

“DEVELOPMENT OF CARBON ADSORBENTS USING PHYSICAL ACTIVATION FOR CO₂ CAPTURE”

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Abstract:

Increase in concentration of Carbon dioxide (CO₂), which is major greenhouse gas, is one of the challenges of the 21st century. Carbon Capture and storage (CCS) technology is attracting higher interest which can lower down this increase in CO₂ concentration. The available capture technologies are absorption, adsorption and many more. Mature technology like absorption has used most but having disadvantages like high regeneration cost, equipment corrosion. Adsorption is believed to be economical due to its easy application, less energy penalty and low equipment cost but suitable low-cost adsorbent need to be developed. Carbon based adsorbents are found to be attractive but very less efforts have been made for development of carbon adsorbents using waste materials. Thus, objectives of our work are to overcome this gap, in which direct carbonization followed by physical activation in development of carbon adsorbents at lower costs and improve the texture properties and CO₂ capture capacity.

Keywords – Waste Carbon material, PET (Polyethylene terephthalate), Physical Activation,

I. INTRODUCTION AND PROBLEM DEFINITION



The increasing demand for energy is causing a rise in the emissions of greenhouse gases and growing environmental concern over global warming and climate change. CO₂ is by far the most important GHG (Green House Gases). As a result of anthropogenic CO₂ emissions, atmospheric concentrations have risen by 35 % from the pre-industrial level of 280 ppm to 387 ppm in 2008, primarily as a consequence of the use of fossil

fuel. According to the IPCC Special Report on CO₂ Capture and Storage, CCS will contribute to 15-55 % of the cumulative mitigation effort worldwide until 2100 (IPCC 2005). CO₂ emissions in power generation can be reduced by three different routes that are at different stages of development: post-combustion, pre-combustion and oxy-fuel combustion. Among the technologies considered for post and pre-combustion capture, absorption, adsorption, membrane separation and cryogenic distillation are the most promising. So, in our current semester project we are using the adsorption technique for CO₂ capture.

PROBLEM DEFINITION

The level of CO₂ has reached up to 441 ppm in 2019. Highly increasing CO₂ levels are because of strong dependence on fossil fuels for meeting the energy requirements, thereby resulting in increase in average global temperature and changes in weather patterns. Stabilization of CO₂ concentration at the level of 450 ppm is considered as threshold to avoid the overshoot of average global temperature rise by 2°C by the year 2100, Hence immediate action needs to be taken to these increasing CO₂ concentrations.

Possible solutions for this can be:

(1) Using renewable energy sources and increasing usage of low carbon fuels, including natural gas, hydrogen or nuclear power. Apply geo engineering approaches, e.g. deforestation and reforestation. Carbon dioxide capture, storage and utilization (CSU) system.

(2) Carbon capture and storage (CCS) is the process of capturing carbon dioxide (CO₂) from large point sources, such as fossil fuel power plants, transporting it to a storage site, and depositing it where it will not enter the atmosphere, normally an underground geological formation.

(3) The aim is to prevent the release of large quantities of CO₂ into the atmosphere (from fossil fuel use in power generation and other industries).

(4) Cost of CO₂ capture and separation is a significant portion (~70–80%) of the total sequestration cost; hence development of an efficient and cost-effective CO₂ capture technology holds the highest priority in the field of CCS.

II. LITRATURE SURVEY

1] Dynamic CO₂ capture by carbon adsorbents: kinetics, isotherm and thermodynamic studies:

In this work, we report carbon adsorbents obtained from MCM-41 (mesoporous zeolite) template and high nitrogen content, melamine-formaldehyde resin as starting material by using Nano casting technique. The material was carbonized and physically activated with CO₂ at different temperatures to obtain different carbon adsorbents. Synthesized adsorbents were characterized using various techniques for their elemental, surface and textural properties. Effect of Nano casting technique was seen by the increase in textural property such as the surface area and pore volume of the adsorbent prepared at 700°C were found to be maximum, i.e. 193.28 m²g⁻¹ and 0.32 cm³g⁻¹, respectively. This was not seen for the sample prepared by direct carbonization (MF-700). Also, development of nanostructured carbon adsorbents was confirmed from XRD and TEM results. Adsorption of CO₂ on carbon adsorbents was evaluated between temperatures (30-100°C) and concentrations (5-12.5%) in a dynamic fixed bed column. Adsorbent prepared at 700°C exhibited highest CO₂ uptake of 0.64

