Mixed Matrix Membrane Incorporating of MgAl-CO$_3$ Layered Double Hydroxide for Enhanced Carbon Dioxide Separation

N. Fajrina$^{1,2}$, N. Yusof$^{1,2,*}$, A.F. Ismail$^{1,2}$, J. Jaafar$^{1,2}$, F. Aziz$^{1,2}$, W.N.W. Salleh$^{1,2}$, N.M. Ismail$^{3}$

$^1$ Advanced Membrane Technology Research Centre (AMTEC), Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor Darul Ta’zim, Malaysia.
$^2$ School of Chemical and Energy Engineering (SCEE), Faculty of Engineering, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor Darul Ta’zim, Malaysia.
$^3$ Faculty of Engineering, Universiti Malaysia Sabah, Jalan UMS, 88400, Kota Kinabalu, Sabah, Malaysia

E-mail: norhaniza@petroleum.utm.my

Abstract. In this study, mixed matrix membranes were fabricated by incorporating MgAl-CO$_3$ layered double hydroxides (LDH) into polysulfone (PSF) coated with low-cost commercial PEBAX polymer for enhancing CO$_2$/CH$_4$ separation. LDH was synthesized via a simple co-precipitation method and flat sheet membranes were fabricated by dry/wet inversion phase. The gas separation performance on pure PSF and LDH/PSF membranes were investigated. The physical property, chemical structure and membrane morphology were characterized by XRD, FTIR, and SEM. The sample membranes were tested with CO$_2$ and CH$_4$ gas for permeance performance and selectivity of CO$_2$/CH$_4$ was calculated. By incorporation of LDH, the CO$_2$ permeance increased about 54.6%. LDH mixed matrix membranes displayed the 18.2 GPU of CO$_2$ permeance and CO$_2$/CH$_4$ selectivity of 18.0. The LDH based membrane produces innovation in membrane technology by improving its morphology and permeance performance with great potential for large-scale CO$_2$ capture and separation.

1. Introduction
The rapid growth of the global economy and the expanding human population urgently requires a sustainable supply of energy [1]. Considering the depletion of fossil fuels, it is imperative to find appropriate alternatives to cope with the energy crisis. Harvesting energy from biogas, a kind of renewable energy source, has attracted a great deal of attention and evolves a potential way to retard the depletion of other energy sources and fight against global warming at the same time [2-4]. However, removing CO$_2$ from the as-produced biogas is necessary to increase the calorific values. Compared with conventional biogas upgrading methods such as water and amine scrubbing [5], membrane separation is considered a more cost-effective technical solution, along with low energy consumption, simple design, environmental friendliness as well as small plant footprint [6, 7]. These advantages have led to extensive exploration in the preparation of CO$_2$ membranes with high separation performance.

Polymeric membranes are processed by a simple, environmentally sustainable process, which is cost-efficient, energy-intensive and easy to scale up [8-10]. However, the substitution of traditional technologies and their positive effect would require a long time for membrane separation, as it is
constrained by the intrinsic restriction in the trade of permeability and selectivity [11]. Inorganic membranes show a better performance in separation but are expensive and hard to turn into uniform films, compared to polymeric membranes [12]. A mixture of inorganic fillers distributed over a polymer matrix called a mixed matrix membrane (MMM) has shown an attractive method to boost the separating characteristics of polymers to help solve the well-known Robeson’s upper bound [13]. Latest studies concentrate on a variety of new filler products in MMM, including carbon nanotube, metal-organic framework (eg: UiO-66), clay, zeolite, silica, metal oxide and carbon molecular sieve [14-19].

