

Review of the use of activated biochar for energy and environmental applications

Hyung Won Lee^{1,*}, Young-Min Kim^{2,*}, Seungdo Kim², Changkook Ryu³,
Sung Hoon Park⁴, and Young-Kwon Park^{1,*}

¹School of Environmental Engineering, University of Seoul, Seoul 02504, Korea

²Department of Environmental Sciences and Biotechnology, Hallym University, Chuncheon 24252, Korea

³School of Mechanical Engineering, Sungkyunkwan University, Suwon 16419, Korea

⁴Department of Environmental Engineering, Suncheon National University, Suncheon 57922, Korea

Article Info

Received 13 September 2017

Accepted 21 November 2017

*Corresponding Author

E-mail: catalica@uos.ac.kr

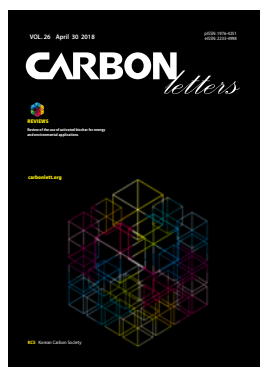
Tel: +82-2-6490-2870

*Co-first authors

Open Access

DOI: [http://dx.doi.org/
10.5714/CL.2018.26.001](http://dx.doi.org/10.5714/CL.2018.26.001)

This is an Open Access article distributed under the terms of the Creative Commons Attribution Non-Commercial License (<http://creativecommons.org/licenses/by-nc/3.0/>) which permits unrestricted non-commercial use, distribution, and reproduction in any medium, provided the original work is properly cited.



<http://carbonlett.org>

pISSN: 1976-4251

eISSN: 2233-4998

Copyright © Korean Carbon Society

Abstract

Biochar obtained from the thermal conversion of biomass has high potential as a substitute material for activated carbon and other carbon-based materials because it is economical, environmentally friendly, and carbon-neutral. The physicochemical properties of biochar can also be controlled by a range of activation methods such as physical, chemical, and hydrothermal treatments. Activated biochar can be used as a catalyst for the catalytic pyrolysis of a biomass and as an adsorbent for the removal of heavy metal ions and atmospheric pollutants. The applications of biochar are also expanding not only as a key component in producing energy storage materials, such as supercapacitors, lithium ion batteries, and fuel cells, but also in carbon capture and storage. This paper reviews the recent progress on the activation of biochar and its diverse present and future applications.

Key words: biochar, activation, energy storage materials, catalyst, adsorbent,

1. Introduction

The worldwide interest in renewable energy sources is being raised by accelerated global warming, air contamination, and fossil fuel shortage. Among the various types of renewable energy sources, biomasses are particularly important because they are the only carbon source that can replace fossil fuels [1-3].

Biomasses can also be converted into fuels and chemicals using suitable thermochemical conversion technologies such as torrefaction, gasification, and pyrolysis [4]. Torrefaction, a mild heat treatment at relatively low temperatures between 200 and 320 °C, can improve the biomass feed property for gasification, combustion, and pyrolysis processes [5-6]. Gasification, which is usually applied to carbonaceous materials, such as a biomass, is a partial oxidation process using gasification agents such as steam, CO₂, and gas mixtures. This process can produce large amounts of gaseous products, such as H₂ and CO, mostly together with oil and solid products (char and ash) [7-8]. Pyrolysis is a thermal decomposition reaction of polymeric materials at temperatures ranging from 300 to 900 °C under a non-oxygen atmosphere producing gas, oil, and solid products. The yields and properties of the gas, oil, and solid products produced by the pyrolysis of a biomass are differentiated not only by the properties of the feeding biomass but also by the pyrolysis reaction conditions such as the temperature, heating rate, and residence time [9-10].

Biochar is a solid product produced as a byproduct of the thermal conversion processes of a biomass. The effective use of biochar has also been emphasized because of its high carbon content and rapid increase in production. The low cost and high porosity are also accelerating research into the use of biochar in a wide range of industries [11]. Biochar has also been

assessed widely as a key material for environmental applications such as soil remediation, waste water treatment, greenhouse gas reduction, biofuel upgrading, and energy storage equipment (e.g., supercapacitors, lithium-ion batteries, and fuel cells) [12]. Recently, improvements in the biochar quality have become an important research area, and various types of activation technologies, such as physical and/or chemical activation, have been applied to the production of high quality biochar depending on the purpose of its use [13,14]. The manufacture of biochar-based nano-composites, such as nano-metal oxide/hydroxide-, magnetic-, and functional biochar nano-composites, is also an important research area [15-18]. As a large number of new studies on the use of biochar are being reported, a systematic review is necessary to provide a better understanding of the recent technical trends of the applications of biochar.

Therefore, in this article, the manufacturing processes of activated biochar and biochar-based nano-composites are reviewed together with their applications in biofuel upgrading, energy storage, and removal of environmental pollutants.

2. Biochar activation

The physico-chemical properties of biochar can be improved by its activation. The methods of activating biochar and the synthesis of biochar-based nano-composites are differentiated by the use of biochar (Table 1).

2.1. Physical activation

The activation of biochar by physical activation is normally processed by a two-step treatment. In the first step, the carbonization step, a relatively low temperature between 700 and 1150 K is applied. A higher temperature (900-1200 K) is applied to the activation of carbonized biochar [19,20]. Due to the high energy and time consumption, the actual application of physical activation is limited, and other activation technologies have been attempted by many researchers.

2.2. Chemical activation

Chemical activation can produce high quality biochar with a higher surface area and porosity than physically activated biochar (Fig. 1). In addition, the chemical activation of biochar can proceed at a lower temperature than the physical activation of biochar. A long processing time and high energy are required in chemical activation during the washing step to eliminate the residual impurities [43,44].

2.3. Hydrothermal carbonization

Hydrothermal carbonization (HTC), which is an effective method to produce nanostructured carbon, can control the morphology, surface chemistry, and functionality of biochar. For structural aromaticity and the high yield of biochar, a relatively low temperature (180-250°C) is applied to the HTC process. The surface area and chemical activity of the biochar can also be further increased by applying the HTC process together with chemical activation [45,46].

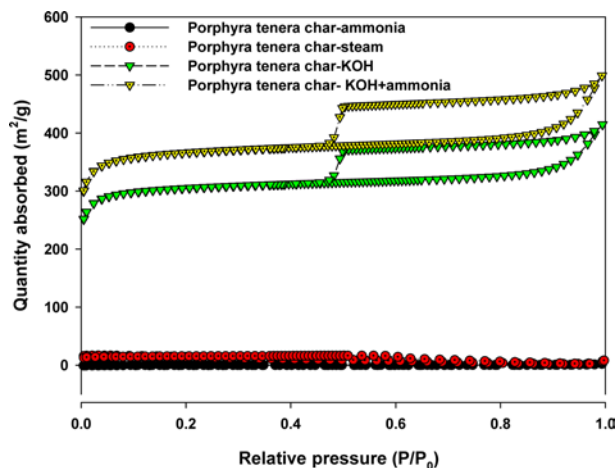


Fig. 1. Nitrogen sorption isotherms of activated biochar [36].

