VOLATILE ORGANIC COMPOUNDS AND METALS ADSORPTION CAPACITY OF WOOD BARK-BASED ACTIVATED CARBONS

YOUNG-KYU LEE, OHKYUNG KWON, WONSIL CHOI SEOUL NATIONAL UNIVERSITY SOUTH KOREA

MYOUNGCHEOL MOON, JAE MIN SO HAPPYHOMEWOODTECH CO. LTD. SOUTH KOREA

VILASIT THITHAI, JOON WEON CHOI, DAYE KIM, IN YANG SEOUL NATIONAL UNIVERSITY SOUTH KOREA

(RECEIVED OCTOBER 2022)

ABSTRACT

This study was conducted to investigate the applicability of wood bark-based activated carbon (AC) for the adsorption of metal ions and volatile organic compounds (VOC) from the atmosphere. Contents of Fe and Al in the AC made with coconut shell, and the bark of larch and cork oak (CSA, LBA and COA, respectively) were higher than those of the unexposed AC and increased with the exposure to various indoor/outdoor spaces when compared to the unexposed AC. However, Fe and Al contents of the exposed AC, which is a coal-based one used as a control (SAA), were lower and scarcely higher than the unexposed SAA. From the results, it is evident that the wood bark-based AC examined in this study is more effective to adsorb metals than SAA. The SEM-EDS analysis exhibited prominent metal-adsorptivity of COA, although its total surface area and pore volume were lower than those of SAA. Total VOC-adsorptivity was the highest in COA followed by CSA, CBA (cypress bark activated carbon), LBA and SAA. In conclusion, wood bark-based AC can be utilized as an effective adsorbent for the removal of metals and VOC from the atmosphere. The optimum AC is COA, an industrial by-product, in view of the techno-economic aspect.

KEYWORDS: Wood bark, activated carbon, adsorptivity, volatile organic compounds, SEM-EDS.

INTRODUCTION

Non-woven fabric filters made with polypropylene (PP) and polyethylene terephthalate (PET) are the most commonly used medium for the reduction of particulate matter (PM) concentration in South Korea due to its cost-effectiveness than other filter media, such as woven fabric, needled felt, plastic, ceramic and metal (http://super.textopia.or.kr:8888/ newsletter//170404/lib0201.pdf). However, PP- and PET-filters are efficient only for the removal of PM, but not suitable for removing volatile organic compounds (VOC) and metals, posing a significant health risk to the public. Therefore, the use of other raw materials as a media for air-cleaning filters is required to remove VOC and metals efficiently.

Activated carbon (AC) plays an important role for removing various air pollutants including VOC and metals because it has a suitable variation of pore size and a high surface area resulting in a high adsorption capacity (Rashidi and Yusup 2017, Ma et al. 2018, Wang et al. 2018). AC also contains functional groups that interact with air-polluting molecules, making it an adsorbent with a high adsorption capacity (Bhatnagar et al. 2013). In addition to the high adsorption feature of AC, lignocellulosic raw material has been considered as raw materials for manufacturing cost-effective AC (Miao et al. 2013, Thue et al. 2016, Dizbay-Onat et al. 2017, Zazycki et al. 2018). In particular, wood bark has been used as a raw material for the production of activated carbons due to its higher carbon content compared to other tree components (Thomas and Martin 2012, Martin et al. 2015, de Aza et al. 2021). In addition, bark is generated in large amounts by wood-based industries, which implies high availability in South Korea. According to the Market Survey of Timber Products published in the Forest Service of the Republic of Korea, approximately 700 million tons of wood bark were generated as waste in 2017 (Forest Service of Republic of Korea 2020). Although the production of AC using wood bark is not a new technology, a low-cost AC can provide an efficient air-cleaning process with an economic advantage (Patnukao and Pavasant 2008, Beets and Garrett 2018, Lütke et al. 2019, Abdulla et al. 2021). Wood bark, which is mostly disposed of as waste in South Korea, is a good resource for AC which offers added value to the waste.

AC impregnated in cellulose filters was shown to be effective in reducing the contents of VOC, metals and harmful microorganisms present in indoor spaces (Kim et al. 2020). Other studies reported on the adsorption of VOCs, which are known to be harmful to human health, by wood-based AC (Das et al. 2004, Kim et al. 2016, Huang et al. 2021). However, the use of AC causes a risk of secondary contamination due to its high dust-generation rate and duration of time required to adsorb VOC and metals (Choi et al. 2018). Hence, the inclusion of AC in a matrix composed of natural fiber is an approach to solve the problems and to collect air pollutants efficiently. However, no studies have investigated the efficiency of wood bark-based AC added in a wood fiber-based matrix as an adsorbent to reduce VOC and metal contents.

Therefore, VOC and metal adsorptivity of the wood bark-based AC exposed in various indoor/outdoor spaces were evaluated by the analysis of metal contents, X-ray combined microscopic observation, surface spatial properties and the ratio of VOC contents to atmospheric circumstances to select an optimal AC to use in the matrix of fiberboard filters.

MATERIAL AND METHODS

Raw materials

Activated carbons made of larch (*Larix kaempferi*, LBA) and cypress (*Chamaecyparis obtusa E.*, CBA) bark and carbonized at a temperature of 700 - 800 for 4 h were purchased from the Ansung Co. Ltd. (Gwangju, South Korea). Cork oak (*Quercus variabilis B.*) activated carbon (COA) was obtained from the Goodsoot Co. Ltd (Songpa, South Korea). The COA was an AC, which is obtained as a by-product in the carbonization process of 3 m long cork and oak logs used as a raw material for the production of barbecuing charcoal. As a reference, coconut shell activated carbon (CSA) was purchased from Ecolife&health Co. Ltd. (Daegu, South Korea). Activated carbon (SAA) obtained from adsorption filters of a commercial air cleaner (CFX-H170D, Samsung, Suwon, South Korea) was used as another reference.

