CARBON DIOXIDE Capture Using Graphene Oxide Membrane and Its Usage

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ABSTRACT

With increase in the emissions of carbon dioxide gas (CO₂), Global warming and climate change have become the deadliest issues to conquer and hence efforts to reduce its atmospheric concentration is made globally. In order to have a positive effect on our environment by reducing carbon dioxide emissions to the atmosphere, carbon dioxide capture and utilization or storage is being researched upon recently to make it more efficient and economical. In this paper, the literature survey gathers light upon the different methods of carbon dioxide capture, its advantages and disadvantages, study on membrane technology, graphene membrane properties and synthesis and suitable graphene based composite membrane for carbon dioxide capture. In this paper, capturing and usage of carbon dioxide gas is discussed along with the economics of it. Sodium chloride (NaCl) and glycerin was recovered from a process waste by-product of an industry named Cardolite for the usage of captured CO₂. The purity of NaCl after recovery was determined using flame photometric estimation of Sodium ion content and titration method using Silver Nitrate for the Chloride ion content & the total purity was found. Sodium carbonate is formed by adding ammonium bicarbonate to the obtained NaCl solution which is one of the methods to form sodium carbonate from NaCl. The other method of forming sodium carbonate from NaCl is by bubbling carbon dioxide through ammoniacal brine solution. This method is highlighted in the carbon dioxide kit in which CO₂ gas is filtered using membrane technology-Graphene Oxide (GO) composite membrane. Graphene oxide is prepared using modified Hummer’s method. The obtained GO was confirmed using various analytical methods viz. SEM, EDAX, and XRD. The GO composite membrane is placed in the carbon dioxide capturing kit and the mixture of gases is passed through. The filtered CO₂ is then tested for its concentration using gas sensors and hence process is repeated till the required efficiency. The pure CO₂ is made to pass through recovered NaCl to obtain sodium carbonate Na₂CO₃ which can be used for commercial purposes.

Keywords: Carbon dioxide capture, Graphene oxide, Solvay process, EDAX, XRD analysis, GO composite, PEBAX Membrane

1. INTRODUCTION

Excessive amount of carbon dioxide emissions from industries and their inevitable outcomes have led to climate change which is of utmost concern today. In accordance with the freight of global warming, one of the ways to reduce carbon dioxide is by carbon capture and sequestration. By using the technique of carbon capturing, CO₂ can be withdrawn from the emissions, which would stop it from entering the atmosphere.

The seized carbon dioxide can then be recycled or can be stored in gas or liquid form, this process is known as sequestration. High-performance membranes can be implemented to trap the Carbon dioxide. These are polymer filters that can pick out CO₂ specifically from a mixture of gases, such as those emitted from a factory's flue. These membranes are environmentally compatible, they don't produce any unwanted substances, they can boost chemical processes, and can be used in a decentralized fashion. To minimize the CO₂ emissions, the membranes are regarded as the most efficient route in terms of energy.

1.1. Methods of Carbon Dioxide Capture

The most popular methods of carbon capturing are membrane separation technology and MEA (monoethanolamine) absorption method.

Membrane separation processes have gained momentum in the membrane separation technology fields. They provide a domination over conventional separation methods. Easy scale up of membrane processes is possible on account of their modular and compact design. They are able to pass on distinct components in a mixture selectively which is the major reason why it’s used in gas separation processes. They operate under moderate temperature conditions which leads to mild treatment of the product. They are also energy efficient systems. The positives of membrane separation technology involve energy savings, can be easily integrated with other processes and operations, clean technology, environmentally compatible, gives rise to high quality products with waiving operating parameters, good flexibility in designing systems with easy scale up, no additives and chemicals. Along with the pros, there are also cons like it has short membrane lifetime, generally low selectivity, fouling, concentration polarization [3].
The second method is CO\textsubscript{2} capture utilizing amine-based solvents, mostly monoethanolamine (MEA). MEA is used extensively as the major solvent for carbon dioxide capture in post-combustion processes like from fossil fuel plants. The advantages of MEA absorption method are that they have a multi-pollutant capture system, use of a non-hazardous and non-volatile solvent, lower fouling and corrosion issues with that amine compounds as compared to the membrane separation process. Apart from this, there are several disadvantages like high pollutant removal, solid and slurry management, slow absorption rate [4].