2.4. Other activation methods

Recently, microwave-induced/assisted activation was also applied to the activation of biochar. Duan *et al.* [47] suggested microwave heating as a better activation method of biochar than conventional heating because the distorted and inhomogeneous microstructure of the biochar activated by conventional heating can be improved by applying microwave heating, which enables a smaller temperature difference between the inside and outside of the biochar particles. In addition, other activation methods using a range of chemicals, such as HNO_3 , H_2O_2 , H_2SO_4 , ammonium peroxydisulfate, and ammonia water, as the activation agent have also been used for biochar activation [48].

3. Biochar for the catalytic pyrolysis of a biomass

Biomass pyrolysis produces large amounts of bio-oil. On the other hand, biomass pyrolysis oil has a few important drawbacks. Its oxygen content is much higher than that of petroleum oil, and it has high acidity and reactivity, because of the high contents of organic acids, and a low heating value, and it is difficult to mix it well with petrochemical fuels such as gasoline. Therefore, the additional catalytic upgrading of biomass pyrolysis oil is considered an essential process to produce high-quality oil containing large amounts of hydrocarbons by decreasing the contents of oxygenated compounds such as organic acids [49-51].

Biomass pyrolysis oil can be upgraded using a range of technologies such as hydrotreating, hydrocracking, catalytic pyrolysis, esterification, emulsification, and steam reforming [52]. Among them, catalytic pyrolysis has been applied widely to produce high quality bio-oil because it can be performed under ambient pressure without the use of hydrogen. The increased content of hydrocarbon, such as aromatic hydrocarbons, in bio-oil by applying a range of catalysts, such as zeolites, activated alumina, fluid catalytic cracking (FCC) catalyst, and transition metal catalysts, to the catalytic py-

Table 1. List of various biochar-based material applications.

Application	Purpose	experimental condition	activation method	Ref	
Catalyst	Biorefinery	corn stover / 650 °C pyrolysis	-	[21]	
		red cedar / 850 °C gasification	KOH (nickel impregnation)	[22]	
	DeNOx	rice straw, sewage sludge / 500 °C pyrolysis	steam, KOH	[23]	
		cotton stalk / 600 °C - 5 °C/min pyrolysis	steam, H ₃ PO ₄	[24]	
		rice husk / 850 °C - 5 °C/min pyrolysis	ZnCl ₂	[25]	
		waste paper / 900 °C - 3 °C/min pyrolysis	HNO ₃	[26]	
		hemp bast fiber / 180 °C HTC	HTC / KOH	[27]	
		cotton cloth / 900 °C pyrolysis	CO ₂	[28]	
		cotton wool / 700-1100 °C multi step pyrolysis	-	[29]	
		Wood / 200°C-350 °C pyrolysis	-	[30]	
Corn cob / 700 °C pyrolysis	-	[31]			
Biochar	Energy storage materials	Pine wood lumber / 1000 °C - 17 °C/min gasification	KOH	[32]	
		Olive stone, almond shells / 800, 750 °C pyrolysis	CO ₂	[33]	
	Sorbent of pollutant	RDF / 500 °C pyrolysis	steam, KOH	[34]	
		Rice husk / 800 °C - 5 °C/min pyrolysis	FeCl ₃ ·6H ₂ O	[35]	
	adsorbent for air pollutants	Porphyra tenera / 500 °C pyrolysis	steam, KOH	[36]	
		CCS	corn straws / 600 °C pyrolysis	KMnO ₄	[37]
			Laminaria japonica / 600 °C electro assisted pyrolysis	MgCl ₂	[38]
		decontamination of waste-water (metals, organic, inorganic)	Oak wood, oak bark / 400, 450 °C pyrolysis	chemical coprecipitation of iron oxides	[39]
			Hickory chip, sugarcane bagasse / 600 °C slow pyrolysis	CNT coating	[40]
			Wheat straw / 600 °C slow pyrolysis	graphene pretreatment	[41]
Bamboo, sugarcane, hickory wood, peanut hull / 600 °C pyrolysis	chitosan coating		[42]		

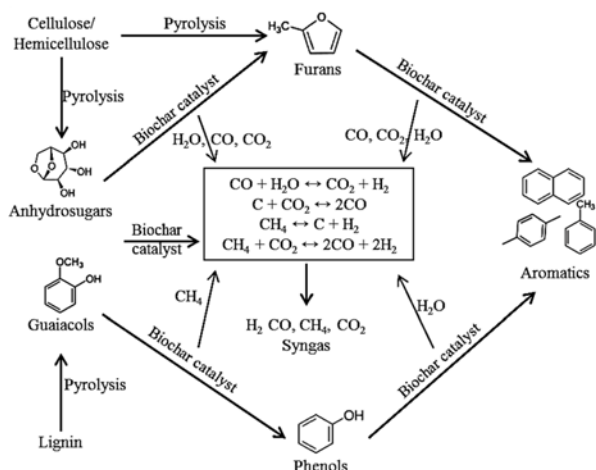


Fig. 2. Reaction pathway of catalytic pyrolysis using biochar catalyst under microwave heating [21].

rolysis of a biomass has been reported [53,54]. The catalytic upgrading of biomass pyrolysis oil by an esterification reaction using WO_3/ZrO_2 , and an Amberlyst catalyst at low temperatures was also used to reduce the total acid number (TAN) and the viscosity of bio-oil [55]. Nevertheless, commercialization of the catalytic pyrolysis of a biomass and the catalytic upgrading of pyrolysis oil is difficult because of the low efficiency and high catalyst price [21].

Biochar is regarded by many researchers as a cost-competitive catalyst for the catalytic pyrolysis of a biomass. Ren *et al.* [21] used corn stover biochar as a catalyst for the microwave pyrolysis of torrefied Douglas fir sawdust pellets. They reported that the yields of phenolics and hydrocarbons in the product oil and the contents of H_2 , CO , and CH_4 were increased using the corn stover biochar shown in Fig. 2.

Li *et al.* [56] examined the effects of activated biochars on the catalytic pyrolysis of lignin using a bubbling fluidized bed reactor. The activated biochars were obtained from the activation of lignin and birch bark in a batch reactor at 800°C under a CO_2 atmosphere. They suggested that the activated biochars produced larger amounts of bio-oil with a lower water content and smaller average molecular weight than the nonactivated chars. The phenolics content was also increased with decreasing acidity by applying the activated biochars as a catalyst. Poggi *et al.* [57] also attempted the catalytic decomposition of acetic acid, which is one of the typical oxygenates in biomass pyrolysis oil, using biochar and a fluid catalytic cracking (FCC) catalyst as the catalyst. They reported that the activated biochars led to higher conversion efficiencies of acetic acid than that of the FCC catalyst.

From these studies, it was concluded that biochar has a strong potential for replacing commercial catalysts using bio-energy products. Despite the potential of biochar catalysts, their actual catalytic performance is still lower than that of conventional zeolite catalysts. Therefore, more intensive research will be needed to increase the performance of activated biochar by increasing its functionality or co-use with high performance catalysts.

