

Effect of the SBA-15 template and KOH activation method on CO₂ adsorption by N-doped polypyrrole-based porous carbons

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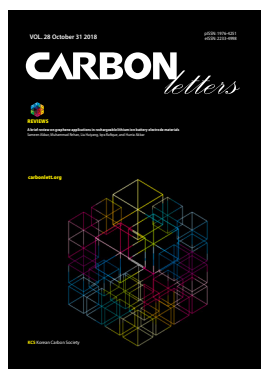
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Abstract

Nitrogen-doped carbons have attracted much attention due to their novel application in relation to gas storage. In this study, nitrogen-doped porous carbons were synthesized using SBA-15 as a template, polypyrrole as the carbon and nitrogen precursor, and KOH as an activating agent. The effect of the activation temperature (600–850°C) on the CO₂ adsorption capacity of the obtained porous carbons was studied. Characterization of the resulting carbons showed that they were micro-/meso-porous carbon materials with a well-developed pore structure that varied with the activation temperature. The highest surface area of 1488 m² g⁻¹ was achieved at an activation temperature of 800°C (AC-800). The nitrogen content of the activated carbon decreased from 4.74 to 1.39 wt% with an increase in the activation temperature from 600 to 850°C. This shows that nitrogen is oxidized and more easily removed than carbon during the activation process, which indicates that C-N bonds are more easily ruptured at higher temperatures. Furthermore, CO₂ adsorption isotherms showed that AC-800 exhibited the best CO₂ adsorption capacity of 110 mg g⁻¹ at 298 K and 1 bar.

Key words: N-doped, SBA-15, polypyrrole, CO₂ adsorption

1. Introduction

Global warming, as a result of rapid industrialization and civilization, has caused unpredictable disasters such as droughts, floods, economic issues, disease, and the destruction of ecosystems and has thus endangered human life [1-3]. The main greenhouse gases that lead to global warming are carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O), fluorocarbons, perfluorocarbons, chlorofluorocarbons, and sulfur hexafluoride (SF₆) [3]. Among these gases, CO₂ is a key anthropogenic greenhouse gas closely linked to the global greenhouse effect. Thus, reducing CO₂ emissions is a priority in the fight against global warming.

In recent years, porous carbon materials have been widely employed as potential adsorbents in many fields, including gas adsorption, catalytic supports, supercapacitors, fuel cells, and lithium ion batteries. This is due to their high specific surface area, large pore volume, low preparation cost, high adsorption capacity, stable chemical and thermal performance, and because modifications are easy to design [4-9].

Mesopores come into play when the adsorbates are polymers, dyes, and vitamins, but a microporous structure is also important to adsorb small gas molecules. Thus, it is essential to control the pore structure of porous carbons [10]. Template methods are recognized as a suitable means of controlling the development of porosity in carbons. Porous carbons with a homogeneous structure and a uniform pore size can be prepared using soft templates, but this method places the following strict requirements on the precursor: (1) the precursor should have the form of a self-assembled nanometer-sized

structure; (2) there must be a guide component to create the pores; (3) the components used to create the pores must tolerate the activation temperature; and (4) the carbon precursor must maintain its nanostructure during decomposition and removal of the pore-creating agents [11]. Additionally, it is not possible to control the size and shape of the products when using a soft template. However, hard-template sources such as ordered mesoporous silicate and zeolites are relatively abundant. In particular, SBA-15 is an efficient hard template due to its well-ordered hexagonal mesoporous structure.

Recently, the presence of certain functional groups containing electron-donating or electron-withdrawing heteroatoms, such as N, B, and Si, has been shown to improve the CO₂ adsorption performance of carbon materials [12]. Nitrogen doping has attracted much interest due to the unique applications of N-doped carbons, particularly in gas adsorption, water purification, catalyst supports, and electrochemistry [13]. Conductive polymers are excellent carbon and nitrogen source materials. Specifically, the monomer of polypyrrole is a C, N five-membered heterocyclic molecule, which is a more common conductive polymer. Recently, it has been reported that polypyrrole can be used as a conductive polymer and combined with other materials as a carbon source and nitrogen source to prepare porous carbons. Thus, significant efforts have been made to synthesize N-doped porous carbons. Hard templating is often employed to prepare heteroatom-doped carbons due to the controllable pore structure and morphology of the obtained carbons and the homogeneous incorporation of nitrogen into the carbon frameworks.