Elemental analysis of activated carbons

For the elementary analysis of LBA, CBA, COA, CSA and SAA, 2 mg of each specimen was put into the reactor chamber and combusted at 990 , with a sufficient supply of oxygen. The specimens were converted into a gas mixture with complete oxidation. The gas mixture was passed to an Elemental Analyzer (Flash 2000, Thermo Fisher Scientific, Waltham, MA, USA) with helium gas as a carrier gas, and separated into CO₂, N₂ and H₂O gases. Each gas was transformed to an electrical signal using a thermal conductivity detector. The gas was calibrated through an elementary analysis of standard samples provided by the instrument manufacturer, and then the content of carbon, hydrogen and nitrogen was measured. The results of the elementary analysis were calculated based on the average of three measurements.

Surface properties of activated carbon

Before determining the characteristics of the Brunauer–Emmett–Teller (BET) surface area, about 200 mg of each activated carbon (AC) was placed in a sample cell and degassed at 350°C for 3 h under vacuum conditions to eliminate its surface functionalities and moisture existing in the AC. Then, it was cooled to room temperature before being purged with nitrogen gas. The texture properties of AC were characterized using BELSORP-max instrument (MicrotracBEL Crop, Japan), with a nitrogen adsorption-desorption isotherm at 77 K (-196°C). The BET method was used to calculate the specific surface area from liquid nitrogen gas adsorption (Thithai et al. 2021). The Barrett–Joyner–Halenda (BJH) and t-plot methods were used to determine the mesopore volume and micropore structure, respectively. In addition, the diameter of the average pore was evaluated using the adsorption branch.

Metals-adsorptivity of activated carbons

Activated carbon of 50 g was placed in a non-woven fabric bag, and the bag then was put in an oven at 95 ± 2.5 overnight. The bag dried fully was stored in an air-tight plastic bag before use. The AC was exposed in various indoor/outdoor spaces, such as a sawmill plant (SAPL), an iron foundry (IRFO), the hallway of a building next to the platform of a railway station (HPRS), a closed smoking room (COSR) and an underground parking lot (UGPL) for 7 days. With the completion of the exposure, amounts of metals (Pb, Cu, Fe, Al, Cr and Zn) adsorbed on the AC were measured according to the standard method for measuring indoor/outdoor air quality designated by the National Institute of Environmental Research of the Republic of Korea (2020). For instance, the AC specimen was smashed through a grinder and 0.5 g was placed in a 100-m ℓ flask. The specimen was pretreated with 10 m ℓ nitric acid (conc. 65%) and 5 m ℓ perchloric acid on a hot plate at 150 to 200 . Distilled water (50 m ℓ) was added to the flask for washing the specimen, and then the mixture was filtered through Whatman filter paper (No. 42). The filtrate was used to measure the content of metals by the inductively coupled plasma (ICP) emission spectrometer with a Perkin-Elmer Optima 4300 DV. For example, the filtering solution was subjected to ICP analysis at a detection wavelength of 324.8 nm to detect copper content.

Microscopic observation of the activated carbons

In order to quantitively identify the metals-adsorptivity difference on the surfaces of CSA and COA, which were unexposed and exposed at HPRS, the AC specimens were examined by energy dispersive X-ray analysis (EDS, FlatQUAD 5060F; Bruker AXS Microanalysis, Berlin, Germany) combined with field emission scanning microscopy (SEM, Auriga, Carl Zeiss, Oberkochen, Germany) at an accelerating voltage of 15 kV. Each specimen was placed on an aluminum stub and then sputter-coated with a thin layer (approximately 20 nm thick) of platinum. The X-rays reflected were collected using a detector fixed at the top of the sample and their intensities were recorded in count per second. The aperture size was 30 µm and the working distance was 10 mm. The surface of each AC specimen was fractioned into 16 sections. The type, number and occupied area of metals distributed on the surface of AC were calculated by the sum of the data obtained from each section.



Fig. 1: Schematic diagram of equipment used for measuring VOC adsorbed onto activated carbons quantitatively.

VOC-adsorptivity of activated carbons

Fig. 1 shows a schematic diagram of equipment used for measuring VOC-adsorptivity of AC. This test was carried out by exposing AC to a mixture of VOCs including benzene, toluene, ethyl benzene, m, p-xylene and styrene (5VOC) and allowed for the investigation of the adsorptivity of AC to remove the VOCs from the polluted atmosphere. The detailed procedure is as follows: VOC standard solution was injected into a micro-chamber with a syringe, and then evaporated at 200 . Gaseous materials produced in the micro-chamber

were purged by supplying hyper-pure nitrogen gas at a 100 ml/min-flow rate. VOCs in the air exhausted from the empty glass tube for 10 min was collected in a Tenax TA tube (Supelco, Merck, Darmstadt, Germany). Prior to testing, the Tenax tubes were conditioned in the tube conditioner (APK 1200, KNR Co. Ltd., Namyangju, South Korea) at 300 with nitrogen gas at a 100 ml/min-flow rate for 4h. The concentration of VOCs for blank values was measured using a TurboMatrix 350 ATD system (PerkinElmer, Shelton, USA) and a Clarus 680 Gas Chromatograph coupled to a Clarus SQ8T Mass Spectrometer (PerkinElmer, Shelton, USA). AC (5 g) that was dried fully in the oven at 95 ± 2.5 overnight was filled in a glass tube. The same procedure as that for obtaining the blank value of each VOC was applied to measure the concentration of the AC adsorbed. VOC-adsorptivity of the AC was calculated as the ratio of the concentration of each VOC measured with AC in a glass tube to that without AC. Determination of the VOC was performed on the basis of the selected ion monitoring (SIM)/scan method developed previously.