4. Biochar as an energy storage material

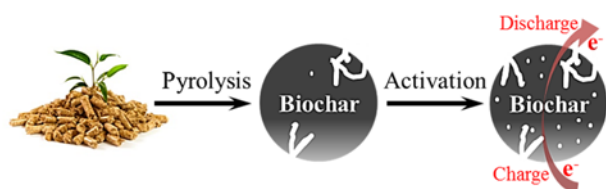
Worldwide energy consumption is increasing, and the importance of energy conversion without increasing the level of environmental contamination has become an important factor in social and economic development. To meet the energy demand, it is necessary to develop a system to store clean energy that can reduce the fossil fuel consumption [58,59]. One of the possible solutions is the development of clean energy storage devices using waste. Typical examples include lithium ion batteries, fuel cells, and supercapacitors (SCs). Among them, SCs are promising electrochemical energy storage systems that can be used in wireless terminals and electric vehicles. Therefore, there has been intensive research into the development of more powerful devices producing stronger forces with rapid charging and discharge performance [60]. On the other hand, SCs are not renewable and sustainable because they use graphite and inorganic materials containing rare metals as the core elements. In contrast, biomass-based materials are environment-friendly and naturally abundant, have inherent mechanical strength and flexibility because of their diverse structure, and can be used together with other materials. Therefore, extensive research on the use of biomass-based materials is being performed to develop SCs with a high power density and batteries with ultrahigh capacity [61].

4.1. SCs

SCs consist of two of the same electrodes (anode and cathode), both of which are attached to electrolytes (bilayers). The charging mechanism of SCs is determined by the charging effect of the double layer. Electrode materials enabling the operation of SCs are classified into three categories: carbon-based materials, transition metal oxide, and conducting polymers. Various kinds of carbon-based materials, such as activated carbon, carbon aerogels, graphite, carbon nanotubes, carbon nanofibers, and nanosized carbon, have been used as the electrode materials in SCs because of their accessibility, easy processability, non-toxicity, high chemical stability, and wide application temperature range. Activated carbon is used mainly as a capacitor because of its high porosity and large surface area, which can increase charging at the contact surface [62]. Most carbon electrodes are produced from fossil fuel-based precursors (e.g., petroleum coke and coal); hence, they are not economical and reproducible. On the other hand, carbon electrodes require high energy consumption because high temperature and vacuum conditions are required for their manufacture. Recently, biomass-based materials and byproducts have been used to develop new carbon electrodes as a potential solution from the view point of the environment and energy. Various types of biomasses, such as wood, plant tissues, agricultural waste, and industrial biomass wastes, can be used for manufacturing electrodes because of their low price. Active research on the production of SCs from biochar is also being performed, whose main purpose is to increase the specific capacitance through the appropriate proper activation of biochar shown in Table 2. Zhao *et al.* [63] synthesized powdered activated carbon (PAC) from potato starch and activated it via stabilization, carbonization, and KOH activation for application in

Table 2. List of carbon derived from biomasses for electrode materials in capacitors.

No	Biomass	Activating agent	Electrolyte	BET surface area (m ² /g)	Specific capacitance (F/g)	ref.
1	Potato starch	KOH	KOH	2342	335	[63]
2	Sunflower	KOH	KOH	1371-2821	311	[64]
3	Walnut shell	Physical/chemical activation	KOH	1197	292	[65]
4	Sugar cane bagasse	ZnCl ₂	H ₂ SO ₄	1788	300	[66]
5	Waste newspaper	pyrolysis (without activation)	KOH	459	300	[67]
6	Waste coffee ground	ZnCl ₂	H ₂ SO ₄	1021	368	[68-69]
7	Eggshell	pyrolysis (without activation)	Acidic	221	284	[70]
			Basic		297	

**Fig. 3.** A schematic diagram of SCs using activated biochar [44, 63].

SCs (Fig. 3). The activated PACs showed a high specific capacitance (335 F/g), and their specific surface area increased with an increasing KOH/PACs ratio and with a decreasing carbonization temperature. They also observed a linear dependence between the specific surface area and specific capacitance. Rufford *et al.* [66] tested the electrochemical performance of activated carbon electrodes synthesized from the activation of sugarcane bagasse by ZnCl₂. They revealed that the activated carbon electrodes in the supercapacitor cell containing 1 M of H₂SO₄ electrolyte has a high specific capacitance (300 F/g) and explained that the high specific capacitance is made by the formation of a high surface area and the presence of mesopores when ZnCl₂ acts as an activator. Rufford *et al.* [68,69] synthesized activated carbon from waste coffee grounds and obtained specific capacitances of 100 and 368 F/g through the activation using organic (C₂H₅)₄NBF₄/CH₃CN and inorganic H₂SO₄ electrolytes, respectively. Jurewicz *et al.* [71] also produced activated carbon with a large specific surface area and high capacitance using coconut shell/melamine as the precursor.

4.2. Electrodes in lithium-ion batteries

Lithium-ion batteries have attracted considerable attention as a secondary battery because of their high energy charging capacity. A lithium-ion battery is composed of a carbon material used as the anode and a lithium transition metal oxide used as the cathode [72]. The theoretical charging capacity of graphitic carbon used as the anode of lithium-ion batteries is 372 mAh/g. The development of a material that can increase the level of lithium ion accumulation is important because the overall capacity of a lithium-ion cell depends strongly on the lithium-ion charging amount of the carbon structure. The lithium metal used as the anode of the lithium secondary bat-

tery has an approximately 10 times higher accumulation amount (3800 mAh/g) than that of the carbon-based LiC₆ anode (372 mAh/g). On the other hand, the overall lifetime of the lithium metal anode is short because it reacts with both aprotic and protic solvents at the surface. This short lifetime can cause many problems, such as electrochemical reactions with the anodes and electrolytes and the loss of electrical contact with the electrodes and the dendritic lithium. Therefore, it is essential to develop a new material that is cheaper, more active, and can provide a higher ion accumulation capacity [73].

Various solid byproducts obtained from the pyrolysis of biomasses, such as rice husk, cherry stones, tea leaves, and sugarcane bagasse, have also been applied to lithium-ion batteries. The low specific capacities of biochar (63-291 mAh/g) obtained from the pyrolysis of biomasses were increased by proper activation using a proprietary porogenic agent, KOH, and ZnCl₂, shown in Table 3. Kuo *et al.* [76,77] examined lithium ion batteries using the biochar of rice husk that had been activated using a proprietary porogenic agent. The specific area of the biochar was increased from 20 to 1597 m²/g by the activation, and its capacity was also increased dramatically. Stephan *et al.* [78] applied banana fiber biochar to lithium ion batteries. They obtained specific capacities of 3,123 and 921 mAh/g by the ZnCl₂ and KOH activation of porogen-treated biochar, respectively. The specific capacity of the biochar was low (625 mAh/g) when a porogen was not used to activate the biochar. Kuo *et al.* [80-81] investigated the porogen treatment of disordered carbon produced from the pyrolysis of peanut shells. They reported that the first-cycle lithium insertion capacity of the porogen-treated carbon was increased by up to 3504 mAh/g because of its high surface area (2099 m²/g) formed by its activation. They also carbonized the peanut shell through a two-step process between 300 and 600 °C and treated it with proprietary porogenic agents. Both untreated and porogen-treated shells produced carbon materials that could be used as a cathode material for lithium-ion batteries. Using porogenic agents as an activator, its surface area was increased 66 fold compared to that of the untreated carbon material, and its initial lithium intake capacity also increased up to 4,765 mAh/g.