Comparing the two methods, MEA absorption method has high energy consumption requirements for the recovery of the solvent and scale up is also difficult [5]. For our project, we considered the membrane technology method of carbon dioxide capture as graphene based membranes have sky-scraping capability in separation of CO\textsubscript{2} from the other gases.

1.2. Graphene Based Membranes

Graphene based membranes are widely being used for water purification, air purification and desalination purposes. This is due to the properties of graphene having mono-atomic thickness, good mechanical strength, thermal stability & chemical inertness. Graphene is used as nanoporous graphene, graphene laminates or graphene based composites for gas purification purposes. It is inferred from the paper that compared to nanoporous graphene, graphene oxide membranes are better due to hydroxyl, epoxy and carboxyl groups present in graphene oxide. The selectivity for CO\textsubscript{2} offered by GO composite membranes is better than that of the pristine graphene oxide laminates because of the showing of a strong conjugated \pi system existing in these membranes. Selectivity of GO membranes can be increased by addition of amine or oxygen functional groups. In the purpose of achieving high quality membranes, spin coating technique should be used [6].

Shen and his team synthesised a GO-PEBA membrane on PVDF substrate [9]. Due to the presence of -N-H-, H-N=O, and O=C=O functional groups in PEBA, high selectivity of CO\textsubscript{2} is observed [4]. Hence, GO-PEBA membrane using PVDF as substrate is to be synthesised for the carbon dioxide capture kit.

2. MATERIALS & METHODOLOGY

2.1. Materials

2.1.1. To Obtain NaCl from Cardolite Waste Solid Sample

Methanol, filter paper, funnel, glass rod, oven to dry the wet NaCl sample obtained, beakers.

2.1.2. To Obtain Sodium Bicarbonate from NaCl Using Ammonium Bicarbonate

Ammonium bicarbonate, beakers, glass rod, deionized water, NaCl obtained from the waste solid sample.

2.1.3. To Prepare Graphene Oxide using Modified Hummers Method

Graphite powder, sulfuric acid, phosphoric acid, potassium permanganate, hydrogen peroxide, hydrochloric acid, measuring cylinders, shaker, centrifuge, deionized water, beakers, conical flask, petri dish, oven to dry the wet graphene oxide.

2.1.4. To Prepare GO-PEBA Membrane on PVDF Substrate

GO powder prepared from Hummers method, ethanol, water, PEBBA pellets, PVDF substrate, spray/spin coating setup, beakers, glass rod, heating mantle.

2.1.5. Carbon Dioxide Capture Kit

GO-PEBA membrane on PVDF substrate, carbon dioxide gas, pressure regulator, non-return valves, safety valve, pipes, steel boxes, gas sensors, pressure gauge, NaCl obtained from Cardolite sample, deionized water, ammonia gas, drain valve, flow meters.

2.2. Methodology

2.2.1. To obtain NaCl from Cardolite Waste Solid Sample

The method used for separation of NaCl from glycerine is Filtration. Methanol is added to the sample obtained from Cardolite industry and is then filtered. The NaCl is then collected from the filter paper and dried in the oven to get a moisture free NaCl sample.

2.2.2. Solvay’s Process

1. To obtain sodium bicarbonate from NaCl using ammonium bicarbonate

Sodium Chloride is reacted with Ammonium bicarbonate to produce sodium bicarbonate with ammonium chloride as the by-product.

\[
\text{NaCl} + \text{NH}_4\text{HCO}_3 \leftrightarrow \text{NaHCO}_3 + \text{NH}_4\text{Cl}
\]

2. To obtain sodium bicarbonate from NaCl using ammonia and carbon dioxide

Sodium chloride is made to react with ammonia and carbon dioxide. This reaction gives rise to sodium bicarbonate and ammonium chloride.

\[
\text{NaCl} + \text{CO}_2 + \text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NaHCO}_3 + \text{NH}_4\text{Cl}
\]