AC (5 g) exposed at various indoor/outdoor spaces was placed in the kit, which was comprised of a stainless-steel chamber for the placement of AC and Tenax TA tube for collecting gaseous materials. The temperature of the micro-chamber was raised to 150 for emitting 5VOC from AC. Then, gaseous materials produced in the chamber were purged with hyper-pure nitrogen gas at a 120 ml/min-flow rate for 10 min. The 5VOC desorbed from the AC was collected to Tenax TA tube. The concentration of the 5VOC was measured using a thermal desorption–gas chromatography–mass spectrometry (TD-GC-MS), which was used for the VOC-adsorptivity analysis of AC as mentioned above (Rodríguez-Navas et al. 2012).

RESULTS AND DISCUSSION

Elementary analysis

Tab. 1 presents the carbon, hydrogen and nitrogen contents of activated carbons (AC) examined in this study. Carbon contents of LBA, CBA and COA were lower than that of CSA, but much higher than that of SAA included in the adsorption filter of a commercial air-cleaner as a VOC-adsorbent. The results indicate that LBA, CBA and COA can be used as a VOC-adsorbent due to its higher carbon content than other wood-based AC and low-cost advantage (Abiko et al. 2010, Danish and Ahmad 2018, Park et al. 2019). In addition, the carbon content of LBA was similar to that (90.7%) of larch bark carbonized at 600 for 1 h (Jo, 2008). At this carbonization condition, the LBA examined in this study can be reproduced.

		,	
Туре	Carbon (%)	Hydrogen (%)	Nitrogen (%)
Coconut shell activated carbon (CSA)	95.6	0.5	0.4
Activated carbon obtained from adsorption	68.2	0.8	1.2
filters of a commercial air cleaner (SAA)	08.2	0.8	1.2
Cork-oak activated carbon (COA)	84.5	0.6	0.3
Larch bark activated carbon (LBA)	92.2	1.7	0.9
Cypress bark activated carbon (CBA)	86.0	1.2	1.7

Tab. 1: Elemental contents of various activated carbons used in this study.

Hydrogen content decreased in the following order: LBA, CBA, SAA, COA and CSA. On the other hand, CBA, SAA and LBA exhibited significant quantity of nitrogen when compared to those of COA and CSA. The high nitrogen contents of CBA and LBA are probably due to the microorganisms grown on cypress and larch bark. For instance, the bark is placed outside as waste for a long duration until it is gathered by collectors, resulting in a high possibility of microorganism growth on the pile of bark. In addition, amino acids included in the living tissue of the xylem and inorganic salts, such as NO₂ and NO₃, attached on the bark seem to play a role for the high nitrogen content of CBA and LBA. For SAA, the high nitrogen content might result from the coal used during its production.

Specific surface area and porosity

The total surface area, total pore volume, micropore volume, mesopore volume and average pore diameter of AC examined for the morphological study of AC surface are given in Tab. 2. The highest surface area was measured on SAA followed by CSA, CBA, LBA and COA. The volumes of total pore and micropore were able to identify the results above. In addition, the nitrogen adsorption-desorption isotherm plot presented in Fig. 2(left) also support the results.

	$S_{BET}^{1}(m^{2}/g)$	V_{total}^2 (cm ³ /g)	V_{micro}^{3} (cm ³ /g)	V_{meso}^{4} (cm ³ /g)	$D_{ave}^{5}(nm)$		
CSA*	526	0.217	0.206	0.026	1.648		
SAA*	839	0.428	0.374	0.137	2.041		
COA*	383	0.184	0.160	0.048	1.919		
LBA*	420	0.187	0.166	0.034	1.785		
CBA*	430	0.202	0.172	0.046	1.879		

Tab. 2: Surface area and pore size analysis of activated carbon examined in this study.

* Refer to Tab. 1. ¹ BET specific surface area was measured by N_2 adsorption data in the P/Po range from 0.06 to 0.20; ² Total pore volume was determined from the adsorption isotherm at P/Po = 0.99; ³ Micropore volume was calculated using a t-plot method; ⁴ Mesopore volume was calculated by using a BJH method; ⁵ Average pore diameter was determined by the adsorption data using a BET-plot method.



Fig. 2: Nitrogen adsorption-desorption isotherms (top) and pore size distribution (bottom) of activated carbon examined in this study.

SAA is a coal-based AC resulting in being more porous than wood-based AC. Larger surface area of CSA compared to CBA, LBA and COA might be due to the severe carbonization on the coconut shell (Efeovbokhan et al. 2019). It can be inferred that CSA has a higher carbon content than CBA, LBA and COA (Tab. 1). Low surface area and large pore diameter of COA are probably due to its difference in anatomical structure from CBA and LBA. For instance, COA is produced with raw materials composed of xylem and bark, contrary to CBA and LBA as mentioned previously, and thus might have a lower surface area and a larger pore diameter than those.

Fig. 2(right) compares the pore size distribution of AC examined in this study. Less developed porous structure was observed in LBA followed by COA and CBA. Pores existing on AC were less than those on SAA and CSA. The results indicate that LBA, CBA and COA have less adsorption sites than SAA and CSA.

Metals adsorptivity

To measure the contents of metals adsorbed on AC, which were exposed at various indoor/outdoor spaces, its quantitative analysis was conducted using an ICP-OES technique. The results are summarized in Tab. 3. For the unexposed AC, Al was detected in all AC, while Fe was detected in CSA, COA and CBA. In the unexposed CBA, Pb and Zn were also found. However, Cr was not found in any unexposed AC specimens. In addition, variations in metal type and content of the unexposed AC are probably due to the raw material used for the production of AC. For example, SAA is a coal-based AC, and thus might have high contents of Al and Fe (Flues et al. 2013). For CBA, Pb and Zn were detected in company with Fe and Al which can be attributed to the high metal-adsorptivity of cypress bark (El-Hasan et al. 2002).