mmol g^{-1} due to high basicity confirms from X-ray photoelectron spectroscopy. Both surface and texture chemistry have a strong influence on the CO₂ adsorption performance. The CO₂ adsorption kinetic study was performed by using three kinetic models and was found that a fractional order fits well with the experimental data with maximum error% of 3.68%. Regeneration study of the adsorbent was carried out by using multiple adsorption-desorption cycles and found that the adsorbent exhibited easy regenerability and stability over multiple cycles. The Temkin isothermal model fitted best among three isotherm models indicating the heterogeneous surface of adsorbent surface. The isosteric heat of adsorption is found to be 15.05 kJ mol⁻¹, which indicates physisorption process and also supports easy regenerability of the adsorbent. Thermodynamic parameters such as ΔH and ΔG were found to be -5.7 kJ mol⁻¹ and 0.033 kJ mol⁻¹ K⁻¹. The thermal energy estimated for CO₂ desorption is 2.15 MJ per kg CO₂. An effective, nitrogen enriched carbon adsorbents have been synthesized from MF resin using mesoporous zeolite as a template through Nano-casting technique, by carbonization and activation at different temperatures. Synthesized adsorbents were characterized using various techniques and found that carbonization and activation temperature have a major impact on textural and surface properties. XRD and TEM results confirm development of nanostructured carbon adsorbents. Elemental analysis, FTIR and XPS confirmed the presence of nitrogen content. The adsorbent prepared at 700 °C showed 0.64 mmol g⁻¹ CO₂ uptake at 30 °C and 12.5% CO₂ concentration. Decrease in CO₂ uptake capacity with temperature confirms exothermic adsorption process. Furthermore, adsorbents show complete regenerability, stability and better selectivity for CO₂. Among three kinetic models, fractional-order-model with error% values within the range of 3.68% provided the best description at various temperatures. The isotherm showing CO₂ adsorption on the adsorbent surface obeying Temkin isotherm indicates heterogeneous nature. Exothermic and spontaneous nature was suggested from thermodynamics parameter values. Energy needed for regeneration, calculated from the isosteric heat of adsorption and sensible heat is equal 2.15 MJ per kg CO₂, which is equivalent to 0.028 kg CO₂ (as energy penalty).

2] A review on Post-Combustion CO₂ Capture Using Solid Sorbents:

Post-combustion CO₂ capture from the flue gas is one of the key technology options to reduce greenhouse gases, because this can be potentially retrofitted to the existing fleet of coal-fired power stations. Adsorption processes using solid sorbents capable of capturing CO₂ from flue gas streams have shown many potential advantages, compared to other conventional CO₂ capture using aqueous amine solvents. In view of this, in the past few years, several research groups have been involved in the development of new solid sorbents for CO₂ capture from flue gas with superior performance and desired economics. A variety of promising sorbents such as activated carbonaceous materials, microporous, mesoporous silica or zeolites, carbonates, and polymeric resins loaded with or without nitrogen functionality for the removal of CO₂ from the flue gas streams have been reviewed. Different methods of impregnating functional groups, including grafting techniques and modifying the support materials, have been discussed to enhance the performance of the sorbents. The performance characteristics of the solid sorbents are assessed in terms of various desired attributes, such as their equilibrium adsorption capacity, selectivity, regeneration, multi cycle durability, and adsorption-desorption kinetics. The potential of metal-organic frameworks (MOFs) is also recognized to determine whether these novel materials provide better CO₂ adsorption capacity under low CO₂ partial pressure. A

comprehensive critical review and analysis of the literature on this subject has been carried out to update the recent progress in this arena. A comparison of different solid sorbents at different stages is made. It also includes a brief review on techno-economic analysis and design aspects of sorbent bed contactor configuration. Finally, a few recommendations have been proposed for further research efforts to progress post-combustion carbon capture. Finally, as more scientific data on these sorbents become available, the system modeling, optimization, and techno-economic analysis needed to estimate the potential improvement in solid sorbents capture technologies will be more precise and reliable.

