and oil industry for removal

of hydrogen sulphide and CO<sub>2</sub> from gas streams. There are many disadvantages of this technique like high energy penalty, solvent degradation, corrosion and need for pretreatment to remove SO<sub>x</sub> and NO<sub>x</sub>. Membrane separation and cryogenic separation are involved with high-energy requirement in the compression step. Thus there is need to explore new separation techniques.

The intermolecular forces between gases such as CO<sub>2</sub> and the surface of certain solid materials permit separation by adsorption. Selective adsorption of the gases depends on temperature, partial pressure, surface forces and adsorbent pore size.

Many researchers have examined adsorption capacity on an equilibrium basis only. However, the dynamic regime of operation is equally important as a material characteristic. This is because most applications of adsorption are run only up to partial bed saturation because of the adsorption dynamics. Therefore, in this study, CO<sub>2</sub> adsorption capacities were determined as a function of time for zeolite 13X, zeolite 5A and activated carbon (AC). Breakthrough adsorption studies were carried out, where feed gas containing CO<sub>2</sub> is passed over the adsorbent and the time required for CO<sub>2</sub> to be detected in the adsorption column outlet (termed

breakthrough time) is monitored. Adsorption by material up to that point is called its breakthrough (BT) adsorption capacity. The breakthrough time (min) is multiplied by CO<sub>2</sub> flow rate (ml/min) and product expressed per g of adsorbent gives the BT adsorption capacity (ml/g). Thus, the material with highest adsorption capacity will take the longest breakthrough time.

Zeolite 13X, zeolite 5A and AC have high surface area, pore volume and commercial availability. The surface areas of zeolite 13X and AC calculated by N<sub>2</sub> adsorption using Brunauer, Emmett and Teller (BET) method are 615 and 917 m<sup>2</sup>/g respectively.

The experimental set-up used in the present study is shown in Figure 1. CO<sub>2</sub> and He gases were fed through mass flow controllers (MFC). A mixer was provided to mix the two gas streams. Adsorbent was placed in a glass tube (diameter = 9 mm and height = 30 cm) and heated using a tubular furnace equipped with a PID temperature controller. Feed gas and product stream were fed through an auto sampler valve to gas chromatogram (GC) using sample selector valve for selecting the desired stream.

In a typical experimental protocol, the adsorbents were dried in an oven at

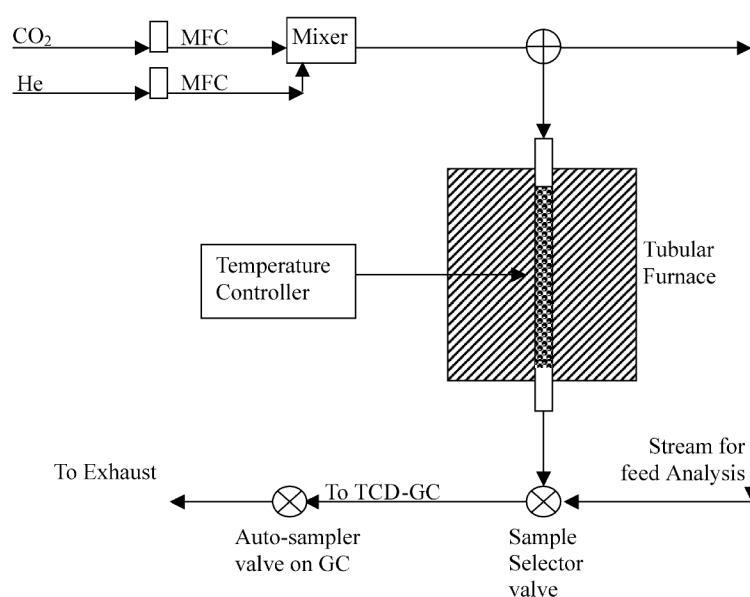
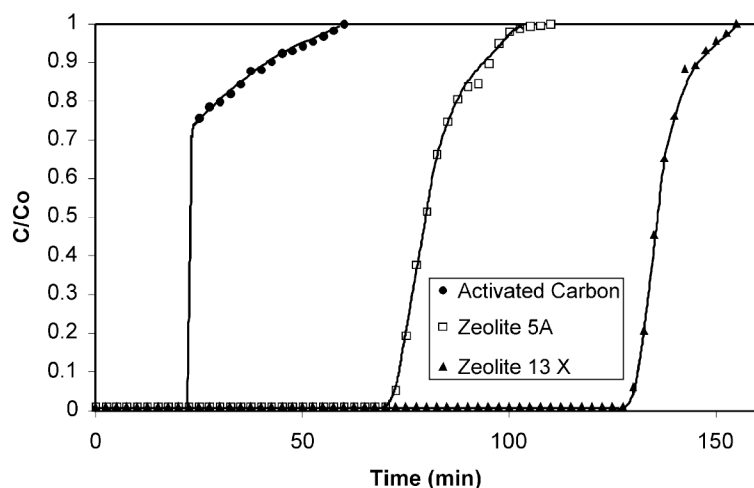


Figure 1. Experimental set-up for breakthrough adsorption study.