The quantities of Fe and Al in most of CSA, COA and LBA exposed at various indoor/outdoor spaces increased when compared to the unexposed AC (Tab. 3). Interestingly, in the HPRS- and COSR-exposed LBA, Pb, which was not detected in the unexposed LBA, was found. For IRFO-exposed CBA, Fe and Al contents were higher than those of the unexposed CBA. Pb in the unexposed LBA and Cu in the unexposed CBA were not detected but in HPRS- and COSR-exposed LBA as well as SAPL-, IRFO- and UGPL-exposed CBA, respectively. Cu and Zn, which were not detected in other AC specimens, were found in SAPL, IRFO- and UGPL-exposed and all exposed CBA, respectively. Meanwhile, Pb, Cu, Cr and Zn were not detected in the unexposed SAA, and Fe and Al contents of the exposed SAA were lower and scarcely higher than the unexposed one. The results indicate that AC produced with woody materials is more effective to adsorb metals than SAA. However, metal adsorptivity of AC is affected largely by the raw material used for AC production and its carbonization conditions.

When the content of each metal adsorbed on AC is compared according to its exposure spaces, Fe content of COSR-exposed CSA showed the highest increasing rate to the unexposed ones, followed by HPRS-, SAPL-, UGPL- and IRFO-exposed ones (Tab. 3). The increasing rates of Al by the exposure space in CSA were similar to those of Fe. For LBA, the highest increasing rates of Fe, Al and Pb also appeared in COSR- followed by HPRS-exposed one. Fe contents of IRFO- and UGPL-exposed CBA and Al content of IRFO-exposed CBA were higher than those of the unexposed CBA. Cu contents of IRFO-, SAPL- and UGPL-exposed

Activated carbon		Dh	Cu	Fo	A 1	Cr	Zn
Туре	Space exposed	10	Cu	Γ¢	AI	CI	ZIII
	SAPL**	ND	ND	5.0	8.0	ND	ND
	IRFO**	ND	ND	0.9	1.9	ND	ND
CS 4 *	HPRS**	ND	ND	5.4	14.7	ND	ND
CSA	COSR**	ND	ND	5.6	11.0	ND	ND
	UGPL**	ND	ND	1.9	4.6	ND	ND
	UNEX**	ND	ND	ND	3.5	ND	ND
	SAPL**	ND	ND	55.6	13.5	ND	ND
C A A *	IRFO**	ND	ND	59.3	15.9	ND	ND
	HPRS**	ND	ND	57.4	15.3	ND	ND
SAA*	COSR**	ND	ND	61.1	16.3	ND	ND
	UGPL**	ND	ND	57.1	16.3	ND	ND
	UNEX**	ND	ND	61.8	16.0	ND	ND
	SAPL**	ND	ND	ND	0.4	ND	ND
COA*	IRFO**	ND	ND	3.2	11.0	ND	ND
	HPRS**	ND	ND	ND	1.8	ND	ND
	COSR**	ND	ND	1.0	4.7	ND	ND
	UGPL**	ND	ND	1.4	6.0	ND	ND
	UNEX**	ND	ND	0.2	2.6	ND	ND
	SAPL**	ND	ND	ND	9.9	ND	ND
	IRFO**	ND	ND	0.6	18.8	ND	ND
LDA	HPRS**	0.1	ND	18.3	28.7	ND	ND
LDA	COSR**	1.1	ND	38.0	53.4	ND	ND
	UGPL**	ND	ND	ND	19.7	ND	ND
	UNEX**	ND	ND	ND	18.7	ND	ND
	SAPL**	0.7	0.7	7.0	2.0	ND	7.5
	IRFO**	1.6	1.6	50.9	7.9	ND	7.2
CDA	HPRS**	ND	ND	ND	3.2	ND	4.6
UBA	COSR**	ND	ND	ND	1.2	ND	4.9
	UGPL**	0.7	0.7	26.0	4.3	ND	7.8
	UNEX**	3.2	ND	25.6	6.6	ND	1.1

Tab. 3: Contents of metals adsorbed on various wood bark-based activated carbons, which were exposed at indoor/outdoor spaces for one week. (unit: mg/kg).

*, ** Refer to Tab. 1 and the chapter of Material and Methods, respectively. ND: not detected (< 0.1 mg/kg).

CBA and Zn contents of all exposed-CBA increased when compared to the unexposed CBA. The highest increasing rates of Fe and Al contents were measured in the exposed COA at IRFO followed by UGPL and COSR. Taken together from the results, COSR or HPRS is the space with the highest Fe and Al contents, and thus the increasing rates of the metals adsorbed in COSR- and HPRS- exposed AC might be higher than those exposed in other spaces. On the contrary, the adsorption contents of Al at IRFO-exposed CSA, Fe and Al at SAPL- and COSR-exposed COA, Al at SAPL-exposed LBA, Pb at SAPL-, IRFO- and UGPL-exposed CBA, Fe at SAPL-exposed CBA and Al at SAPL-, HPRS-, COSR- and UGPL-exposed CBA

reduced with the exposure to the spaces. The reductions are likely to result from three inferences; 1) a specimen of 0.5 g from the AC exposed (50 g) was used for the ICP-EOS analysis, 2) the repetition number for the quantitative analysis was not enough to measure the content of metals adsorbed on AC precisely and 3) the exposure period (1 week) was too short to adsorb metals on AC. To identify the speculations and investigate the difference in metals distributed on the AC, the microscopic observation of the unexposed and exposed AC was conducted using SEM-EDS.