3] Development of adsorbents for CO₂ capture from waste materials, a review.:

In recent years, a number of scientific papers have been published on the use of residues from industrial and agricultural operations to develop adsorbents for CO₂ capture at low, medium, and high temperatures. This is mainly because these waste materials are low-cost and abundant, and may contribute to a reduction of the total costs in carbon capture technologies. In addition, environmental concerns may also be addressed by developing strategies that can use these waste materials instead of burning or sending them to landfills. This review analyses the recent progress made in the development of CO₂ adsorbents made from waste precursors. The different preparation approaches developed for the synthesis of adsorbents, including type of raw waste-material, experimental methods, and further modifications, are reviewed.

4] Comparative adsorption study on carbons from polymer precursors:

The effect of the precursor polymer on nitrogen adsorption properties, pore size distribution and the hydrophilic /hydrophobic character of both the pyrolyzed char and the activated carbon was studied in the case of three basically different polymers, i.e. polyacrylonitrile, polyethylene terephthalate and cellulose. Pyrolyzed samples were produced from these polymers and activated by steam at 900°C. After a 50% burn-off, the pore volume and the specific surface area increase significantly and the pore size distribution is determined by that of the pyrolyzed char, i.e. the starting polymer. The activated sample derived from polyacrylonitrile is microporous, while the other two carbons contain both micro- and mesoporous. The properties of polymer carbons prepared from the different precursors depend on the starting polymer. The behavior of PET during the manufacturing is similar to CEL as well as to PAN. The products obtained in the carbonization process show a low pressure hysteresis characteristic to non-rigid structures. This feature is practically eliminated during the activation. The activation significantly increases the surfaces. The highest improvement is achieved in the case of PAN of low oxygen content, but its surface is still far beyond the other two carbons made of polymers with high oxygen content. The pore size distribution in the micro pore range if there is any can be described by bimodal functions. As a result of the activation process, the distribution function can be applied for the PAN-derived sample as well. In the other two cases the position, the ratio of the peaks as well as their intensity change. In PET the position of the first peak shifts toward smaller size, but the position of the other one is not affected by the activation. The ratio of the smaller pores increases from ca. 63% to 72% by the activation. In CEL char only the intensity and the ratio of the peaks changes, their position is not affected. The ratio of the smaller pores decreases from 93% to 80% during the activation process. The finer pores show the lowest size inactivated PAN, where the wider pores have about the same size as in the other two samples. In this case the ratio of the smaller pores is only 58%. The variation of the pore size during the activation supports

that the pores are formed by the out burn of forming graphite layers. Characteristic mesoporosity was experienced only in PET and CEL derivatives, especially in their activated form. Activation creates pores which are equally available for methanol and benzene. The surface of all the samples is heterogeneous, exhibiting affinity toward both methanol and benzene, but in different range of concentration. The regime of benzene affinity increases with the activation and the shift of the azeotropic composition is different in each polymer carbon. The more preferential adsorption of benzene is the result of the extension of the graphite-like region and/or the increasing amount of benzophilic CO₂-complexes. No direct relation could be established between the measured parameters and the concentration of O and N. The N content seems not to effect the immersion enthalpy in benzene. In contradiction to the monolayer being formed on the nitrogen-free surfaces, a multilayer adsorption takes place on the PAN surface from benzene methanol mixtures.

III. IMPLEMENTATION

(1) Why Post-Combustion?

We preferred post-combustion technique for capturing CO₂ because it gets rendered to the surviving power plants without further upgradation. I found out that adsorption is the technique of adhesion of liquid.