For MMM to achieve the best performance, the good compatibility between filler with polymer is the key factor. Layered double hydroxide (LDH) has similar properties to clay but, it can be finely tuned and has high CO\textsubscript{2} affinity resulting in easy CO\textsubscript{2} capture. Although less research can be found on CO\textsubscript{2} separation using LDH as filler, the LDH is reported to be excellent as an adsorbent for CO\textsubscript{2} capture. Gouveia et al. [20] have shown that the combination of high surface area and basic sites have resulted in the maximum adsorption capacity of CO\textsubscript{2} (159.1 mg/g\textsubscript{cat}). The large specific surface area with the availability of basic sites in LDH will certainly bring an advantage as a nanofiller in MMM for CO\textsubscript{2} capture as CO\textsubscript{2} is known as acidic gas. Liu et al. [21] successfully fabricated a 2D-LDH membrane and built CO\textsubscript{2}-selective transport nanochannels for CO\textsubscript{2} separation. The intercalator of CO\textsubscript{2}\textsuperscript{2-} ions have reduced the nanochannel size from 0.7 nm to 0.3 nm and thus, provided the membrane a molecule sieving ability for CO\textsubscript{2}/CH\textsubscript{4} separation. The results showed high performance with 150 GPU of CO\textsubscript{2} permeability and 33 of CO\textsubscript{2}/CH\textsubscript{4} selectivity.

Polysulfone (PSF) is the most used polymer due to its properties such as good chemical stability and high mechanical strength. Kiadehi et al. [22] successfully fabricated nanofibers (CNF)/PSF MMM. The finding showed that the increasing of CNF concentration in MMM led to the increasing of CO\textsubscript{2} permeability and CO\textsubscript{2}/CH\textsubscript{4} selectivity with 12.04 Barrer and 12.17, respectively. Waheed et al. [23] fabricated MMM by incorporating PSF with mesoporous silica particles extracted from rice husk ash and the results have shown 8.46 Barrer of CO\textsubscript{2} permeability, 0.258 Barrer of CH\textsubscript{4} permeance and 32.79 CO\textsubscript{2}/CH\textsubscript{4} selectivity using 40% filler loading. However, there is still a membrane defect, such as pinholes, which reduces CO\textsubscript{2}/CH\textsubscript{4} selectivity. This problem can be prevented by coating the MMM with PEBAX to seal pinholes and improve the permeance of selective gas. The previous research indicated the ideal range of PEBAX is about 3% to 5% [24-27]. Researchers claimed in this range that although there is a risk of pore penetration, it also makes excellent transport of gas. Jamil et al. [28] showed that membrane defects on the surface can be minimized by PEBAX coating. Their finding exposed that the PEBAX on MMM has the highest CO\textsubscript{2}/CH\textsubscript{4} selectivity with 38.45 at 5 bar in room temperature.

Up to date, the incorporation of LDH in MMM for CO\textsubscript{2} capture is still recent and as for the author’s knowledge, there is no research on coated MgAl-CO\textsubscript{3} LDH/PSF MMM fabrication has been done. Herein, in this research, the compatibility of LDH with PSF was investigated. The fabricated MMM was coated with 3 wt% PEBAX to seal pinholes and improve the gas permeances.

2. Methodology

2.1. Materials

\text{Al(NO}_3\text{)}_3\cdot9\text{H}_2\text{O and Mg(NO}_3\text{)}_2\cdot6\text{H}_2\text{O were provided by Fisher Scientific (M) Sdn Bhd. Acetone, Na}_2\text{CO}_3 and NaOH were purchased from Sigma-Aldrich (Malaysia). Polysulfone polymer (Udel-P3500) and PEBAX MH 1657 were purchased from Solvay Advanced Polymers (USA). Deionized water (DI water) was used during the whole experiment. Without further purification, all chemical compounds were used.}