Fig. 3: Scanning electron microscopic-energy dispersive X-ray spectrometer (SEM-EDS) images of surface of coconut shell (top) and cork oak (bottom) activated carbon, which were unexposed (left) and exposed at the hallway of building next to the platform of a railway station (right). Light blue, cobalt, red, pink, green and yellow spots mean the existence of iron, copper, chromium, lead, aluminum and zinc, respectively. Bars = 10 μ m. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Microscopic observation

The contents of Fe and Al adsorbed on the unexposed CSA were lower than those of HPRS-exposed CSA. For COA, Fe and Al contents decreased after HPRS-exposure. Therefore, microscopic observation on the AC specimens was conducted to elucidate the relationship between the AC and the adsorption of Fe and Al. Fig. 3 shows SEM-EDS maps providing

a distribution of metals adsorbed on surface of CSA and COA. Metals contents of HRPS-exposed CSA seem to be reduced rather than those of unexposed CSA. On the other hand, SEM-EDS analysis of COA showed that the most metals distribute widely throughout the surface of HPRS-exposed COA when compared to the unexposed COA.

When the distribution of metals observed on the surface of CSA and COA was measured quantitatively, the number of metal clusters and the proportion of area that the metals occupy in the scanned surface area increased after the AC was exposed at HPRS (Tab. 4). However, the number and the occupied area of Pb on HPRS-exposed CSA to the unexposed one were abruptly reduced. The results indicate that Cu, Cr and Zn might be adsorbed on CSA and COA exposed at HPRS in addition to Fe and Al. Therefore, the assumption on the metal adsorptivity of CSA and COA needs to be identified in further studies using a repetition of the ICP-EOS analysis on all AC specimens unexposed and exposed at various indoor/outdoor spaces.

Tab. 4: Number of iron, lead, copper, aluminum, chromium and zinc existing on the surface of coconut shell (CSA) and cork oak activated carbons (COA), which were unexposed (UNEX) and exposed at the hallway of building next to the platform of a railway station (HPRS), detected by the measurement of SEM-EDS.

	CSA – UNEX	CSA – HPRS	COA – UNEX	COA – HPRS
Fe	25 (10.6 10 ⁻⁴)	$115(12.5 10^{-4})$	ND^1	11 (5.1 10 ⁻⁴)
Pb	801 (65.8 x 10 ⁻⁴)	43 (2.6 x 10 ⁻⁴)	17 (0.3 x 10 ⁻⁴)	995 (104.9 x 10 ⁻⁴)
Cu	18 (0.9 x 10 ⁻⁴)	138 (9.2 x 10 ⁻⁴)	34 (1.0 x 10 ⁻⁴)	151 (23.8 x 10 ⁻⁴)
Al	32 (3.5 x 10 ⁻⁴)	134 (6.9 x 10 ⁻⁴)	31 (0.7 x 10 ⁻⁴)	71(9.9 x 10 ⁻⁴)
Cr	2 (0.2 x 10 ⁻⁴)	3 (0.8 x 10 ⁻⁴)	9 (0.2 x 10 ⁻⁴)	23 (3.1 x 10 ⁻⁴)
Zn	$1 (0.1 \times 10^{-4})$	4 (0.9 x 10 ⁻⁴)	20 (0.5 x 10 ⁻⁴)	23 (4.6 x 10 ⁻⁴)
Others	2 (0.9 x 10 ⁻⁴)	4 (0.2 x 10 ⁻⁴)	18 (0.6 x 10 ⁻⁴)	65 (21.7 x 10 ⁻⁴)
Total	881 (72.3 x 10 ⁻⁴)	441 (33.1 x 10 ⁻⁴)	129 (3.3 x 10 ⁻⁴)	1,339 (173.1 x 10 ⁻⁴)

* Number in parenthesis means the proportion of area that each metal occupies in total area scanned. ¹ ND: not detected.

Туре	Total volatile organic compounds	Benzene	Toluene	Ethyl benzene	m,p- xylene	Styrene	o-xylene
CCA*	95.9%	93.5%	98.9%	99.7%	99.8%	100%	99.9%
SAA*	79.8%	97.9%	98.9%	99.7%	99.7%	99.7%	99.8%
COA*	96.2%	88.8%	99.2%	99.9%	99.9%	99.6%	100%
LBA*	92.0%	97.2%	100%	100%	100%	100%	100%
CBA*	95.5%	100%	100%	100%	100%	100%	100%

Tab. 5: Volatile organic compounds adsorptivity of activated carbons used in this study.

* Refer to Tab. 1.

Volatile organic compounds adsorptivity

Tab. 5 shows the adsorptivity of AC to total volatile organic compounds (TVOC) and 5VOC. The highest TVOC adsorptivity was observed in COA and the lowest in SAA. TVOC adsorptivity of CSA and CBA were as high as that of COA, but LBA had a lower TVOC adsorptivity than COA, CSA and CBA. For 5VOC, CBA exhibited the highest adsorptivity followed by LBA, CSA, SSA and COA, but the differences were not significant. The low

5VOC adsorptivity of COA results from the low content of benzene adsorbed on the COA. In addition, there were no significant differences in the adsorptivities of toluene, ethylbenzene, m, p, o-xylene and styrene. The results indicate that wood materials-based AC tested in this study can adsorb VOC existing in the atmosphere effectively.