A lithium-sulfur battery with a theoretical ultrahigh specific capacity of 1650 mAh/g and an energy density of 2600 Wh/kg is a next-generation high-energy battery that is particularly suit-

Table 3. List of carbon derived from biomasses for electrode materials in lithium-ion batteries.

No.	Biomass	Activation method	Temperature (°C)	specific capacity (mAh/g)	Progenic treatment	Ref.
1	Pinecone hull	CO ₂	450	357	-	[74]
2	Coffee shells	pyrolysis (without activation)	800	1150	KOH	[75]
			900	1200	KOH	
3	Rice husk	pyrolysis (without activation)	500-900	1190-3253	Proprietary porogenic agent	[76-77]
4	Banana fibers	pyrolysis (without activation)	800	921	KOH	[78]
				3123	ZnCl ₂	
5	Coconut shell	pyrolysis (without activation)	800	950	KOH&ZnCl ₂	[79]
			900	1714	KOH&ZnCl ₂	
6	Peanut shells	pyrolysis (without activation)	900	3504	Proprietary porogenic agent	[80]
7	Peanut shells	pyrolysis (without activation)	500	4765	Proprietary porogenic agent	[81]
			600	3504	Proprietary porogenic agent	
			700	2783	Proprietary porogenic agent	
			800	2977	Proprietary porogenic agent	
8	Cotton cloth	CO ₂	900	1400	-	[82]

able for applications requiring a higher energy transfer such as electric vehicles and grid scale stationary storage. Sulfur, which is rich in nature, inexpensive, and environmentally friendly, is a core component of lithium-sulfur batteries. On the other hand, its commercialization is limited due to several problems including low sulfur utilization, rapid capacity decay, and low cycling stability. These problems are caused by the dissolution of lithium polysulfides and the large volume change between sulfur and sulfide during the electrochemical process [44, 83].

Until now, a variety of approaches, such as new electrolyte development, separator modification, lithium anode protection, and new configuration design, have been adopted to mitigate the 'shuttle effect' of polysulfides and extend the circulation cycle. Among the various approaches, the most effective way has been to hybridize sulfur with conductive carbon substrates to produce C/S composites. For this, various carbon materials, such as microporous carbon, mesoporous carbon, interconnected pore-structured hierarchical carbon, graphene nanosheets, carbon nanotubes, and hollow carbon fibers, have been found to exhibit excellent conductivity, chemical stability, and mechanical durability [44].

4.3. Fuel cells

Fuel cells exhibit relatively high efficiencies and can contribute to the decrease in greenhouse gas emissions if renewable fuels are used. Recently, a direct carbon fuel cell (DCFC) converting a molten carbonaceous solid fuel into electricity has been developed using biochar and coal as the carbonaceous solid fuel for the DCFC [31]. A DCFC using biochar showed a relatively

high current (64.2 mA/cm²) and power density (32.8 mW/cm² at 0.5 V) compared to commercial hard coal and carbon black (about 55 mA/cm² and 28 mW/cm² at 0.5V) [84]. Elleuch *et al.* [85-86] used almond shell biochar in a DCFC and compared its efficiency with that of commercial activated carbon. They reported that the almond shell biochar had a current density of 480 mA/cm² and a maximum power output of 127 mW/cm², which is double the efficiency of commercial activated carbon. Biochar is normally used as a low-cost anode material and catalyst in different types of fuel cells, such as microbial fuel cells (MFC). Although biochar has shown lower efficiencies (532-457 mW/m²) than activated carbon (674 mW/m²) and graphite (566 mW/m²), it can provide an economical advantage due to its low cost because the power output cost of biochar (17-35 \$/W) is much lower than that of activated carbon (402 mW/m²) and graphite (392 mW/m²) [87]. Research into the use of biochar as a catalyst for MFCs has also been reported. The catalytic layer-coated cathode is used for MFCs, and wet-proofed carbon is used as the catalytic layer. Yuan *et al.* [88] used sewage sludge-derived biochar and Pt/C as the cathode of MFCs. Although sewage sludge-derived biochar showed a similar efficiency as Pt/C, it had a better stability in terms of the change in voltage output and anti-depolarization ability.

Despite the high potential and extensive studies of biochar, its commercialization as an energy storage material is limited by its lower performance compared to conventional energy storage materials. To increase the energy storage efficiency, more study will be needed to understand the interactions between the biochar properties and energy storage as well as to increase the overall efficiency.

5. Biochar as an environmental material

The importance of biochar in environmental applications has increased in recent decades. One of the applications is carbon capture and storage (CCS) to decrease the levels of greenhouse gases such as carbon dioxide (CO_2). The use of biochar as an absorbent to eliminate pollutants in an air or water matrix is a potential application that has been studied intensively.

5.1. Carbon capture and storage

CO_2 is the dominant greenhouse gas emitted from the combustion of fossil fuels. Research on CCS is being actively performed to reduce greenhouse gas emissions from large stationary sources such as coal-fired power plants. In CCS, carbon materials can be used efficiently because of their higher stability and higher regeneration. The development of new materials is necessary because of the relatively high cost of the carbon materials used in CCS. In this aspect, biochar can be a solution thanks to its low price. Creamer *et al.* [89] produced biochar from the pyrolysis of sugarcane bagasse and hickory wood at 300, 450, and 600°C and tested their CO_2 sorption efficiencies. The biochar produced at the highest temperature (600°C) showed the highest CO_2 adsorption efficiency (73.55 mg/g at 25°C). Most of the CO_2 was adsorbed onto the biochar by weak physical adsorption. Creamer *et al.* [90] used biochar pretreated with metal ions for CCS. Aluminum hydroxide, magnesium hydroxide, and iron oxide were used for the pretreatment during the synthesis of carbon composites from the pyrolysis of cottonwood at 600°C. The synthesized material consisted of biochar and metal oxyhydroxide nanoparticles and showed a much larger CO_2 capture capacity than the untreated biochar. Among the various kinds of composites, aluminum hydroxide-biochar composite revealed the highest CO_2 adsorption capacity (71 mg/g at 25°C) because of its large surface area and metal nanoparticles.