2.2. Synthesis of LDH

MgAl-CO\textsubscript{3} LDH was prepared via the co-precipitation method. Firstly, 9.6 g of Mg(NO\textsubscript{3})\textsubscript{2}\cdot6H\textsubscript{2}O and 4.78 g of Al(NO\textsubscript{3})\textsubscript{3}\cdot9H\textsubscript{2}O were dissolved in 50 ml DI water by magnetic stirring at room temperature as Solution A. For solution B, 2.65 g of Na\textsubscript{2}CO\textsubscript{3} was dissolved in 50 ml of DI water using magnetic stirring while for solution C, 8g of NaOH pellets were dissolved in 50 ml of DI water. With continuous stirring,
solution A was titrated into solution B and the pH of the mixture solution was maintained at about 9-10 by adding Solution C to the above-mentioned mixture. The mixture was stirred for a further 30 min after solution A was completely added to solution B. Then, the solution was aged at 60°C for 24 hr. The sample was consequently separated by centrifuge (6000 rpm). The LDH obtained was washed with DI water repeatedly until pH approached 7 and centrifuge each time. The LDH was further washed intensively with acetone to prevent LDHNPs agglomeration. After that, the obtained sample was dried in the oven for 24 h at 60°C and then grounded using a mortar and pestle.

2.3. Fabrication LDH/PSF MMM

PSF dope solution was prepared by simple mixing. 1.5 g MgAl-CO$_3$ LDH was dispersed in 23 ml NMP solvent by sonicator for 1 h. Then, the mixture was heated to 65°C. 6 g PSF was added slowly and stirred at a stirring rate of 130 rpm. The dope solution was continually stirred for a further 24 h after the PSF was completely dissolved. The casting solution was degassed by sonicator for 4 h followed by cooling at room temperature for another 24 h. For bare PSF, the procedure is the same without included the LDH powder.

Next, the membrane was prepared by dry/wet phase inversion. The dense membrane was cast at room temperature using a casting glass rod on a smooth glass plate and was then immediately immersed in the coagulant bath. The fabricated membrane was transferred and immersed in the fresh water for 24 h and then, drying it for 24 h at room temperature.

2.4. Coating PEBAX layer

The single layer of 3 wt% PEBAX layer was coated by the dip-coating method to seal the membrane defect. PEBAX coating solution was prepared with a mass ratio of 70:30 of ethanol/water. In the mixed solvent at 70°C, PEBAX pellets were first added and stirred for 2 h followed by sonicated for 4 h. The ready solution was subsequently cooled to room temperature. Next, the solution was used to coating MMM with PEBAX. The dope solution of PEBAX was pour into the glass petri dish around 5 ml to damp the dish. Small amount of PEBAX solution is used to make sure the solution just coated one side surface dip, and not overflow and cover both side of membrane. Then, the shiny surface of the flat sheet membrane was faced the solution then dip coated for 30 sec. After that, the membrane was hanged for 3 min to remove the excess solution before dried in the oven for 2 h at 60°C to allow solvent vaporization.

2.5. Characterization Technique

X-ray diffraction (XRD) was used to determine the crystallinity of the sample using an X-Ray Diffractometer (Model Rigaku SmartLab). The X-ray diffractometer was conducted at a 2-theta range from 3°≥2θ≥100° in room temperature. To determine the functional group that exists in LDH-based MMM, the Fourier transform infrared (FTIR) analysis was tested. FTIR spectra were obtained by Bruker TENSOR27 impact spectrometer. The Scanning Electron Microscope (SEM) was used to characterize the morphology of the membrane in the lower magnification. Before testing, the samples were also frozen fractured under cryogenic conditions in liquid nitrogen and gold/platinum coat. The surface area and cross-sectional morphology analysis of the flat sheet MMM was conducted using a scanning electron microscope (TM3000, Hitachi) fitted with different magnifications.

2.6. Gas Permeance Test

To assess the membrane efficiency in terms of gas permeance and selectivity, a gas permeation test was performed. The sample membrane was put inside the tailored flat sheet membrane housing before processing. At 5 bar, single gas CO$_2$ and CH$_4$ with a purity of 99.99% were then supplied from a gas cylinder to the membrane housing. The pressure was adjusted by a two-stage pressure regulator. The flow rate was measured using a soap bubble flowmeter after the gas had permeated through the membrane.