Activated carbon		Benzene	Toluene	Ethyl	m,p-	Styrene	o-xylene
Туре	Space			benzene	xylene		
	SAPL**	ND	ND	ND	ND	ND	ND
	IRFO**	ND	ND	ND	ND	ND	ND
CSA*	HPRS**	11.6	13.0	2.7	3.8	0.6	2.2
CBA	COSR**	11.3	5.8	0.9	1.7	0.4	0.7
	UGPL**	ND	ND	ND	ND	ND	ND
	UNEX**	8.5	6.3	1.6	3.0	0.5	1.4
	SAPL**	51.0	381.2	76.7	447.3	9.0	124.1
	IRFO**	19.9	74.3	13.0	86.8	2.2	17.3
C A A *	HPRS**	17.6	56.3	12.6	61.2	1.5	12.4
SAA*	COSR**	37.6	150.4	27.1	139.5	3.5	31.0
	UGPL**	44.7	178.6	38.4	277.2	5.4	58.3
	UNEX**	22.6	84.6	28.1	161.5	3.2	32.3
	SAPL**	ND	ND	ND	ND	ND	ND
	IRFO**	1.4	67.6	ND	ND	ND	ND
CO.4.*	HPRS**	9.1	ND	ND	ND	ND	ND
COA*	COSR**	ND	ND	ND	ND	ND	ND
	UGPL**	14.0	26.2	ND	ND	ND	ND
	UNEX**	10.3	1.7	0.5	1.2	0.6	0.4
	SAPL**	23.5	287.0	29.8	117.8	4.8	69.1
	IRFO**	29.9	111.9	28.6	79.4	3.4	59.0
	HPRS**	41.8	262.6	18.8	37.0	2.6	20.5
LBA	COSR**	47.4	233.9	22.1	43.4	4.0	21.6
	UGPL**	84.6	412.8	56.7	143.9	7.3	98.2
	UNEX**	15.9	89.8	30.3	236.5	7.6	90.5
	SAPL**	59.6	288.5	265.2	1,045.5	49.1	498.7
	IRFO**	38.7	471.5	48.1	130.8	6.6	70.9
	HPRS**	61.4	396.9	79.9	167.6	6.6	103.0
СВА	COSR**	43.9	357.1	45.0	97.8	2.6	77.4
	UGPL**	67.6	416.8	66.0	135.5	9.0	64.8
	UNEX**	22.4	249.7	91.5	732.3	28.2	318.7

Tab. 6: Contents of volatile organic compounds adsorbed on activated carbons, which were exposed at various indoor/outdoor spaces, for one week. (unit: $\mu g/m^3$).

*, ** Refer to Table 1 and the chapter of Material and Methods, respectively. ND: not detected.

Tab. 6 shows the contents of 5VOC emitted from the AC unexposed or exposed at various indoor/outdoor spaces. Among the unexposed AC, the highest 5VOC content was measured in CBA followed by LBA, SAA, CSA and COA. The high 5VOC contents of CBA and LBA are likely because of the high content of volatile matters including extractives in cypress and larch

bark itself (El-Hasan et al. 2002, Jo 2008, Jiang et al. 2011). For instance, the volatile matters are decomposed by a thermal treatment (150) during testing, and thus might attribute to the increasing 5VOC content of CBA and LBA. High content of volatile matters contained in coal-based SAA also might result in the higher content of 5VOC emitted from itself than from CSA and COA (Rahman et al. 2019). CSA and COA have a volatile matter less than CBA and LBA (Mostapha and Husseinsyah 2011). In particular, COA is an AC composed of bark and parts of xylem in contrast to CBA and LBA (Ferreira et al. 2018). Consequently, the chemical composition of CSA and COA might contribute to the low content of 5VOC emitted from the AC. Among the 5VOC emitted from the exposed AC, toluene showed the highest content, followed by benzene and ethylbenzene. Since the relative evaporation rate of toluene is greater than that of benzene and ethylbenzene (Karimnezhad et al. 2014). Inferences of the adsorptive and desorptive mechanisms on o-, m-, p-xylene and styrene are excluded in this article because the contents of the VOCs adsorbed onto the exposed AC were lower than those on the unexposed one.

As shown in Tab. 6, 5VOC contents of CSA exposed at HPRS, SAA at SAPL, COSR and UGPL, COA at IRFO and UGPL, LBA at SAPL and UGPL and CBA at SAPL were higher than the unexposed ones. The higher contents are probably due to the effective adsorption of the AC to 5VOC. However, 5VOC was not detected in SAPL-, IRFO- and UGPL-exposed CSA as well as SAPL- and COSR-exposed COA, and the contents of 5VOC adsorbed on the remainder of the AC exposed were even lower than those on the unexposed ones. The results might be due to experimental errors, such as the amount of AC used as a specimen, sampling error, insufficient time of exposure for AC specimens and lack of 5VOC existing in the spaces exposed, as mentioned above. In addition, although the exposed AC was stored in an air-tight plastic bag after the exposure, steady evaporation of 5VOC adsorbed onto the AC prior to testing is likely to have an effect of its 5VOC adsorptivity. Nevertheless, the 5VOC adsorptivity of the exposed AC was affected by the exposure spaces. For example, the 5VOC adsorptivities of several AC specimens including IRFO- and UGPL-exposed COA and HPRS-exposed CSA were much higher than those of the unexposed ones, and similar results appeared in the metals adsorptivities of the AC (Tab. 3). From the results, it is assumed that differences of the 5VOC contents might exist to some extent in accordance with the exposure spaces. However, such speculation is hardly supportive to draw further conclusions as the 5VOC adsorptivity of AC would be affected by other factors.