**Figure 2.** Comparison of adsorption capacities of activated carbon, zeolite 5A and zeolite 13X at 30°C.

**Table 1.** Adsorption capacity of materials

Adsorbent	Pretreatment temperature (°C)	Adsorption temperature (°C)	Breakthrough adsorption capacity (ml/g)
Activated carbon	140	30	16
		50	12
		80	8
		120	4
Zeolite 13X	140	30	28
		50	18
		80	10
		120	4
Activated carbon	200	30	18
Zeolite 13X	200	30	100
Zeolite 5A	200	30	56

120°C for 3 h. Then 10 g of the material was filled in the adsorption column and ceramic wool was filled at the top and bottom of the material to ensure good packing. The material was pretreated at 200°C or 140°C in He gas at a flow rate of 20 ml/min for 6 h. The material was then cooled to a predetermined adsorption temperature. Feed gas stream consisting of 15 mol% CO<sub>2</sub> in the balance He was passed over the material and the outlet was analysed continuously. Feed gas flow rate (CO<sub>2</sub> = 8, He = 44 ml/min) was 52 ml/min. The effluent gas was analysed using thermal conductivity detector–gas chromatogram (TCD–GC) on Porapak-Q column and a pneumatically controlled sample injector. Experiments were continued until saturation was reached, i.e. outlet stream CO<sub>2</sub> concentration equals that of the inlet.

Zeolite 13X was pretreated at 140°C and 200°C to study the effect of pretreatment temperature on adsorption capacity at 30°C. The BT adsorption capacity of zeolite 13X had dropped from 100 ml/g for pretreatment at 200°C to 28 ml/g at 140°C. The difference can be attributed to better removal of volatiles, moisture and other impurities that are pre-adsorbed on strongly polar zeolite 13X at higher pretreatment temperatures. The breakthrough curves obtained are in agreement with those from earlier published literature<sup>8</sup>. Pretreatment temperature of 140°C and 200°C had little effect on adsorption capacities of AC, where adsorption capacities were 16 and 18 ml/g respectively. This indicated that nonpolar AC was free from preadsorbed species even at 140°C.

Adsorption capacities of AC, zeolite 5A and zeolite 13X were compared at

30°C after pretreatment at 200°C. Figure 2 shows the fraction of CO<sub>2</sub> concentration in the effluent gas from the adsorption column,  $C$ , over that in the feed,  $C_0$ . As can be seen, zeolite 13X showed highest BT adsorption capacity of 100 ml/g followed by zeolite 5A at 56 ml/g and AC at 18 ml/g.

AC pretreatment was carried out for each run at 140°C and adsorption was studied at four temperatures (30, 50, 80, 120°C). The adsorption capacity decreases with temperature. This is because adsorption, being an exothermic process, is favoured at lower temperatures. The BT adsorption capacity dropped from 16 ml/g at 30°C to 4 ml/g at 120°C. Similarly, for zeolite 13X, BT adsorption capacity dropped from 28 ml/g at 30°C to 4 ml/g at 120°C. Table 1 shows adsorption capacities of materials under different conditions. Typical range of power plant flue gas temperatures is 120–160°C. Cyclic CO<sub>2</sub> adsorption capacity of about 2 mmol/g is desired for the plant-scale application of these materials<sup>9</sup>. Thus, some new modification techniques like functionalization and pore engineering for the application of materials in CO<sub>2</sub> removal from flue gas are required. These are being pursued at NEERI, Nagpur to improvise adsorption efficiency of materials at high temperatures.

Attempts are being made to enhance adsorbent affinity of CO<sub>2</sub> over N<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>O, with better physico-chemical stability towards other potentially fouling components (NO<sub>x</sub>, SO<sub>x</sub>) of industrial emissions. The materials being developed show encouraging results for capture of CO<sub>2</sub>. Further improvisations in their selectivity and affinity are being attempted by functionalizing zeolites as well as mesoporous materials based on silicates and carbons with different types of sterically hindered and unhindered amines.

Zeolite 13X, zeolite 5A and AC were evaluated for CO<sub>2</sub> breakthrough adsorption capacity from a 15 mol% stream. Under experimental conditions, these materials had capacities 100, 56 and 18 ml/g respectively at 30°C. Zeolite 13X with highest adsorption capacity comes out as the best adsorbent among the studied materials. However, at 120°C, the BT adsorption capacity of zeolite 13X dropped to 4 ml/g, similar to that of AC. Thus for the application of these materials in CO<sub>2</sub> removal from power plants flue gas (with typical temperatures in the range 120–160°C), novel modification techniques

need to be considered. Efforts are being made at NEERI to functionalize the materials to enhance adsorption efficiency.