The gas permeance (P$_i$/l) and the gas selectivity (α$_i$) were calculated using equations (1) and (2).
\[
\left( \frac{P_i}{l} \right) = \frac{Q_i}{A \Delta P} \frac{273.15 \times 10^6}{T} 
\]

\[\alpha_{ij} = \frac{(P_i/l)}{(P_j/l)}\]  

where \(i\) and \(j\) are the penetrating gas \(i\) and \(j\), respectively, \(P_i/l\) is the gas permeance across the membrane (GPU), \(Q_i\) is the volumetric flow rate of gas permeated across the membrane at STP (cm\(^3\)/s), \(A\) is the effective surface area of membrane (cm\(^2\)) and can be determined by \(A = \pi r^2\), where \(\pi\) is Archimedes’ constant (\(\pi = 3.14\)) and \(r\) is the radius of the flat sheet membrane (cm), \(\Delta P\) is the pressure difference (cm Hg) as the gas passes through the membrane, and \(T\) is the ambient temperature (K) at which the permeation experiment is performed.

3. Results and Discussion

3.1. Characterization Analysis

Figure 1 shows the XRD spectra of MgAl-CO\(_3\) LDH, PSF and LDH/PSF MMM. From the XRD pattern, it was confirmed that MgAl-CO\(_3\) LDH shows the crystalline structure while membrane samples show an amorphous phase. For LDH, there are sharp peaks at 11.38\(^\circ\), 22.92\(^\circ\), and 34.56\(^\circ\) which are ascribed to (003), (006) and (009), respectively. The other peaks are at 38.80\(^\circ\), 45.76\(^\circ\), 60.50\(^\circ\) and 61.80\(^\circ\) [29]. These peaks correspond with MgAl-CO\(_3\) LDH JCPDS reference patterns (JCPDS No: 00-014-0191) [30] and deduced that the LDH has been successfully synthesized. The amorphous PSF membrane shows the broad peak diffraction at 2\(\theta\)=17.70\(^\circ\) and the addition of peak at 23.90\(^\circ\) corresponding to the crystalline phase of PEBAX [31]. This shows PEBAX is successfully coated on the surface of PSF. The LDH/PSF MMM has the obvious peak of LDH, PSF and PEBAX spectra. This shows that coated MMM has been successfully prepared.
Figure 2 presents the FTIR spectra for MgAl-CO$_3$ LDH, PSF and LDH/PSF MMM. The MgAl-CO$_3$ LDH FTIR spectra show the obvious broad band at 3451.59 cm$^{-1}$ corresponds to the OH group stretching in coordination with the cations. While, at 2980.51 cm$^{-1}$, the bending assign to the H-bond between water and CO$_3^{2-}$ ions in the interlayer. For the band at 1631.33 cm$^{-1}$, it is related to the water bending in the interlayer. The sharp band at 1360.87 cm$^{-1}$ concerns the stretching of the carbonate group. The signal below the 700 cm$^{-1}$ band is related to the Mg-O and Al-O vibration in the lattice of LDH [32]. The membrane sample shows an absorption band at 1236.61 cm$^{-1}$ assign to the O=S=O group stretching vibration which is representing for PSF polymer. There is strong band at 1098.79 cm$^{-1}$ for the PEO segment for the (-C=O-) group. The absorption band at 3296.37 cm$^{-1}$, 1731.84 cm$^{-1}$ and 1636.37 cm$^{-1}$ corresponding to (-N–H), (-O–C=O-) and (-H–N–C=O-) have been observed and it belongs to the functional group in the hard polyamide (PA) segment of PEBAX while 2867.27 cm$^{-1}$ in the soft and hard segment representing (-C–H-) group. Thus, it can be deduced that the PEBAX coating has been successfully prepared on the PSF surface membrane. For the composition of LDH on the MMM, the FTIR spectra show a similar pattern with PSF. Since the amount of LDH added is low around 5 wt% and MMM surface was coated with PEBA, the FTIR spectra has high intensity absorption band for functional group and bond exist on the PEBAX.