3. To obtain sodium carbonate by heating sodium bicarbonate

The dry product- Sodium bicarbonate is then heated in a furnace which gives rise to sodium carbonate. The carbon dioxide can be recycled again to use in the process.

\[
\text{NaHCO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O}
\]

2.2.3. To Prepare Graphene Oxide Using Modified Hummers Method

Modified Hummers method is used to synthesise graphene oxide from pure graphite powder. To the mixture of sulfuric and phosphoric acid,
pure graphite powder is added along with potassium permanganate to oxidise the graphite powder to oxides. This mixture is stirred or shaken for 6 hours. Hydrogen peroxide is added to it to eliminate excess of potassium permanganate. This is further cooled down. HCl and deionized water are added gradually and the solution is centrifuged. The supernatant liquid is separated and the sample is dried in the oven to achieve graphene oxide powder.

2.2.4. To Prepare GO-PEBA Membrane on PVDF Substrate

GO is dispersed in ethanol and water by ultrasonication. PEBA pellets are added to the GO solution which is further sprayed onto the PVDF substrate.

![Flowsheet for the fabrication of Graphene Oxide](image)

**Figure 2.** Flowsheet for the fabrication of Graphene Oxide

2.3. Procedure

2.3.1 Cardolite Sample Preparation

150 g Sample containing NaCl and Glycerin was separated for testing individual purity and for further usage of the compounds obtained. The solid was diluted using methanol and the liquid so obtained, was filtered separating the methanol-glycerin mixture from NaCl. Purity of NaCl was determined using Flame Photometric Estimation of Sodium ion content and Titration method using Silver Nitrate for the Chloride ion content & was found to be 99% purity. [4]

![Separated glycerin& sodium chloride](image)

**Figure 3.** Separated glycerin& sodium chloride

2.3.2. Modified Solvay Process to Produce Sodium Bicarbonate

58g of recovered NaCl was dissolved in water to make a NaCl solution of 1 mole. 79g of ammonium bicarbonate was then added to the NaCl solution to give ammonium chloride and ammonium bicarbonate. Precipitate of sodium bicarbonate is formed which is filtered out and dried. It is weighed and calculation of the number of moles of sodium bicarbonate is done. Theoretically, one mole of sodium bicarbonate should be formed.

\[
\text{NaCl} + \text{NH}_4\text{HCO}_3 \to \text{NaHCO}_3 + \text{NH}_4\text{Cl} \\
\text{NaHCO}_3 \to \text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2
\]

2.3.3. Preparation of Graphene Oxide (GO)

Graphene oxide (GO) was synthesised making use of the modified hummers method using pure graphite powder. In this method, 27 ml of sulfuric acid (H$_2$SO$_4$) and 3 ml of phosphoric acid (H$_3$PO$_4$) (volume ratio 9:1) were mixed and made to stir for several minutes after which 0.225 g of graphite powder was dropped into the solution mixture under stirring condition. 1.32 g of potassium permanganate (KMnO$_4$) was then added gradually into the solution. This mixture was shaken for 6 hours until the solution turned dark green.

![Dark green mixture, shaken for 6 hours](image)

**Figure 4.** Dark green mixture, shaken for 6 hours

0.675 ml of hydrogen peroxide (H$_2$O$_2$) was enumerated slowly by stirring for 10 minutes to eradicate excess of KMnO$_4$. The reaction was found to be exothermic, hence it was allowed to cool down. 10 ml of hydrochloric acid (HCl) and 30ml of deionized water (DIW) was added and centrifuged at 2500 rpm for 15 minutes. Supernatant layer was decanted and the obtained residue was washed with a mixture HCl and Water thrice. The solution was kept for drying in an oven maintained at 90°C for 1 day, for obtained dried graphene oxide powder. The GO powder was analysed using SEM and XRD analysis. 5 batches of GO powder were prepared using modified Hummers method and 0.8g of GO powder was obtained totally.
2.3.4. Preparation of GO Membrane

10g of PVDF was dissolved in 100ml of DMA at 180°C to form a clear viscous solution. 0.1g of GO powder was added to this and sprayed to the cellulose acetate membrane.