CONCLUSIONS

Activated carbon (AC) produced from wood bark was characterized to examine its application towards metals and VOC adsorption from the atmosphere. The higher carbon content was observed in coconut shell AC than wood bark-based AC. The quantities of Fe and Al in the majority of wood bark-based AC exposed at various indoor/outdoor spaces increased when compared to the unexposed AC. Metal adsorptivity of the AC is affected largely by the raw material used for AC production and its carbonization conditions. Based on

the microscopic analysis of the exposed AC using SEM-EDS, it is evident that cork oak bark-based AC adsorbed metals existing in the hallway of a building next to the platform of a railway station effectively. The total surface area and pore volume of wood bark-based AC were lower than those of AC used as a control in this study. The TVOC adsorptivity measured by the VOC-detecting equipment, which was devised for this study, was higher in cork oak bark-based AC than other AC specimens. However, for 5VOC, the cork oak bark-based AC exhibited the lowest adsorptivity compared to other AC specimens, but the differences were not significant. The contents of 5VOC emitted from the unexposed AC were the lowest on cork oak bark-based AC. On the other hand, 5VOC contents of the AC exposed at certain indoor/outdoor spaces were higher than those of the unexposed ones. Therefore, it was concluded that wood bark-based AC examined in this study can be utilized as an effective adsorbent for the removal of metals and VOC from the atmosphere. Among the wood bark-based AC, the optimum one is considered cork oak bark-based AC, an industrial by-product, in view of the techno-economic aspect.

ACKNOWLEDGMENTS

This research was funded by the Korea Forest Service (Korea Forestry Promotion Institute) through R&D program for Forest Science Technology (Project No. 2020227D10-2222-AC01).

REFERENCES

- RASHIDI, N.A. & YUSUP, S. (2017): Potential of palm kernel shell as activated carbon precursors through single stage activation technique for carbon dioxide adsorption. In: J. Clean. Prod. 168, 474-486 pp.
- [2] MA, J., QIN, G., ZHANG, Y., SUN, J., WANG, S. & JIANG, L. (2018): Heavy metal removal from aqueous solutions by calcium silicate powder from waste coal fly-ash. In: J. Clean. Prod. 182, 776-782 pp.
- [3] WANG, W., HUANG, G., AN, C., ZHAO, S., CHEN, X. & ZHANG, P. (2018): Adsorption of anionic azo dyes from aqueous solution on cationic gemini surfactant-modified flax shives: Synchrotron infrared, optimization and modeling studies. In: J. Clean. Prod. 172, 1986-1997 pp.
- [4] BHATNAGAR, A., HOGLAND, W., MARQUES, M. & SILLANPÄÄ, M. (2013): An overview of the modification methods of activated carbon for its water treatment applications. In: Chem. Eng. J. 219, 499-511 pp.
- [5] MIAO, Q., TANG, Y., XU, J., LIU, X., XIAO, L. & CHEN, Q. (2012): Activated carbon prepared from soybean straw for phenol adsorption. In: J. Taiwan Inst. Chem. Eng. 44, 458–465 pp.
- [6] THUE, P.S., ADEBAYO, M.A., LIMA, E.C., SIELIECHI, J.M., MACHADO, F.M., DOTTO, G.L., VAGHETTI, J.C.P. & DIAS, S.L.P. (2016): Preparation, characterization

and application of microwave-assisted activated carbons from wood chips for removal of phenol from aqueous solution. In: J. Mol. Liq. 223, 1067–1080 pp.

- [7] DIZBAY-ONAT, M., VAIDYA, U.K. & LUNGU, C.T. (2017): Preparation of industrial sisal fiber waste derived activated carbon by chemical activation and effects of carbonization parameters on surface characteristics. In: Ind. Crops. Prod. 95, 583–590 pp.
- [8] ZAZYCKI, M.A., GODINHO, M., PERONDI, D., FOLETTO, E.L., COLLAZZO, G.C. & DOTTO, G.L. (2018): New biochar from pecan nutshells as an alternative adsorbent for removing reactive red from aqueous solutions. In: J. Clean. Prod. 171, 57–65 pp.
- [9] DE AZA, H., TURRIÓN, M. & BRAVO, P. (2011): Carbon in heartwood, sapwood and bark along the stem profile in three Mediterranean Pinus species. In: Ann. For. Sci. 68, 1067–1076 pp.
- [10] THOMAS, S.C. & MARTIN, A.R. (2012): Carbon Content of Tree Tissues: A Synthesis. In: Forests 3, 332-352 pp.
- [11]MARTIN, A.R., GEZAHEGN, S. & THOMAS, S.C. (2015): Variation in carbon and nitrogen concentration among major woody tissue types in temperate trees. In: Can. J. For. Res. 45(6), 150217143629002 p.
- [12] FOREST SERVICE OF REPUBLIC OF KOREA, 2020: Market survey of timber products. Administrative Report 11-140000-000709-10: Daejon, Republic of Korea.
- [13] ABDULLAH, A.H., KASSIM, A., ZAINAL, Z., HUSSIEN, M.Z., KUANG, D., AHMAD, F. & WOOI, O.S. (2021): Preparation and Characterization of Activated Carbon from Gelam Wood Bark (*Melaleuca cajuputi*). In: Malaysian J. Anal. Sci. 7 (1), 65-68 pp.
- [14] PATNUKAO, P. & PAVASANT, P. (2008): Activated carbon from *Eucalyptus camaldulensis Dehn* bark using phosphoric acid activation. In: Bioresour. Technol. 99 (17), 8540-8543 pp.
- [15] BEETS, P.N. & GARRETT, L.G. (2018): Carbon fraction of Pinus radiata biomass components within New Zealand. In: N. Z. J. For. Sci. 48, 14 p.
- [16]LÜTKE, S.F., IGANSI, A.V., PEGORARO, L., DOTTO, G.L., PINTO, L.A.A. & CADAVAL JR., T.R.S. (2019): Preparation of activated carbon from black wattle bark waste and its application for phenol adsorption. In: J. Environ. Chem. Eng. 7, 103396 p.
- [17]KIM, M., JANG, Y. & PARK, D. (2020): Determination of the optimum removal efficiency of fine particulate matter using activated carbon fiber (ACF). In: Int. J. Environ. Res. Public Health 17 (21), 8230 p.
- [18]DAS, D., GAUR, V. & VERMA, N. (2004): Removal of volatile organic compound by activated carbon fiber. In: Carbon 42, 2949–2962 pp.
- [19]KIM, S.Y., YOON, Y.H. & KIM, K.S. (2016): Performance of activated carbon-impregnated cellulose filters for indoor VOCs and dust control. In: Int. J. Environ. Sci. Technol. 13, 2189–2198 pp.
- [20] HUANG, S., CHUNG, T. & WU, H. (2021): Effects of molecular properties on adsorption of six-carbon VOCs by activated carbon in a fixed adsorber. In: ACS Omega 6 (8), 5825–5835 pp.
- [21] CHOI, Y.J., LEE, Y.S. & IM, J.S. (2018): Effect of pore structure of activated carbon fiber on mechanical properties. In: Appl. Chem. Eng. 29, 318–324 pp.