Figure 3 displays the SEM micrographs of the PSF and LDH/PSF MMM. The membranes were shown to be invariably asymmetric, consisting of the PEBAX-coated layer on the membrane surface structure of the sponge and the finger. The size and shape of the porous membrane were adjusted when LDH was incorporated into the membrane matrix. Comparing with PSF, the MMM was less dense with longer, smoother and narrower pores. This adjustment because of the presence of LDH in the PSF membrane as the number of finger-like pores increased and grew with the addition of filler. LDH may have lowered the polymer/solvent interaction and reduced the interface strain between non-solvent to polymer dope, resulting, during process inversion, an increase in the solvent/solvent exchange rate [33]. Similar analysis carried out by Vatanpour et al. [34] has also shown that inserting filler into a polymer membrane increases porosity as well as macro-void structures. The SEM indicates that the one side
surface of membrane is covered with a layer and it deduces the successful coating of PEBAX on the surface of LDH/PSF MMM.

![SEM micrographs of the PSF and LDH/PSF MMM](image)

3.2. Gas Permeance Test

Figure 4 presents the permeance and selectivity of CO$_2$ and CH$_4$ gasses for PSF and LDH/PSF MMM under 5 bar at room temperature. The results show LDH loading has a high CO$_2$/CH$_4$ selectivity with the better CO$_2$ permeance. The finding obtained has shown the CO$_2$ permeance increased and CH$_4$ permeance decreased with LDH loading. This meant that the PSF membrane chain packing had been interrupted by the LDH filler. This in turn enhances vacancy in the membrane, facilitates the transport of gas across the membranes. The increase in CO$_2$ permeance is because the LDH has a greater affinity with polar gas (CO$_2$) than non-polar gas (CH$_4$), which the presence of open metal sites in LDH would provide interaction between its electrostatic field and quadrupole moment of CO$_2$ while having no specific interaction with CH$_4$. Also, the structure of the LDH affects gas permeance. The interlayer channel dimensions of the 2D LDH membrane are regulated by the intercalated CO$_3^{3-}$ to 0.3 nm (3.0Å), which restricts the transport of CH$_4$ molecules of a complex diameter of 0.38 nm (3.8Å). Although the little channel can also retard the 0.33 nm (3.3Å) of CO$_2$ molecules, the LDH laminar channel will be used to relay CO$_2$ molecules, which are in CO$_3^{3-}$ shape with an ionic radius of 0.136 nm which not influenced by the sieving [21]. Furthermore, the PEBAX can also seal all the defects and pores that may be due to LDH filler at the PSF MMM surface and thus increases the membrane selectivity [28]. Thus, the gas-filler relationship, transport channel and coated membrane contributed to a large increase in selectivity between CO$_2$ and CH$_4$ up to 129.5%.
Figure 4 Permeance and selectivity of CO\textsubscript{2} and CH\textsubscript{4} gasses for PSF and LDH/PSF MMM under 5 bar at room temperature

4. Conclusion

The LDH/PSF MMM was successfully fabricated and the effect of the incorporation of LDH filler into the PSF membrane was investigated in this work. The addition of LDH fillers has been shown to improve CO\textsubscript{2} gas permeance by 54.5% and increase CO\textsubscript{2}/CH\textsubscript{4} selectivity up to 18.0 compared to 7.8 for pristine PSF membrane. The morphology of the MMM membrane shows the filler altering the membrane structure to be less dense and narrow pores which provide a better channel for CO\textsubscript{2} permeance, thus explain the best performance of CO\textsubscript{2}/CH\textsubscript{4} gas separation. For future study, the different loading of LDH and another operating parameter can be investigated as LDH filler has great potential in membrane application.