In recent work, Wahby et al. [14] demonstrated that porous carbons with a high surface area can capture a large amount of CO₂ [15]. KOH is usually used as a chemical activation agent because it produces activated carbon with an extremely high surface area, a predominantly microporous structure, and a narrow micropore distribution. Here, a series of N-doped porous carbons were synthesized using SBA-15 as the template, polypyrrole as the carbon and nitrogen precursor, and KOH as an activating agent. We expect that the porous carbon produced using this method will combine a high density of nitrogen functionality and a large surface area, thus displaying improved CO₂ capturing outcomes.

The effect of the KOH activation temperature on the CO₂ adsorption capacity of the obtained porous carbons was also studied at temperatures of 600, 700, 800, and 850°C. The prepared N-doped porous carbons had large specific surface areas (663–1488 m² g⁻¹) and, furthermore, these carbon materials showed relatively high CO₂ adsorption capacities of up to 110 mg g⁻¹ at 298 K and 1 bar.

2. Experimental

Porous carbons were synthesized by impregnating the inorganic mesoporous silica SBA-15 with polypyrrole by means of KOH activation at different temperatures (600, 700, 800, and 850°C). The polypyrrole was prepared using FeCl₃ as an oxidant. In brief, the porous carbons were prepared as follows: first, 10 g of SBA-15 and 10 g of FeCl₃ were added to a solution of HCl (1.0 M, 15 mL), and the mixture was dried for 2 h at 90°C; pyrrole vapor was then added to the mixture for 2 h. The obtained samples were put into a tube furnace and activated by heating under Ar; the temperature was raised at a rate of 5°C/min up to the desired temperature in the range of 600 to 850°C, which was then maintained for 5 h. The resultant samples were washed with HCl and HF to remove FeCl₃, KOH, and SBA-15 and were then washed with distilled water. The prepared porous carbons were defined as AC-600, AC-700, AC-800, and AC-850, where the number indicates the heating temperature. The detailed scheme of the experimental process is shown in Fig. 1.

Scanning electron microscopy (SEM; Hitachi/S-3500) and transmission electron microscopy (TEM; JEM2100F, JEOL) were used to examine the SBA-15 and AC-800 morphologies. The textural properties of the carbon materials were characterized by nitrogen adsorption-desorption isotherms at 77 K. The specific surface area and total pore volume were determined with a surface area analyzer (Beishide Instrument Technology Co.). The elemental composition on the carbon surface was determined by X-ray photoelectron spectroscopy (XPS; Escalab 220i-XL VG Scientific, UK) measurements. CO₂ adsorption was measured at 298 K and 1 atm.

3. Results and Discussion

The external pore structure of the prepared activated carbons studied was observed using SEM and TEM, as shown in Fig. 2. The SBA-15 (Fig. 2a and b) and AC-800 activated carbon (Fig. 2c and d) morphologies were characterized using SEM. Fig. 2e exhibits TEM images of the AC-800 activated carbon. The AC-800 morphology is not similar to that of SBA-15, which consists of interconnected short bars to necklace-like connected spherical particles. Fig. 2b shows that SBA-15 has a well-ordered hexagonal mesoporous structure. This morphology provides a large pore canal that is essential for achieving good pore development and in which polypyrrole can react uniformly with KOH. As shown in Fig. 2e, AC-800 largely follows the pore structure of SBA-15, which indicates that the activated carbons have a replicated two-dimensional hexagonal mesoporous

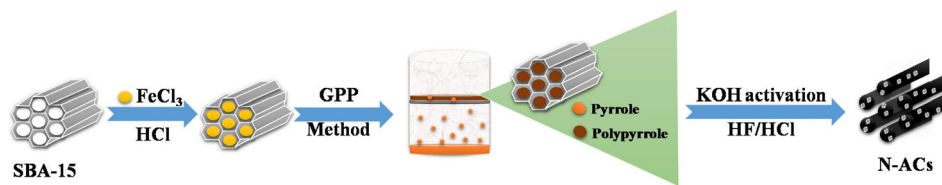


Fig. 1. Schematic illustration of the synthesis procedure used to produce the activated carbons.