5.2. Removal of heavy metal ions

Many studies have used biomasses or biomass composites to remove heavy metals and other water pollutants [91-96] and found that biochar is a more powerful absorbent for removing pollutants in wastewater than biomasses. The effective removal of heavy metals such as Cu, Pb, As, Cr, and mercury using biochar and biochar-nano composites has been reported [97-98]. Various types of biochar obtained from sunflower plates, pomegranate husk, and sugarcane bagasse have also been used to remove phenol, 4-chlorophenol, p-nitrophenol p-benzoquinone, tetracycline, and polyvinyl alcohol as well as heavy metals such as mercury, Pb and Cr in wastewater [99-101]. Park *et al.* [102] used red macroalga porphyra tenera pyrolysis char for the removal of copper ions. They improved the surface properties of the porphyra tenera pyrolysis char by activation with steam and KOH. The steam-activated biochar showed a higher copper removal efficiency due to the increased quantity of exchangeable cations in the biochar. In addition, although the KOH-activated char had an increased surface area and pore volume, its exchangeable cation quantity and copper removal efficiency were low. Lee

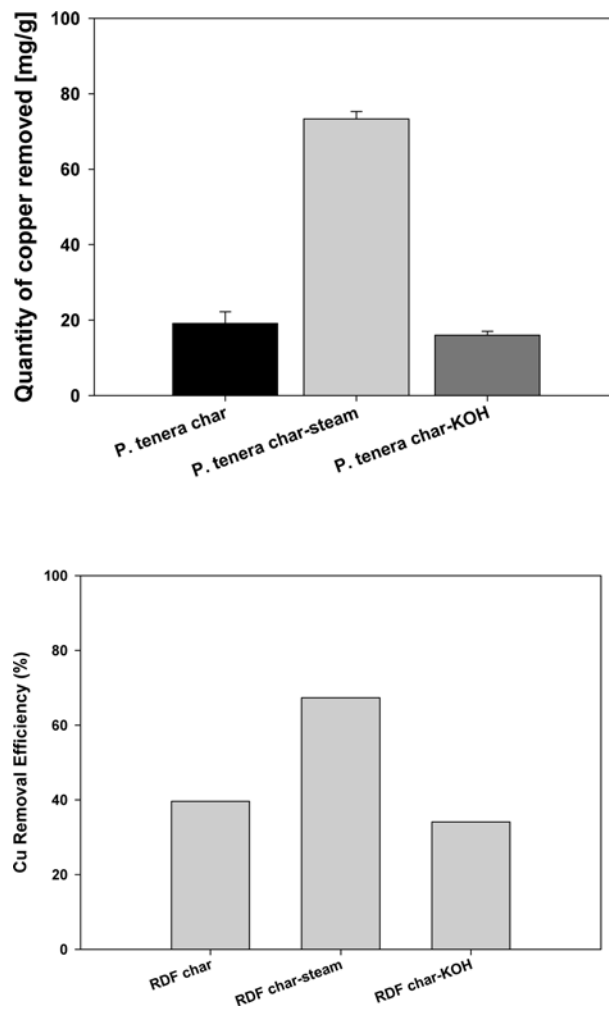


Fig. 4. Comparison of the copper removal capabilities of biochars [34, 102].

et al. [34] applied the biochar produced from the pyrolysis of refuse derived fuel (RDF) to copper ion removal. The activation of the RDF biochar using steam and KOH increased its surface area, pore volume, and metal cation quantity. They reported that the steam-activated RDF char had the best performance for the removal of copper (38.17 mg/g) (Fig. 4). Zhou *et al.* [103] also reported the use of magnetic gelatin-modified biochar for the removal of arsenic in wastewater. They used chestnut shells for the production of pyrolysis biochar and modified the biochar using magnetic gelatin to increase its surface area and improve its magnetic properties. The arsenic adsorption capacity of the biochar was increased from 17.5 to 45.8 mg/g by the activation of the biochar. The synthesis of magnetic biochar from empty palm oil bunches with FeCl_3 and from agricultural waste rice husk with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ was also investigated to remove Cd and Cr [104]. In addition, the removal of Pb and methylene green was attempted using hydrochar produced from the hydrothermal treatment of corn straw black liquor, golden shower pods, coconut shells, and orange peels [105-106].

5.3. Removal of atmospheric pollutants

Due to the increased number of vehicles and factories together with rapid urbanization, the quantities of air pollutants, such as NO_x and volatile organic compounds, have also increased. They need to be removed by the appropriate environmental technologies. Several studies using biochar for the removal of air pollutants have been reported [23, 107-108]. Lee *et al.* [36] used porphyra tenera biochar to replace activated carbon for the removal of NO and formaldehyde. They activated the biochar using KOH, KOH with ammonia, and steam. The biochar activated using KOH with ammonia showed the highest formaldehyde removal efficiency. In the case of NO removal, the KOH-activated biochar had a higher efficiency than that of the other biochars shown in Fig. 5.

Kang *et al.* [109] compared the efficiencies of various nanoporous carbon materials for the removal of acetaldehyde, a major source of food waste odor. They activated the Geodae-Uksae pyrolysis char using steam or KOH and compared the acetaldehyde removal efficiencies of the activated biochars with that of nanoporous CMK-8. The activated biochars showed higher acetaldehyde removal efficiencies than that of the CMK-8 because

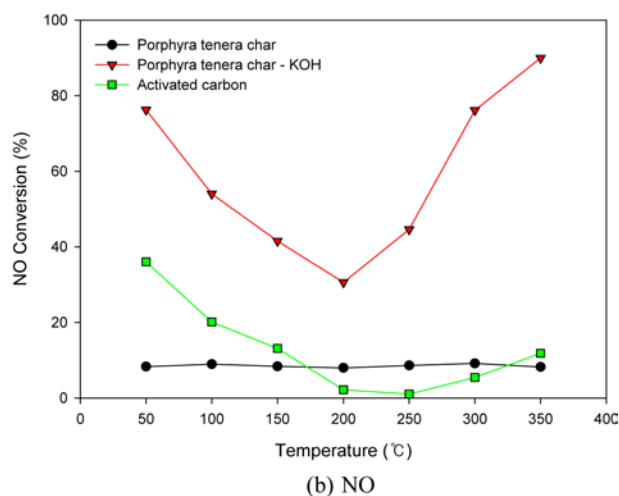
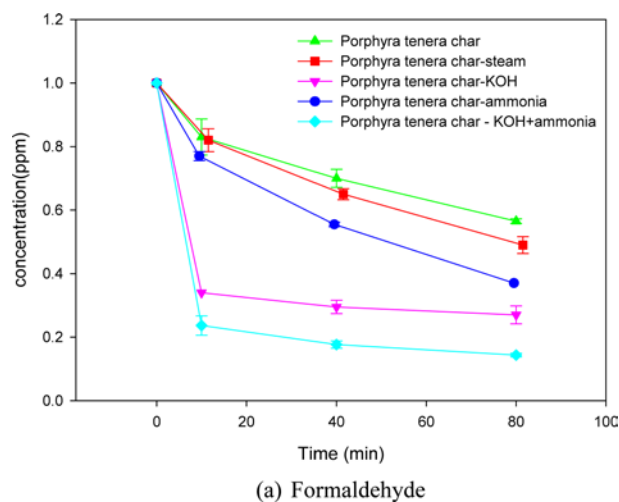


Fig. 5. Formaldehyde and NO removal using biochar [36].

of their large number of nitrogen and oxygen functional groups. The high adsorption capacity of the activated biochar was also applied to methane adsorption. Syed-Hassan *et al.* [110] used ZnCl₂ as the chemical agent for the activation of palm kernel shell pyrolysis char and applied the activated biochar to methane gas adsorption. The methane adsorption efficiency of the activated char was found to be dependent on the activation conditions such as the temperature and activation time. They suggested the possibility of using methane adsorbed on biochar as a fuel or energy.