2.3.5. Preparation of GO-PEBA on PVDF Membrane

This will be done by dispersing GO powder in ethanol & water in 70:30 ratio to form 0.1 wt % GO solution with sonication of 1 hour. PEBA pellets will be added to it with continuous stirring at 80 degree Celsius for 12 hours. This mixture will then be cast on PVDF substrate [9].

2.3.6. CO₂ Capture Kit to Produce Sodium Carbonate Implementing Graphene Oxide Membrane

This is a small scale model that can be implemented first to check the efficiency and performance which later can be used in industries for large scale purposes. The filtered carbon dioxide gas is passed into a closed container through an inlet pipe from the CO₂ cylinder. A graphene oxide membrane is inserted which lets carbon dioxide gas pass through it because of Knudsen Diffusion. The CO₂ is collected in a chamber following the membrane [11]. From this compartment, a connection is made to another compartment having NaCl solution. Ammonia gas is passed to this, hence forming sodium carbonate using Solvays process. Gas pressure regulator is connected with its outlet passage which is also connected to the first compartment. When the inlet suction is closed, exhaust is opened hence releasing the carbon dioxide gas which didn’t pass through the membrane. CO₂ gas sensor modules will be used to analyse the CO₂ content in the inlet and outlet and the efficiency of the membrane will be calculated.

3. Results & Discussion

3.1. SEM, EDAX, and XRD Analysis Image Result

3.2. Results and Inference from SEM, EDAX, and XRD

1. From the SEM analysis, GO particle size was found to be between 12.73-22μm.

2. Comparing the graphite and GO chemical analysis, it is observed that the carbon content has decreased from 98 to 66.3% and the oxygen content has increased from 0 to 27.57%. Hence graphite has been oxidized to graphene oxide.

3. From the XRD results, a sharp tall peak was observed at 10 degrees and it is known that GO forms a peak at 10 degrees. Hence, GO formation can be confirmed.

3.1. GO-PVDF on Cellulose Acetate Membrane Spray Coating Result

Cellulose Acetate membrane was consumed by PVDF substrate which shows that they are not compatible. GO-PEBA would be more suitable as a membrane and compatible with the PVDF substrate.
Table 1. Chemical analysis of graphite

| Element | Weight % |
|---------|----------|
| C K     | 98.0     |
| Fe K    | 0.4      |
| S K     | 0.1      |
| P K     | Traces   |
| Ash content | 0.5 |

Particle size - 100 mesh

Table 2. Chemical analysis of GO

| Element | Weight % | Atomic % |
|---------|----------|----------|
| C K     | 66.30    | 74.25    |
| O K     | 27.57    | 23.18    |
| Al K    | 0.63     | 0.31     |
| Si K    | 2.27     | 1.09     |
| Ca K    | 1.05     | 0.44     |
| Cl K    | 1.40     | 0.53     |
| Fe K    | 0.77     | 0.18     |

4. CONCLUSION

4.1. Recovery of NaCl

NaCl and Glycerin were obtained from Cardolite industry in the form of waste solid. Purity of NaCl was found to be 99.9%, and was further reacted with ammonium bi-carbonate to produce sodium bicarbonate.

4.2. Graphene Oxide Synthesis, its Characterization, and Membrane Fabrication

Graphene oxide was synthesised using Modified Hummers method and was analysed using scanning electron microscopy, EDAX and X-ray diffraction setup. The particle size of graphene oxide in SEM was found to range between 12.73-22μm. The XRD analysis of graphene oxide resulted in a sharp peak at 10 degrees which infers that GO is produced.

From literature survey, it was observed that GO-PEBA on PVDF membrane was a suitable membrane to proceed the project with.