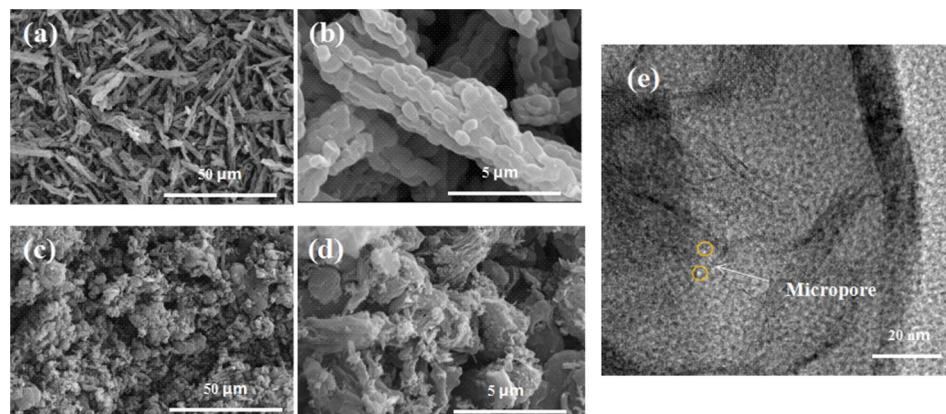


Fig. 2. SEM and TEM images of mesoporous silica SBA-15 and the prepared activated carbons (activated 800°C). SEM: (a, b), SBA-15; (c, d), AC-800. TEM: (e), AC-800.

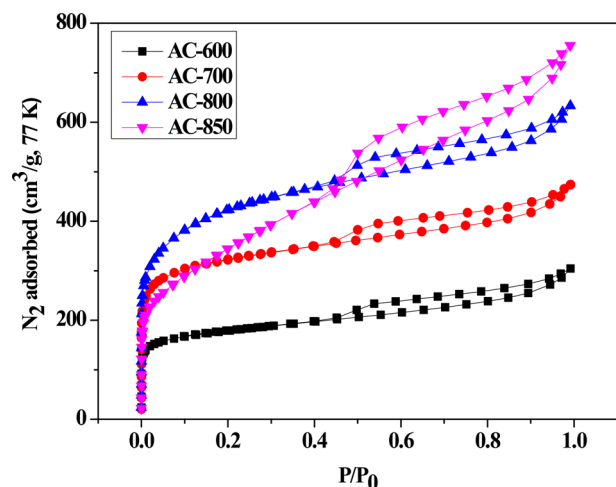


Fig. 3. The N_2 adsorption/desorption isotherms of the prepared activated carbons at different activation temperatures.

structure.

The textural properties of the activated carbons prepared at different temperatures (600, 700, 800, and 850°C) were characterized from their nitrogen adsorption-desorption isotherms, as displayed in Fig. 3. The isotherm shape changes with an increase in the activation temperature from 600 to 850°C, which indicates a change in the porous structure of the activated carbons. All of the isotherms are basically identical as type I or IV, according to the IUPAC nomenclature, with the corresponding type of hysteresis loop, indicative of the mesoporous nature of the SBA-15 template, which indicates that polypyrrole was actually inserted inside of the SBA-15 channels. In addition, some micropores are present in the activated carbons, which may be a result of interaction in the carbon framework inducing a pore-wall collapse and blocking some of the mesoporous channels.

The pore-structure parameters of the activated carbons as a function of the activation temperature are summarized in Table 1. The synthesized activated carbons have high specific surface areas, large mesopore volumes, and large total volumes. The

specific surface area increased with an increase in the activation temperature up to 1488 $m^2 g^{-1}$ (AC-800) and then decreased to 1235 $m^2 g^{-1}$ (AC-850). The pore diameter was controlled in the range of 2.42 to 3.77 nm and the pore volume increased significantly when increasing the activation temperature from 0.467 to 1.164 $cm^3 g^{-1}$. Micropore formation can be attributed to thermo-decomposition of the carbon precursor (polypyrrole), while the mesoporous framework results from the replication of the SBA-15 template [16]. It was unusual to find that the mesopore volume of AC-800 is much lower than that of AC-850, whereas the specific surface area of AC-800 is much higher than that of AC-850. This may be due to the collapse of the template structure at high temperatures, resulting in the production of vast numbers of mesopores despite the greater activation of the carbon source at the higher temperatures. The micropores prevalently derive from the activation of the carbon precursor, while mesopores mainly stem from the replication of the SBA-15 template. Furthermore, some mesopores will form due to the collapse of the thinner micropore walls in the carbon frameworks during the HF etching of the SBA-15 template as a result of the high temperatures achieved during this process [17].