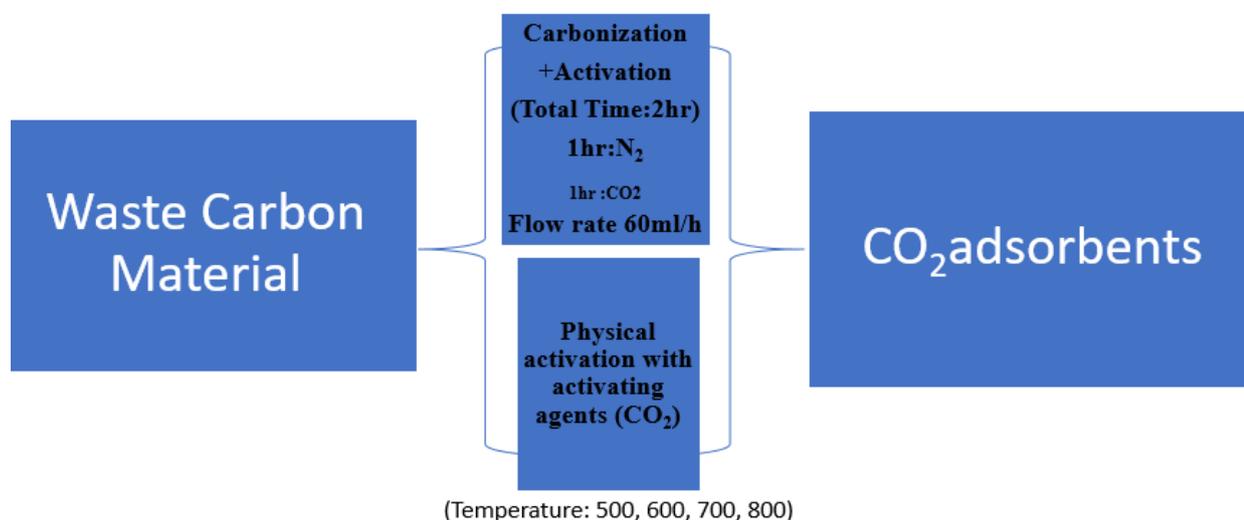
(2) Why Adsorption?

We prefer adsorption since in CO₂ capture via carbon-based adsorbents has a superiority of complete regeneration of adsorbents over multiple adsorption cycles, high surface area, good thermal/mechanical stabilities, and hydrophobicity while in absorption there were the drawbacks such as high corrosion, oxidation–reduction of the absorbent, and energy penalty for regeneration.

(3) Why Plastic waste?

Around 15000 tons of plastic is generated every day. Disposal of plastic waste especially (Polyethylene terephthalate) i.e. PET wastes a serious challenge for waste and environment management as it takes around 500-700 years to biodegrade. There is need to search new processes to use PET wastes due to the vast amount of solid waste generated and to avoid generation of hazardous emissions.

IV. PREPARATION AND ANALYSIS



(1) First of all we took our PET sample in pellet form to perform physical activation. The equipment which we used was the tubular furnace.

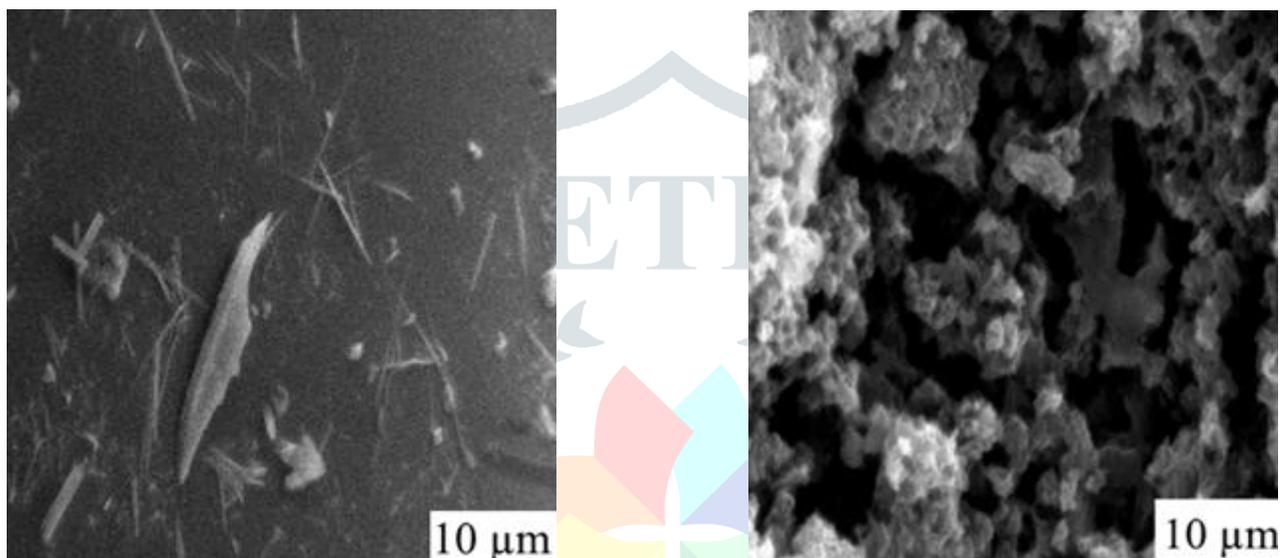
(2) The material was then carbonized for 2 hours with 1 hour CO₂ and 1 hour N₂. The temperature while carrying this process was 700°C.