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## Screening and isolation of cyclosporine-related compound producing soil fungi from the Western Ghats, Tamil Nadu

The fungal kingdom has enormous biodiversity, with around 70,000 known species and an estimated total of about 1.5 million species, presenting a wide scope for further research. The fungal species are known for the production of enzymes and secondary metabolites, which have not been exploited completely. The best-known fungal secondary metabolites that are subjected to commercial production are the  $\beta$ -lactam antibiotics. The fungal genus *Tolypocladium*, first described by Gams in 1971, encompasses fungi imperfecti occurring in soil or litter habitats. This species is well characterized by white, hyaline or bright coloured, relatively slow-growing cottony colonies<sup>1,2</sup>.

The species *T. inflatum* is unique and important as it produces the 11-amino acid cyclic peptide compound, cyclosporine<sup>3</sup>. This product was identified in the 1970s originally as an anti-fungal and later exploited as an immunosuppressant, revolutionizing organ transplant surgery<sup>4</sup>. However, the quantity of production of these metabolites varies with strains of *T. inflatum*<sup>5,6</sup>. Here we report *T. inflatum*-related fungi from the soil of the Western Ghats, producing cyclosporine-related metabolite. We have isolated wild-type fungus showing a three-fold increase in cyclosporine-related metabolite production compared to the MTCC reference culture (Ti) obtained from IMTECH (Chandigarh). Furthermore, these metabolites were tested for their antimicrobial activity and compared with commercially available cyclosporine drug (*cys* Sandimmune Neoral, Novartis).

Six hundred soil samples were collected in sterile plastic bags from various places in the Shola forest, Kodaikanal hills, Western Ghats (lat. 10°12'N, long. 77°30'E), Tamil Nadu, India. The soil samples were initially dissolved in sterile water and the supernatant was subsequently plated in potato dextrose agar medium. The suspected colonies were then plated in the selective malt extract agar medium. Three isolates of *Tolypocladium* spp. were finally isolated from the suspected colonies. Fungi were identified by analysing the morphological structure, colour of the colonies (white, red, orange) and their spores by agar block technique. The microscopic and morphological characteristics of the isolates (Ti-1, Ti-2 and Ti-3) were compared with Ti received from IMTECH for confirmation.

These fungal isolates were grown on malt extract medium for 6 days at 28°C. The red and orange pigmented colonies were selected and grown in 250 ml Erlenmeyer flask containing 100 ml of malt extract broth and were incubated at 28°C with an aeration speed of 200 rpm for 14 days. The cultures of the three different isolates and Ti were inoculated in separate sets of 100 ml malt extract medium in 250 ml Erlenmeyer flask. From these cultures, samples were collected at 2 days interval from the first day till the twelfth day. The samples were centrifuged (650 g for 15 min), pelletized and dry biomass was estimated. The supernatant was filtered through Sartorius cellulose membrane filter (0.2  $\mu$ m) to get cell-free extract for the estimation of cyclosporine.

Presence of cyclosporine was characterized by High pressured or High Performance Liquid Chromatography (HPLC) technique (Central Electrochemical Research Institute, Karaikudi).

Subsequently, it was compared with the *cys* drug for confirmation. Secondary metabolite produced by isolates *T. inflatum*, Ti-1, Ti-2, Ti-3, Ti and *cys* drug showed antimicrobial activity against a battery of microorganisms (Kirby–Bauer disc diffusion method).

For testing the antimicrobial activity, bacterial cultures such as *Escherichia coli*, *Proteus vulgaris*, *Klebsiella pneumoniae*, *Serratia marcescens* and *Salmonella* spp., and fungal cultures such as *Aspergillus niger*, *Cryptococcus neoformis*, *Penicillium chrysogenum*, *Aspergillus flavus*, *Candida albicans* and *Trichoderma virgii* were used. The lawn was made in Mueller–Hinton Agar for bacterial cultures and Potato Dextrose Agar for fungal cultures. Nitrocellulose paper discs of size 0.6 mm were made, dipped in the filtrate and placed at the centre of a petri dish plated with the test microbial cultures. The plates were then incubated at 37°C for 24 h and 24°C for 48–72 h for the bacterial and fungal plates respectively.

The minimal inhibitory concentration (MIC) for Ti-1, Ti-2, Ti-3, Ti and *cys* drug was assessed (Agar dilution technique). Results showed that the isolate Ti-3 had maximal antimicrobial activity compared to other isolates (Ti-1 and Ti-2), but lower than Ti. Both Ti-3 and Ti have more microbicidal activity than the commercially available *cys* drug (Table 1). Secondary