As shown above, there have been many studies on the use of biochars in environmental applications as well as on the appropriate activation method depending on its purpose. A more detailed optimization to increase the functionality of biochars needs to be performed and its research scaled up. In addition, the availability of the biochar used needs to be further investigated to make the carbon cycle safer.

6. Conclusion

Biochar produced from biomass pyrolysis is a carbon-rich porous solid that already has applications as a fuel, low quality adsorbent, soil ameliorator, and additive with good physical and chemical properties. The material can be upgraded further to a value-added product by physical, chemical, or hydrothermal treatments. Activated biochars, obtained through diverse treatments, are being applied to the removal of heavy metal ions and atmospheric pollutants. Biochar can also be used for carbon capture and storage as well as a core substitute in energy storage materials such as supercapacitors, lithium ion batteries, and fuel cells. Although biochar has the potential to be used as carbon materials, it is still difficult to replace commercial materials because of its low activities.

To meet the growing needs for biochar in many applications, further studies on commercial technologies of biochar production are required. The existing slow pyrolysis technologies are mostly for small-scale biochar production at a few tons per day or smaller which often has difficulties in fully utilizing the by-products of the pyrolysis (tar and non-condensable gases) and in controlling the reaction conditions for desirable biochar properties. For the increased use of biochar, it is essential to develop advanced pyrolysis processes with accurate control of the reaction conditions, high energy efficiency, and low environmental impact at a lower cost. Additional study of the biochar used will also be needed to make the carbon cycle safer.

Acknowledgements

This research was supported by a grant (17IFIP-B113506-02) from the Development of Plant Program funded by the Ministry of Land, Infrastructure and Transport of the Korean government.

References

- [1] Y.M. Kim, T.U. Han, B.A. Hwang, B. Lee, H.W. Lee, Y.K. Park, S. Kim, *Korean J. Chem. Eng.*, 33, 2350 (2016).