For better characterization of the change in the pore structure of the activated carbons studied here, the pore size distributions in the micro-/meso-pore regions are shown for the prepared porous carbons obtained using different activation temperatures. Fig. 4 shows the effect of the activation temperature on the pore size distribution of the prepared activated carbons. All of the carbons obtained at different activation temperatures possessed a mostly narrow pore size distribution mainly concentrated in the 0.5 to 2 nm range. On the one hand, mesopore formation arises from removal of the template; on the other hand, the micropores originate from the activation of the carbon source. In particular, AC-800 possesses a significant fraction of narrower micropores (<0.7 nm), which has an important effect on its gas-capture properties.

The details of the textural properties and chemical compositions of the prepared activated carbons at different temperature are shown in Table 1. As shown in Table 1, the nitrogen content of the activated carbons decreased from 4.74 to 1.39 wt% as the activation temperature increased from 600 to

Table 1. Pore structure parameters and elemental compositions of the prepared activated

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$) ^{a)}	V_{Total} ($\text{cm}^3 \text{g}^{-1}$) ^{b)}	V_{Mes} ($\text{cm}^3 \text{g}^{-1}$) ^{c)}	D (nm) ^{d)}	Chemical composition (wt%)		
					N	C	O
AC-600	663	0.467	0.270	2.82	4.74	83.89	11.36
AC-700	1204	0.729	0.349	2.42	2.15	88.18	9.67
AC-800	1488	0.976	0.545	2.62	1.18	91.57	7.24
AC-850	1235	1.164	1.006	3.77	1.39	91.14	7.47

carbons at different activation temperatures from the N₂ adsorption isotherms

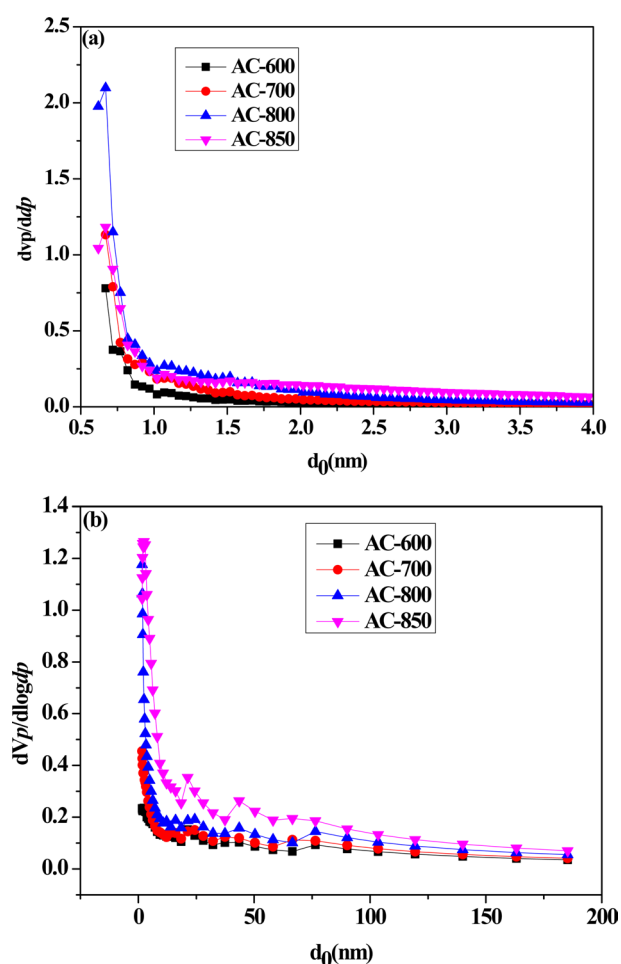


Fig. 4. Micropore size distributions (a) and mesopore size distributions (b) of the prepared activated carbons at different activation temperatures.

850°C, which shows that nitrogen is oxidized and more easily removed than carbon during the KOH activation process [14]. This also indicates that C-N bonds are more easily ruptured at higher temperatures. Moreover, the existence of alkaline nitrogen functional groups favors increased CO₂ adsorption.