Acknowledges

The authors would like to recognize the financial support provided by UTM-UTP-UMP-UMS Collaborative Research Grants (CRG) (Q.J130000.2451.08G26) and (Q.J130000.2451.08G72), and UTM Prototype Research Grants (UTMPR) (Q.J130000.2851.00L41) by the Malaysian Ministry of Education and Universiti Teknologi Malaysia.

References

[1] Owusu P A, Asumadu-Sarkodie S and Dubey S 2016 A review of renewable energy sources, sustainability issues and climate change mitigation Cogent Engineering 3

[2] Wasajja H, Lindeboom R E F, van Lier J B and Aravind P V 2020 Techno-economic review of biogas cleaning technologies for small scale off-grid solid oxide fuel cell applications Fuel Processing Technology 197 106215

[3] Sahota S, Shah G, Ghosh P, Kapoor R, Sengupta S, Singh P, Vijay V, Sahay A, Vijay V K and Thakur I S 2018 Review of trends in biogas upgradation technologies and future perspectives Bioresource Technology Reports 1 79-88
[4] Singhal S, Agarwal S, Arora S, Sharma P and Singhal N 2017 Upgrading techniques for transformation of biogas to bio-CNG: a review *International Journal of Energy Research* **41** 1657-69

[5] Baena-Moreno F M, le Saché E, Pastor-Pérez L and Reina T R 2020 Membrane-based technologies for biogas upgrading: a review *Environmental Chemistry Letters* **18** 1649-58

[6] Ma C, Wang M, Wang Z, Gao M and Wang J 2020 Recent progress on thin film composite membranes for CO\(_2\) separation *Journal of CO\(_2\) Utilization* **42**

[7] Li H, Feng X, Ma D, Zhang M, Zhang Y, Liu Y, Zhang J and Wang B 2018 Stable aluminum metal–organic frameworks (Al-MOFs) for balanced CO\(_2\) and water selectivity *ACS Appl. Mater. Interfaces* **10** 3160-3

[8] Lei L, Lindbråthen A, Zhang X, Favvas E P, Sandru M, Hillestad M and He X 2020 Preparation of carbon molecular sieves: I. Preparation and experimental results *J. Membr. Sci.* **211** 311-34

[9] Habib N, Shamair Z, Tara N, Nizami A, Koros W J and Fleming G 1993 Membrane processes for gases *Ind. Eng. Chem. Res.* **32** 1-80

[10] Robeson L M 2008 The upper bound revisited *J. Membr. Sci.* **320** 390-400

[11] Koros W J and Miller S J 2003 Mixed matrix membranes using carbon molecular sieves: I. Preparation and experimental results *J. Membr. Sci.* **211** 311-34

[12] Vu D Q, Koros W J and Miller S J 2003 Mixed matrix membranes using carbon molecular sieves: I. Preparation and experimental results *J. Membr. Sci.* **211** 311-34

[13] Susanti I 2019 Polysulfone Membrane with Zeolite Filler for CO\(_2\)/CH\(_4\) Gas Separation: a Review *Sci. Educ. App. J.* **1** 10-6

[14] Jiang Y, Liu C, Caro J and Huang A 2019 A new UiO-66-NH\(_2\) based mixed-matrix membranes with high CO\(_2)/CH\(_4\) separation performance *Microporous Mesoporous Mater.* **274** 203-11

[15] Ismail N, Ismail A, Mustafa A, Zulhairun A, Aziz F, Bolong N and Razali A 2019 Polymer Clay Nanocomposites For Gas Separation: A Review *Environ. Contam. Rev.* **2** 01-5

[16] Reina T R 2017 Novel composite membranes for gas separation *J. Ind. Eng. Chem.* **41** 118529

[17] Mousavinejad A, Rahimpour A, Shirzad Kebria M R, Khoshhal Salestan S, Sadrzadeh M and Tavajohi Hassan Kiadeh N 2020 Nickel-Based metal–organic frameworks to improve the CO\(_2)/\text{CH}_4\) separation capability of thin-film pebab membranes *Ind. Eng. Chem. Res.* **59** 12834-44