(3) The flow of CO₂ and N₂ gases in above step was 60ml/min.

(4) The product we got from the process was PET-700.

ANALYSIS

(SEM Scanning Electron Microscopy)



(Figure-1)

(Figure-2)

(Pores of Carbon adsorbents from SEM)

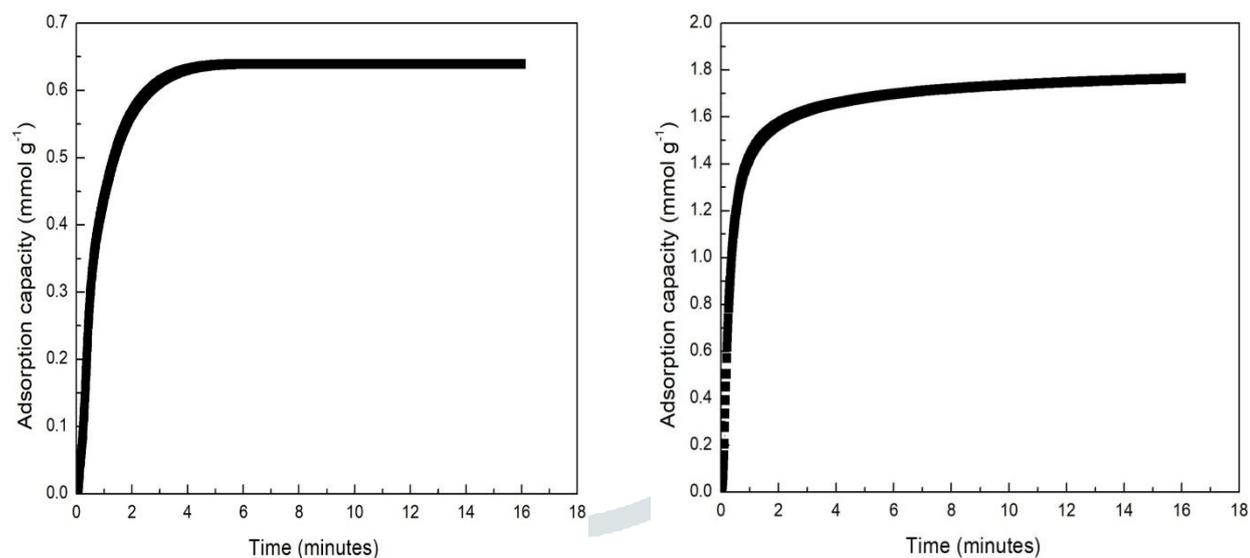
(1) The SEM result of our reference carbon material is shown in Figure-1 which shows the presence of very less amount of pores.

(2) The Figure-2 shows that after activation the porosity of the sample is increasing which is due to physical activation performed with large amount of CO₂ and N₂ gases.

V. RESULT

Elemental Content	O	C	H	N
PET-R	43.24	23.63	1.23	31.9
PET-700	48.03	22.27	1.29	28.41

CO₂ ADSORPTION STUDY



(Figure-A: Before activation)

(Figure-B: After activation)

- (1) The adsorption capacity of the sample (Figure-A) before activation is lesser due to lower porosity.
- (2) The adsorption capacity of the sample (Figure-B) after activation is higher due to process of physical activation which grants higher porosity.

VI. CONCLUSION

- (1) High nitrogen containing carbon adsorbents have been synthesized from PET.
- (2) Synthesized adsorbents were characterized using various techniques and found that carbonization and activation temperature has a major impact on surface properties.
- (3) Presence of nitrogen content was confirmed from elemental analysis. The adsorbent synthesized at 700°C exhibited highest CO₂ uptake of 1.8mmolg⁻¹.
- (4) This shows the synthesis process used in this work produces an effective adsorbent surface property.

VII. REFERENCES

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