The CO₂ adsorption capacities of the activated carbons were measured using CO₂ adsorption isotherms at 298 K, and the obtained results are shown in Fig. 5. All of the porous carbons show high CO₂ adsorption capacities (at least 30 mg g⁻¹) in the order

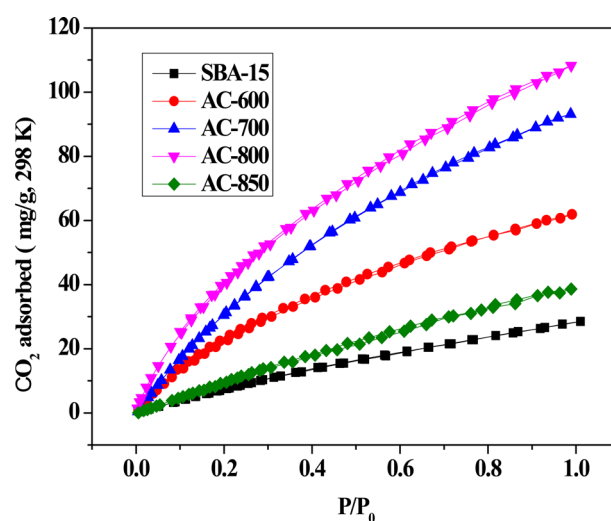


Fig. 5. CO₂ adsorption capacities of the prepared activated carbons at different activation temperatures (at 298 K and 1 bar).

of AC-800 > AC-700 > AC-600 > AC-850 > SBA-15. This indicates that a relatively high activation temperature is favorable for CO₂ adsorption. AC-800 exhibits the best CO₂ adsorption capacity at 110 mg g⁻¹, which is attributed to its high surface area. As the carbon surface is the CO₂ adsorption site and the pore volume is the volume available for trapping CO₂, a large number of adsorption sites and a high trapping volume lead to a high CO₂ adsorption capacity [18-20]. CO₂ adsorption not only relies on the pore structure and surface area of the carbons but also on the surface functional groups. In this study, the prepared porous carbons contained basic nitrogen functional groups, which can act as chemical adsorption sites for CO₂. The basic functional groups increase the surface interactions with acidic CO₂ gas, thereby enhancing the CO₂ adsorption capacity.

4. Conclusions

In summary, nitrogen-doped porous carbons were directly prepared from a polypyrrole carbon precursor, with SBA-15 serving as a template, via chemical activation with KOH. The effect of the activation temperature on the pore structure and CO₂ adsorption capacity of the obtained porous carbons was studied. We found that the N-doped carbons had high surface

areas (up to 1488 m² g⁻¹), large pore volumes (up to -1.164 cm³ g⁻¹), and porosities within the micropore-mesopore range.

Interestingly, porous carbons with narrow microporosity and a high nitrogen content (up to 4.744 wt%) in the form of N basic sites (pyridonic-N groups) can be obtained using the method presented here. These mildly activated carbons exhibit a high efficiency for CO₂ capture, with a maximum CO₂ uptake of 110 mg g⁻¹ obtained at room temperature when using an activation temperature of 800°C. This maximum CO₂ adsorption capacity was attributed to the narrow microporosity of AC-800 together with its high density of basic N groups.

Conflict of Interest

No potential conflict of interest relevant to this article was reported.