- [2] T.U. Han, Y.M. Kim, A. Watanabe, N. Teramae, Y.K. Park, S. Kim, *Korean J. Chem. Eng.*, 34, 1214 (2017).
- [3] H. Lee, Y.M. Kim, I.G. Lee, J.K. Jeon, S.C. Jung, J.D. Chung, W.G. Choi, Y.K. Park, *Korean J. Chem. Eng.*, 33, 3299 (2016).
- [4] C.H. Ko, S.H. Park, J.K. Jeon, D.J. Suh, K.E. Jeong, Y.K. Park, *Korean J. Chem. Eng.*, 29, 1657 (2012).
- [5] S. Wang, G. Dai, H. Yang, Z. Lou, *Prog. Energy Combust. Sci.*, 62, 33 (2017).
- [6] H.W. Lee, Y.M. Kim, J. Jae, J.K. Jeon, S.C. Jung, S.C. Kim, Y.K. Park, *Energy Conv. Manag.*, 129, 81 (2016).
- [7] A.V. Bridgwater, *Chem. Eng. J.*, 91, 87 (2003).
- [8] M. Shahbaz, S. Yusup, A. Inayat, D.O. Patrick, A. Pratama, M. Ammar, *Bioresour. Technol.*, 241, 284 (2017).
- [9] S. Czernik, A.V. Bridgwater, *Energy Fuels*, 18, 590 (2004).
- [10] D. Mohan, C.U. Pittman Jr, P.H. Steele, *Energy Fuels* 20, 848 (2006).
- [11] J.S. Cha, S.H. Park, S.C. Jung, C. Ryu, J.K. Jeon, M.C. Shin, Y.K. Park, *J. Ind. Eng. Chem.*, 40, 1 (2016).
- [12] K. Qian, A. Kumar, H. Zhang, D. Bellmer, R. Huhnke, *Renew. Sust. Energ. Rev.*, 42, 1055 (2015).
- [13] R. Azargohar, A.K. Dalai, *Micropor. Mesopor. Mat.*, 110, 413 (2008)
- [14] J. Lee, K.H. Kim, E.E. Kwon, *Renew. Sust. Energ. Rev.*, 77, 70 (2017).
- [15] A. Bhatnagar, M. Sillanpaa, *Adv. Colloid Interface Sci.*, 152, 26 (2009).
- [16] M. Zhang, B. Gao, Y. Yao, Y. Xue, M. Inyang, *Chem. Eng. J.*, 210, 26 (2012).
- [17] O.S. Amuda, A.A. Giwa, I.A. Bello, *Biochem. Eng. J.*, 36, 174 (2007).
- [18] X. Tan, Y. Liu, Y. Gu, Y. Xu, G. Zeng, X. Hu, S. Liu, X. Wang, S. Liu, J. Li, *Bioresour. Technol.*, 212, 318 (2016).
- [19] A.N.A. El-Hendawy, S.E. Samra, B.S. Girgis, *Colloid Surf. A-Physicochem. Eng. Asp.*, 180, 209 (2001).
- [20] B.S. Kim, H.W. Lee, S.H. Park, K. Baek, J.K. Jeon, H.J. Cho, S.C. Jung, S.C. Kim, Y.K. Park, *Environ. Sci. Pollut. Res.*, 23, 985 (2016).
- [21] S. Ren, H. Lei, L. Wang, Q. Bu, S. Chen, J. Wu, *RSC Adv.*, 4, 10731 (2014).
- [22] K. Qian, A. Kumar, *Fuel*, 162, 47 (2015).
- [23] J.S. Cha, J.C. Choi, J.H. Ko, Y.K. Park, S.H. Park, K.E. Jeong, S.S. Kim, J.K. Jeon, *Chem. Eng. J.*, 156, 321 (2010).
- [24] B. Shen, J. Chen, S. Yue, G. Li, *Fuel*, 156, 47 (2015).
- [25] X. He, P. Ling, M. Yu, X. Wang, X. Zhang, M. Zheng, *Electrochim. Acta* 105, 635 (2013).
- [26] M.C. Liu, L.B. Kong, C. Lu, X.M. Li, Y.C. Luo, L. Kang, *RSC Adv.*, 2, 1890 (2012).
- [27] H. Wang, Z. Xu, A. Kohandehghan, Z. Li, K. Cui, X. Tan, T.J. Stephenson, C.K. King'ondeu, C.M.B. Holt, B.C. Olsen, J.K. Tak, D. Harfield, A.O. Anyia, D. Mitlin, *ACS Nano*, 7, 5131 (2013).
- [28] I. Isaev, G. Salitra, A. Soffer, Y.S. Cohen, D. Aurbach, J. Fischer, *J. Power Sources*, 119-121, 28 (2003).
- [29] E. Peled, V. Eshkenazi, Y. Rosenberg, *J. Power Sources*, 76, 153 (1998).
- [30] S.Y. Ahn, S.Y. Eom, Y.H. Rhie, Y.M. Sung, C.E. Moon, G.M. Choi, D.J. Kim, *Appl. Energy*, 105, 207 (2013).
- [31] J. Yu, Y. Zhao, Y. Li, *J. Power Sources*, 270, 312 (2014).
- [32] T.M. Huggins, J.J. Pietron, H. Wang, Z.J. Ren, J.C. Biffinger, *Bioresour. Technol.* 195, 147 (2015).
- [33] A.S. Gonzalez, M.G. Plaza, F. Rubiera, *Chem. Eng. J.*, 230, 456 (2013).
- [34] H.W. Lee, R.S. Park, S.H. Park, S.C. Jung, J.K. Jeon, S.C. Kim, J.D. Chung, W.G. Choi, Y.K. Park, *Carbon Lett.*, 18, 49 (2016).
- [35] Y. Fan, R. Yang, Z. Lei, N. Liu, J. Lv, S. Zhai, B. Zhai, L. Wang, *Korean J. Chem. Eng.*, 33, 1416 (2016).
- [36] H. Lee, R.S. Park, H.W. Lee, Y. Hong, Y. Lee, S.H. Park, S.C. Jung, K.S. Yoo, J.K. Jeon, Y.K. Park, *Carbon Lett.*, 19, 1 (2016).
- [37] Z. Song, F. Lian, Z. Yu, L. Zhu, B. Xing, W. Qiu, *Chem. Eng. J.*, 242, 36 (2014).
- [38] K.W. Jung, T.U. Jeong, M.J. Hwang, K. Kim, K.H. Ahn, *Bioresour. Technol.*, 198, 603 (2015).
- [39] D. Mohan, H. Kumar, A. Sarswat, M. Alexandre-Franco, C.U. Pittman Jr., *Chem. Eng. J.*, 236, 513 (2014).
- [40] M. Inyang, B. Gao, A. Zimmerman, M. Zhang, H. Chen, *Chem. Eng. J.*, 236, 39 (2014).
- [41] J. Tang, H. Lv, Y. Gong, Y. Huang, *Bioresour. Technol.*, 196, 355 (2015).
- [42] Y. Zhou, B. Gao, A.R. Zimmerman, J. Fang, Y. Sun, X. Cao, *Chem. Eng. J.*, 231, 512 (2013).
- [43] A. Ros, M.A. Lillo-Rodenas, E. Fuente, M.A. Montes-Moran, M.J. Martin, A. Linares-Solano, *Chemosphere*, 65, 132 (2006).
- [44] Z. Gao, Y. Zhang, N. Song, X. Li, *Mater. Res. Lett.*, 5, 69 (2017).
- [45] A. Saba, P. Saha, M.T. Reza, *Fuel Process. Technol.*, 167, 711 (2017).
- [46] M. Titirici, M. Antonietti, *Chem. Soc. Rev.*, 39, 103 (2010).
- [47] D. Xin-hui, C. Srinivasakannan, P. Jin-hui, Z. Li-bo, Z. Zheng-yong, *Biomass Bioenerg.*, 35, 3920 (2011).
- [48] A.M. Abioye, F.N. Ani, *Renew. Sust. Energ. Rev.*, 52, 1282 (2015).
- [49] H. Shafaghhat, P.S. Rezaei, D. Ro, J. Jae, B.S. Kim, S.C. Jung, B.H. Sung, Y.K. Park, *J. Ind. Eng. Chem.*, 54, 447 (2017).
- [50] W. Won, C.T. Maravelias, *Renew. Energy*, 114, 357 (2017).
- [51] C. Hu, R. Xiao, H. Zhang, *Bioresour. Technol.*, 243, 1133 (2017).
- [52] Z. Qi, C. Jie, W. Tiejun, X. Ying, *Energy Convers. Manage.*, 48, 87 (2007).
- [53] H.W. Lee, Y.M. Kim, J. Jae, B.H. Sung, S.C. Jung, S.C. Kim, J.K. Jeon, Y.K. Park, *J. Anal. Appl. Pyrolysis*, 122, 282 (2016).
- [54] Y.M. Kim, J. Jae, B.S. Kim, Y. Hong, S.C. Jung, Y.K. Park, *Energy Conv. Manag.*, 149, 966 (2017).
- [55] Y. Lee, H. Shafaghhat, J.K. Kim, J.K. Jeon, S.C. Kim, I.G. Lee, Y.K. Park, *Korean J. Chem. Eng.*, 34, 2180 (2017).
- [56] D. Li, C. Briens, F. Berruti, *Bioresour. Technol.* 189, 7 (2015).
- [57] L.A. Poggi, K. Singh, *Biomass Bioenerg.*, 90, 243 (2016).
- [58] R.M. Dell, D.A.J. Rand, *J. Power Sources*, 100, 2 (2001).
- [59] N. Linares, A.M. Silvestre-Albero, E. Serrano, J. Silvestre-Albero, J. Garcia-Martinez, *Chem. Soc. Rev.*, 43, 7681 (2014).
- [60] L. Wei, M. Sevilla, A.B. Fuertes, R. Mokaya, G. Yushin, *Adv. Energy Mat.*, 1, 356 (2011).
- [61] W.J. Liu, H. Jiang, H.Q. Yu, *Chem. Rev.*, 115, 12251 (2015).
- [62] G. Wang, L. Zhang, J. Zhang, *Chem. Soc. Rev.*, 41, 797 (2012)
- [63] S. Zhao, C.Y. Wang, M.M. Chen, J. Wang, Z.Q. Shi, *J. Phys. Chem. Solids*, 70, 1256 (2009).
- [64] X. Li, W. Xing, S. Zhuo, J. Zhou, F. Li, S.Z. Qiao, G.Q. Lu, *Bioresour. Technol.*, 102, 1118 (2011).
- [65] J. Yang, Y. Liu, X. Chen, Z. Hu, G. Zhao, *Acta Phys.-Chim. Sin.*, 24, 13 (2008).
- [66] T.E. Rufford, D. Hulicova-Jurcakova, K. Khosla, Z. Zhu, G.Q. Lu, *J. Power Sources*, 195, 912 (2010).
- [67] Rohit Misra. Recycled waste paper-an inexpensive carbon material