[18] Zohdi S, Anbia M and Salehi S 2019 Improved CO\(_2\) adsorption capacity and CO\(_2)/\text{CH}_4\) and CO\(_2)/\text{N}_2\) selectivity in novel hollow silica particles by modification with multi-walled carbon nanotubes containing amine groups *Polyhedron* **166** 175-85

[19] Gouveia L G T, Agustini C B, Perez-Lopez O W and Gutterres M 2020 CO\(_2\) adsorption using solids with different surface and acid-base properties *J. Environ. Chem. Eng.* **8**

[20] Liu Y, Wu H, Min L, Song S, Yang L, Ren Y, Wu Y, Zhao R, Wang H and Jiang Z 2020 2D layered double hydroxide membranes with intrinsic breathing effect toward CO\(_2\) for efficient carbon capture *J. Membr. Sci.* **598**

[21] Ahmadpour E, Shamsabadi A A, Behbahani R M, Aghajani M and Kargari A 2014 Study of CO\(_2\) separation with PVC/Pebax composite membrane *Journal of Natural Gas Science and Engineering* **21** 518-23
[25] Sutrisna P D, Hou J, Li H, Zhang Y and Chen V 2017 Improved operational stability of Pebax-based gas separation membranes with ZIF-8: A comparative study of flat sheet and composite hollow fibre membranes J. Membr. Sci. 524 266-79

[26] Wang L, Li Y, Li S, Ji P and Jiang C 2014 Preparation of composite poly(ether block amide) membrane for CO$_2$ capture Journal of Energy Chemistry 23 717-25

[27] Wahab M A, Sunarti A, Ramli N H and Ahmad A 2019 24 fractional factorial design for PVDF/Pebax film composite synthesis on gas selectivity study. In: IOP Conference Series: Materials Science and Engineering: IOP Publishing) p 012046

[28] Jamil N, Othman N H, Shahrudin M Z, Razlan M R M, Alias N H, Marpani F, Jye L W, Goh P S and Ismail A F 2020 Effects of Pebax Coating Concentrations on CO$_2$/CH$_4$ Separation of RGO/ZIF-8 PES Membranes J. Teknol. 82

[29] Rezaei B, Heidarbeigy M, Ensafi A A and Dinari M 2016 Electrochemical Determination of Papaverine on Mg-Al Layered Double Hydroxide/ Graphene Oxide and CNT Modified Carbon Paste Electrode IEEE Sens. J. 16 3496-503

[30] Shang S, Hanif A, Sun M, Tian Y, Ok Y S, Yu I K M, Tsang D C W, Gu Q and Shang J 2019 Novel M (Mg/Ni/Cu)-Al-CO$_3$ layered double hydroxides synthesized by aqueous miscible organic solvent treatment (AMOST) method for CO$_2$ capture J Hazard Mater 373 285-93

[31] Norahim N, Faungnawakij K, Quitain A T and Klaysom C 2019 Composite membranes of graphene oxide for CO$_2$/CH$_4$ separation J. Chem. Technol. Biotechnol. 94 2783-91

[32] Cardinale A M, Carbone C, Consani S, Fortunato M and Parodi N 2020 Layered Double Hydroxides for Remediation of Industrial Wastewater from a Galvanic Plant Crystals 10

[33] Pal A, Kar S, Debnath A K, Aswal D K, Bindal R C and Tewari P K 2015 Reinforcement of nanostructured reduced graphene oxide: a facile approach to develop high-performance nanocomposite ultrafiltration membranes minimizing the trade-off between flux and selectivity RSC Adv. 5 46801-16

[34] Vatanpour V, Shockravi A, Zarrabi H, Nikjavan Z and Javadi A 2015 Fabrication and characterization of anti-fouling and anti-bacterial Ag-loaded graphene oxide/polyethersulfone mixed matrix membrane J. Ind. Eng. Chem. 30 342-52