Acknowledgements

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References

- [1] Joos F. Global warming: growing feedback from ocean carbon to climate. *Nature*, **522**, 295 (2015). <https://doi.org/10.1038/522295a>.
- [2] Lee YC, Lee SM, Hong WG, Huh YS, Park SY, Lee SC, Lee J, Lee JB, Lee HU, Kim HJ. Carbon dioxide capture on primary amine groups entrapped in activated carbon at low temperatures. *J Ind Eng Chem*, **23**, 16 (2015). <https://doi.org/10.1016/j.jiec.2014.08.020>.
- [3] Hwang DG, Jeong E, Lee SG. Density functional theory study of CH₄ and CO₂ adsorption by fluorinated graphene. *Carbon Lett*, **20**, 81 (2016). <https://doi.org/10.5714/cl.2016.20.081>.
- [4] Antolini E. Nitrogen-doped carbons by sustainable N- and C-containing natural resources as nonprecious catalysts and catalyst supports for low temperature fuel cells. *Renewable Sustainable Energy Rev*, **58**, 34 (2016). <https://doi.org/10.1016/j.rser.2015.12.330>.
- [5] Xia KS, Tian XL, Fei SX, You K. Hierarchical porous graphene-based carbons prepared by carbon dioxide activation and their gas adsorption properties. *Int J Hydrogen Energy*, **39**, 11047 (2014). <https://doi.org/10.1016/j.ijhydene.2014.05.059>.
- [6] Gibson JAA, Gromov AV, Brandani S, Campbell EEB. The effect of pore structure on the CO₂ adsorption efficiency of polyamine impregnated porous carbons. *Microporous Mesoporous Mater*, **208**, 129 (2015). <https://doi.org/10.1016/j.micromeso.2015.01.044>.
- [7] Hu XM, Chen Q, Zhao YC, Laursen BW, Han BH. Facile synthesis of hierarchical triazine-based porous carbons for hydrogen storage. *Microporous Mesoporous Mater*, **224**, 129 (2016). <https://doi.org/10.1016/j.micromeso.2015.11.046>.
- [8] Zhang YF, Zhang CX, Huang GX, Xing BL, Duan YL. Tailoring the textural properties of hierarchical porous carbons for supercapacitors. *Mater Lett*, **159**, 377 (2015). <https://doi.org/10.1016/j.matlet.2015.07.020>.
- [9] Ru HH, Bai NB, Xiang KX, Zhou W, Chen H, Zhao XS. Porous carbons derived from microalgae with enhanced electrochemical performance for lithium-ion batteries. *Electrochim Acta*, **194**, 10 (2016). <https://doi.org/10.1016/j.electacta.2016.02.083>.
- [10] Choma J, Jedynak K, Fahrenholz W, Ludwinowicz J, Jaroniec M. Microporosity development in phenolic resin-based mesoporous carbons for enhancing CO₂ adsorption at ambient conditions. *Appl Surf Sci*, **289**, 592 (2014). <https://doi.org/10.1016/j.apsusc.2013.11.051>.
- [11] Wang HL, Gao QM. Template synthesis, activation and energy storage application of porous carbon materials. *Chem J Chin Univ*, **32**, 462 (2011).
- [12] Shi Q, Zhang RY, Lv Y, Deng YY, Elzatahrya AA, Zhao DY. Nitrogen-doped ordered mesoporous carbons based on cyanamide as the dopant for supercapacitor. *Carbon*, **84**, 335 (2015). <https://doi.org/10.1016/j.carbon.2014.12.013>.
- [13] Huang X, Wang Q, Chen XY, Zhang ZY. N-doped nanoporous carbons for the supercapacitor application by the template carbonization of glucose: the systematic comparison of different nitridation agents. *J Electroanal Chem*, **748**, 23 (2015). <https://doi.org/10.1016/j.jelechem.2015.04.024>.
- [14] Wahby A, Ramos-Fernández JM, Martínez-Escandell M, Sepúlveda-Escribano A, Silvestre-Albero J, Rodríguez-Reinoso F. High-surface-area carbon molecular sieves for selective CO₂ adsorption. *ChemSusChem*, **3**, 974 (2010). <https://doi.org/10.1002/cssc.201000083>.
- [15] Sevilla M, Valle-Vigón P, Fuertes AB. N-doped polypyrrole-based porous carbons for CO₂ capture. *Adv Funct Mater*, **21**, 2781 (2011). <https://doi.org/10.1002/adfm.201100291>.
- [16] Wan K, Liu MY, Yu ZP, Liang ZX, Liu QB, Piao JH, Zheng YY. Synthesis of nitrogen-doped ordered mesoporous carbon electrocatalyst: nanoconfinement effect in SBA-15 template. *Int J Hydrogen Energy*, **41**, 18027 (2016). <https://doi.org/10.1016/j.ijhydene.2016.07.169>.
- [17] Wang AP, Kang FY, Huang ZH, Guo ZC. Preparation of natural zeolite template carbon and its nanopore formation mechanism. *Carbon*, **45**, 2323 (2007). <https://doi.org/10.1016/j.carbon.2007.06.039>.
- [18] Lee CH, Hyeon DH, Jung H, Chung W, Jo DH, Shin DK, Kim SH. Effects of pore structure and PEI impregnation on carbon dioxide adsorption by ZSM-5 zeolites. *J Ind Eng Chem*, **23**, 251 (2015). <https://doi.org/10.1016/j.jiec.2014.08.025>.
- [19] Bai BC, Kim JG, Im JS, Jung SC, Lee YS. Influence of oxyfluorination on activated carbon nanofibers for CO₂ storage. *Carbon Lett*, **12**, 236 (2011). <https://doi.org/10.5714/cl.2011.12.4.236>.
- [20] Yuan H, Meng LY, Park SJ. KOH-activated graphite nanofibers as CO₂ adsorbents. *Carbon Lett*, **19**, 99 (2016). <https://doi.org/10.5714/cl.2016.19.099>.
- [21] Islam MS, Ang BC, Gharekhani S, Afifi ABM. Adsorption capability of activated carbon synthesized from coconut shell. *Carbon Lett*, **20**, 1 (2016). <https://doi.org/10.5714/cl.2016.20.001>.