4.3. Carbon Dioxide Capture from Flue Gas in Industries

Graphene oxide membrane GO-PEBA on PVDF substrate to be used to separate carbon dioxide from the flue gas. The flue gas is cooled and then filtered to remove ash and other small solid particles. The gas mixture is then regulated to the GO based composite membrane such that only carbon dioxide passes through the GO based composite membrane. CO₂ gas sensors and flow meters are used to measure the CO₂ content and flow rate. Ammoniacal brine is formed by passing ammonia gas through NaCl solution. This CO₂ is then sent to a chamber where it is bubbled through the ammoniacal brine to form sodium bicarbonate. This is the Solvay’s process. The sodium bicarbonate formed is then heated at 110 Degree Celsius to get sodium carbonate. The ammonium chloride formed in this process can be used as a fertilizer or ammonia can be recovered from ammonium chloride by heating it. CO₂ captured can also be used to create energy or useful chemicals using suitable catalysts.

Prevention of leakage of ammonia and CO₂ gas in the Solvay process should be taken care of, otherwise this factor leads to air pollution.

CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest related to the publication of this article.

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Figure 9. XRD results of GO
REFERENCES

[1] K. M. Wagialla, I. S. Al-Mutaz, and M. E. El-Dahshan, “The manufacture of soda ash in the Arabian Gulf,” Int. J. Prod. Econ., vol. 27, no. 2, pp. 145–153, 1992, doi: 10.1016/0925-5273(92)90007-T.

[2] N. I. Zaaba, K. L. Foo, U. Hashim, S. J. Tan, W. W. Liu, and C. H. Voon, “Synthesis of Graphene Oxide using Modified Hummers Method: Solvent Influence,” in Procedia Engineering, 2017, vol. 184, pp. 469–477, doi: 10.1016/j.proeng.2017.04.118.

[3] P. Onsekizoglu, “Membrane Distillation: Principle, Advances, Limitations and Future Prospects in Food Industry,” in Distillation - Advances from Modeling to Applications, 2012.

[4] G. Liu, L. Kou, C. Li, “Absorption performance for CO2 capture process using MDEA-AMP aqueous solution,” 2nd International Conference on Advances in Energy Resources and Environment Engineering, pp. 01201, 2017.

[5] F. Vega, M. Cano, S. Camino, L. M. G. Fernández, E. Portillo, B. Navarrete, “Solvents for Carbon Dioxide Capture,” Carbon Dioxide Chemistry, Capture and Oil Recovery, pp. 142-163, 2018.

[6] A. Ali, R. Pothu, S. H. Siyal, S. Phulpoto, M. Sajjad, and K. H. Thebo, “Graphene-based membranes for CO2 separation,” Mater. Sci. Energy Technol., vol. 2, no. 1, pp. 83-88, 2019, doi: 10.1016/j.mset.2018.11.002.

[7] J. Lyu, X. Wen, U. Kumar, Y. You, V. Chen, and R. K. Joshi, “Separation and purification using GO and r-GO membranes,” RSC Advances, vol. 8, no. 41. pp. 23130–23151, 2018, doi: 10.1039/C8RA03156H.

[8] X. He, “A review of material development in the field of carbon capture and the application of membrane-based processes in power plants and energy-intensive industries,” Energy, Sustainability and Society, vol. 8, no. 1. 2018, doi: 10.1186/s13705-018-0177-9.

[9] J. Shen, M. Zhang, G. Liu, K. Guan, and W. Jin, “Size effects of graphene oxide on mixed matrix membranes for CO2 separation,” AIChE J., vol. 62, no. 8, pp. 2843–2852, 2016, doi: 10.1002/aic.15260.

[10] C. Kim et al., “Efficient CO2 Utilization via a Hybrid Na-CO2 System Based on CO2 Dissolution,” iScience, vol. 9, pp. 278–285, 2018, doi: 10.1016/j.isci.2018.10.027.

[11] CO2 Removal Machine || Reducing Carbon Dioxide Level in Atmosphere, Feb 12, 2019. Accessed on: Nov 27, 2019 https://www.youtube.com/watch?v=M03xM9jpWHs

[12] H. Naims, “Economics of carbon dioxide capture and utilization—a supply and demand perspective,” Environ. Sci. Pollut. Res., vol. 23, no. 22, pp. 22226–22241, 2016, doi: 10.1007/s11356-016-6810-2.