- [22] THITHAI, V., JIN, X., AHMED, M.A. & CHOI, J.W. (2021): Physicochemical properties of activated carbons produced from coffee waste and empty fruit bunch by chemical activation method. In: Energies 14, 1-15 pp.
- [23] NATIONAL INSTITUTE OF ENVIRONMENTAL RESEARCH 2020-23, 2020: Standard method for measuring indoor/outdoor air quality.
- [24]RODRÍGUEZ-NAVAS, C., FORTEZA, R. & CERDÀ, V. (2012): Use of thermal desorption–gas chromatography–mass spectrometry (TD–GC–MS) on identification of odorant emission focus by volatile organic compounds characterization. In: Chemosphere 89 (11), 1426-1436 pp.
- [25] ABIKO, H., FURUSE, M. & TAKANO, T. (2010): Reduction of adsorption capacity of coconut shell activated carbon for organic vapors due to moisture contents. In: Ind. Health 48 (4), 427-437 pp.
- [26] DANISH, M. & AHMAD, T. (2018): A review on utilization of wood biomass as a sustainable precursor for activated carbon production and application. In: Renew. Sust. Energ. Rev. 87, 1-21 pp.
- [27] PARK, J.E., KIM, E.J., PARK, M. & LEE, E.S. (2019): Adsorption capacity of organic compounds using activated carbons in zinc electrowinning. In: Energies 12, 2169 p.
- [28] JO, T. (2008): Removal of harmful gas with wood or bark charcoal. In: Mokchae Konghak 36 (6), 69-76 pp.
- [29] EFEOVBOKHAN, V.E., ALAGBE, E.E., ODIKA, B., BABALOLA, R., OLADIMEJI, T.E., ABATAN, O.G. & YUSUF, E.O. (2019): Preparation and characterization of activated carbon from plantain peel and coconut shell using biological activators. In: J. Phys. Conf. Ser. 1378, 032035 p.
- [30] FLUES, M., SATO, L.M., SCAPIN, M.A., COTRIM, M.E.B. & CAMARGO, I.M.C. (2013): Toxic elements mobility in coal and ashes of Figueira coal power plant, Brazil. In: Fuel 103, 430-436 pp.
- [31]EL-HASAN, T., AL-OMARI, H., JIRIES, A. & AL-NASIR, F. (2002): Cypress tree (*Cupressus semervirens L.*) bark as an indicator for heavy metal pollution in the atmosphere of Amman City, Jordan. In: Environ. Int. 28 (6), 513-519 pp.
- [32] JIANG, G.Q., FANG, G.Z., PANG, J.Y. & HAN, S.Y. (2011): Analysis and evaluation on chemical composition of the larch bark. In: Adv. Mat. Res. 183, 2046-2049 pp.
- [33] RAHMAN, R., WIDODO, S., AZIKIN, B. & TAHIR, D. (2019): Chemical composition and physical characteristics of coal and mangrove wood as alternative fuel. In: J. Phys. Conf. Ser. 1341, 052008 p.
- [34] MOSTAPHA, M. & HUSSEINSYAH, S. (2011): The effect of filler content on properties of coconut shell filled polyester composites. In: MPJ 6 (1), 87-97 pp.
- [35]FERREIRA, J.P.A., MIRANDA, I., SOUSA, V.B. & PEREIRA, H. (2018): Chemical composition of barks from *Quercus faginea* trees and characterization of their lipophilic and polar extracts. In: PLoS One 13 (5), e0197135 p.
- [36] KARIMNEZHAD, L., HAGHIGHI, M. & FATEHIFAR, E. (2014): Adsorption of benzene and toluene from waste gas using activated carbon activated by ZnCl₂. In: Front. Environ. Sci. Eng. 8, 835-844 pp.

YOUNG-KYU LEE, OHKYUNG KWON, WONSIL CHOI SEOUL NATIONAL UNIVERSITY NATIONAL INSTRUMENTATION CENTER FOR ENVIRONMENTAL MANAGEMENT 1 GWANAK-RO, GWANAK-GU SEOUL, 08826 SOUTH KOREA

MYOUNG CHEOL MOON, JAE MIN SO HAPPYHOMEWOODTECH CO. LTD 40-7 CHENGGYEGONGDAN-GIL MUAN, 58544 SOUTH KOREA

VILAYSIT THITHAI, JOON WEON CHOI* SEOUL NATIONAL UNIVERSITY GRADUATE SCHOOL OF INTERNATIONAL AGRICULTURAL TECHNOLOGY 1447 PYEONGCHANGDAE-RO PYEONGCHANG-GUN, 25354 SOUTH KOREA *Corresponding author: cjw@snu.ac.kr

> DAYE KIM, IN YANG* SEOUL NATIONAL UNIVERSITY INSTITUTES OF GREEN BIO SCIENCE & TECHNOLOGY, 1447 PYEONGCHANGDAE-RO PYEONGCHANG-GUN, 25354 SOUTH KOREA *Corresponding author: dahadad@snu.ac.kr