- for supercapacitor applications, Masters thesis. Chitrakoot (M.P.): Mahatma Gandhi Chitrakoot Gramodaya Vishwavidyalaya; 2006.
- [68] T.E. Rufford, D. Hulicova-Jurcakova, E. Fiset, Z. Zhu, G.Q. Lu, *Electrochem. Commun.*, 11, 974 (2009).
- [69] T.E. Rufford, D. Hulicova-Jurcakova, Z. Zhu, G.Q. Lu, *Electrochem. Commun.*, 10, 1594 (2008).
- [70] Z. Li, L. Zhang, B.S. Amirkhiz, X. Tan, Z. Xu, H. Wang, B.C. Olsen, C.M.B. Holt, D. Mitlin, *Adv. Energy Mater.*, 2, 431 (2012).
- [71] K. Jurewicz, K. Babel, *Energy Fuels*, 24, 3429 (2010).
- [72] M.A. Hannan, M.S.H. Lipu, A. Hussain, A. Mohamed, *Renew. Sust. Energ. Rev.*, 78, 834 (2017).
- [73] P. Kalyani, A. Anitha, *Int. J. Hydrogen Energy*, 38, 4034 (2013).
- [74] Z. Yu, Z. Feng, L.G. Dong, C.J. Sheng, *Mater. Lett.*, 61, 5209 (2007).
- [75] Y.J. Hwang, S.K. Jeong, K.S. Nahm, J.S. Shin, A.M. Stephan, *J. Phys. Chem. Solids*, 68, 182 (2007).
- [76] G.T.K. Fey, C.L. Chen, *J. Power Sources*, 97-98, 47 (2001).
- [77] G.T.K. Fey, Y.D. Cho, C.L. Chen, Y.Y. Lin, T.P. Kumar, S.H. Chan, *Pure Appl. Chem.* 82, 2157 (2010).
- [78] A.M. Stephan, T.P. Kumar, R. Ramesh, S. Thomas, S.K. Jeong, K.S. Nahm, *Mater. Sci. Eng. -A*, 430, 132 (2006).
- [79] Y.J. Hwang, S.K. Jeong, J.S. Shin, K.S. Nahm, A.M. Stephan, *J. Alloy. Comp.*, 448, 141 (2008).
- [80] G.T.K. Fey, Y.Y. Lin, K.P. Huang, Y.C. Lin, P.T. Kumar, Y.D. Cho, H.M. Kao, *Adv. Mater. Res.*, 415-417, 1572 (2011).
- [81] G.T.K. Fey, D.C. Lee, Y.Y. Lin, T.P. Kumar, *Synth. Metals*, 139, 71 (2003).
- [82] I. Isaev, G. Salitra, A. Soffer, Y.S. Cohen, D. Aurbach, J. Fischer, *J. Power Sources*, 119-121, 28 (2003).
- [83] A. Manthiram, Y. Fu, S.H. Chung, C. Zu, Y.S. Su, *Chem. Rev.*, 114, 11751 (2014).
- [84] A. Kacprzak, R. Kobylecki, R. Wlodarczyk, Z. Bis, *J. Power Sources*, 255, 179 (2014).
- [85] A. Elleuch, A. Boussetta, J. Yu, K. Halouani, Y. Li, *Int. J. Hydrog. Energy*, 38, 16590 (2013).
- [86] A. Elleuch, A. Boussetta, K. Halouani, Y. Li, *Int. J. Hydrog. Energy*, 38, 16605 (2013).
- [87] T. Huggins, H. Wang, J. Kearns, P. Jenkins, Z.J. Ren, *Bioresour. Technol.*, 157, 114 (2014).
- [88] Y. Yuan, T. Yuan, D. Wang, J. Tang, S. Zhou, *Bioresour. Technol.*, 144, 115 (2013).
- [89] A.E. Creamer, B. Gao, M. Zhang, *Chem. Eng. J.* 249, 174 (2014).
- [90] A.E. Creamer, B. Gao, S. Wang, *Chem. Eng. J.* 283, 826 (2016).
- [91] S.A. Jafari, A. Jamali, A. Hosseini, *Korean J. Chem. Eng.*, 32, 2053 (2015).
- [92] A. Talebian, A.R. Keshtkar, M.A. Moosavian, *Korean J. Chem. Eng.*, 33, 2205 (2016).
- [93] A. Gupta, C. Balomajumder, *Korean J. Chem. Eng.*, 33, 559 (2016).
- [94] H. Haroon, T. Ashfaq, S.M.H. Gardazi, T.A. Sherazi, M. Ali, N. Rashid, M. Bilal, *Korean J. Chem. Eng.*, 33, 2898 (2016).
- [95] B. Kumar, U. Kumar, *Korean J. Chem. Eng.*, 32, 1655 (2015).
- [96] J. Zhu, J. Yu, J. Chen, J. Zhang, J. Tang, Y. Xu, Y. Zhang, R. Chi, *Korean J. Chem. Eng.* 34, 1721 (2017).
- [97] M. Ahmadi, E. Kouhgardi, B. Ramavandi, *Korean J. Chem. Eng.*, 33, 2589 (2016).
- [98] H. Zhang, H. Shi, J. Chen, K. Zhao, L. Wang, Y. Hao, *Korean J. Chem. Eng.*, 33, 3134 (2016).
- [99] Z. Zhang, X. Feng, X.X. Yue, F.Q. An, W.X. Zhou, J.F. Gao, T.P. Hu, C.C. Wei, *Korean J. Chem. Eng.*, 32, 1564 (2015).
- [100] X. Jiang, D. Shen, *Korean J. Chem. Eng.*, 34, 2619 (2017).
- [101] G. Li, W. Zhu, L. Zhu, X. Chai, *Korean J. Chem. Eng.*, 33, 2215 (2016).
- [102] S.H. Park, H.J. Cho, C. Ryu, Y.K. Park, *J. Ind. Eng. Chem.* 36, 314 (2016).
- [103] Z. Zhou, Y. Liu, S. Liu, H. Liu, G. Zeng, X. Tan, C. Yang, Y. Ding, Z. Yan, X. Cai, *Chem. Eng. J.*, 314, 223 (2017).
- [104] M. Ruthiraan, N.M. Mubarak, R.K. Thines, E.C. Abdullah, J.N. Sahu, N.S. Jayakumar, P. Ganesan, *Korean J. Chem. Eng.*, 32, 446 (2015).
- [105] Y. Sun, J.P. Zhang, F. Guo, L. Zhang, *Korean J. Chem. Eng.*, 33, 2703 (2016).
- [106] H.N. Tran, S.J. You, H.P. Chao, *Korean J. Chem. Eng.*, 34, 1708 (2017).
- [107] J.H. Ko, Y.H. Kwak, K.S. Yoo, J.K. Jeon, S.H. Park, Y.K. Park, *J. Mater. Cycles Waste Manag.*, 13, 173 (2011).
- [108] J.Y. Lee, S.H. Park, J.K. Jeon, K.S. Yoo, S.S. Kim, Y.K. Park, *Korean J. Chem. Eng.* 28, 1556 (2011).
- [109] B.S. Kang, Y. Hong, H. Lee, Y.M. Kim, S.C. Kim, J.K. Jeon, S.C. Jung, Y.K. Park, *J. Nanosci. Nanotechnol.*, 18, 1492 (2018).
- [110] S.S.A. Syed-Hassan, M.S.M. Zaini, *Korean J. Chem. Eng.*, 33, 2502 (2016).