

Adsorption characteristics of heavy metals ions by physical activation on coal tar pitch-based activated carbon fibers

Bo-kyung Choi^{1,2}, Jae-Kyoung Ko³, Soo-Jin Park^{2,*} and Min-Kang Seo^{1,*}

¹Korea Institute of Carbon Convergence Technology, Jeonju 54853, Korea

²Department of Chemistry, Inha University, Incheon 22212, Korea

³Korea Institute of Convergence Textile, Iksan 54588, Korea

Article Info

Received 24 November 2016

Accepted 9 January 2017

*Corresponding Author

E-mail: seomk721@kctech.re.kr
sjpark@inha.ac.kr

Tel: +82-63-219-3730
+82-32-876-7234

Open Access

DOI: <http://dx.doi.org/10.5714/CL.2017.22.096>

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

Due to the increasing population growth of modern society, along with rapid industrial development and urbanization, environmental pollution continues to worsen and has become an important issue, not only domestically but also worldwide. In particular, toxic substances such as heavy metal ions are present in the wastewater produced by various industries. This wastewater flows into rivers, pollutes water supplies, and can contaminate the drinking water supplied to people [1-3].

Powder or activated carbons are being widely used today to mitigate polluted water from industrial sources and contaminated supplies. To make up for the limitations of such materials, there has been strong interest in the use of activated carbon fibers (ACFs) as adsorbents, because they offer excellent adsorption performance and processability [4-6].

In particular, ACFs are considered to be particularly promising materials based on the controlled manipulation of their nano-structure, including abundant micrometer porosity, and properties such as high specific surface area and narrow pore size distribution [7-9].

The raw materials for ACFs include various types of carbon fibers, such as acrylics, rayons, phenols, and pitch. Pitches in particular are considered promising low-cost carbon precursors because they offer high carbon content, lower volatility, and high yield, and can be utilized in various ways. In recent years, pitch fiber, as high-density graphitizable carbon material precursors, have been suitably activated and used in the fields of adsorption, catalysis, energy storage and conversion [10,11].

The purpose of this study was to investigate the effects of structural changes in ACFs, such as specific surface area and micropore volume, on their adsorption of heavy metal ions.

The coal tar pitch fibers used in this study were prepared from a pitch precursor using a melt-spinning procedure (fusion radiation temperature, 325°C; discharge rate, 0.25 g/min; winding speed, 550 m/min; diameter, 24.4 μm). The coal tar pitch fibers were supplied by the OCI Company in Korea. The obtained isotropic pitch had a softening point of 280°C, viscosity of 400,000 cP, a carbon yield of 80–85 wt%, and quinolone insoluble of 19–24.

To prepare the ACFs, initially 1.0 g of the pitch fibers was oxidized and stabilized in 180–360°C at a heating rate of 1°C/min. The pitch fibers were then carbonized after being heated up to 1000°C at a heating rate of 10°C/min under a nitrogen environment, where they were maintained for an hour.

The physical activation conditions of the pitch fibers were as follows. Water (0.5 mL/min) and CO₂ (300 mL/min) were supplied to the pitch fibers to complete their oxidation, stabilization, and carbonization processes, and nitrogen (100 mL/min) was used as a carrier gas to manufacture the specimens. To obtain various grades of ACFs, the steam activation temperature was fixed at 900°C and the CO₂ activation temperature was fixed at 1000°C, respectively; the ACFs activation time was set at 20, 40, and 60 min. The ACFs were labeled according to their activation time: CF (as-received), ACF-20 (steam-activated 20 min), ACF-40 (steam-activated 40 min), ACF-60 (steam-activated 60 min), ACF-C20 (CO₂-activated 20 min), ACF-C40 (CO₂-activated 40 min), and ACF-C60 (CO₂-activated 60 min).

The adsorption efficiency of Cu(II), Ni(II), and Cr(VI) on the ACFs was measured using stoppered flasks containing 0.05 g of the ACFs in 100 mL of aqueous solution with 1

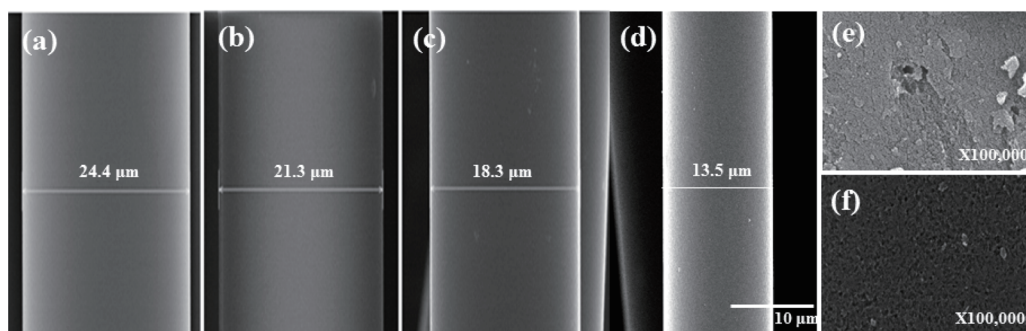


Fig. 1. Scanning electron microscopy images of oxidized, carbonized, and activated pitch fibers; (a) carbon fiber, (b) oxidation, (c) carbonization, (d) activation, (e) H₂O-activated activated carbon fiber (ACF), and (f) CO₂-activated ACF.

mM concentrations of CuSO₄·5H₂O, NiCl₂·6H₂O and K₂Cr₂O₇, respectively. In the case of Cu(II), Ni(II), and Cr(VI) adsorption, the initial pH of the solution was adjusted to about 3, 5 and 1 by using 0.1 M HCl and 0.1 M NaOH. The bottles were sealed with glass stoppers and then shaken for a given time (10, 20, 40, and 60 min) at 25±1 °C at a frequency of 200–250 rpm.

The surface morphology and features of the ACFs were observed by scanning electron microscopy (SEM; JSM 0840A, JEOL). Elemental analysis (EA) was used to measure changes in the oxygen, hydrogen, carbon, and nitrogen contents of the pitch fibers that had been stabilized and carbonized at particular temperatures.

The porous textural characterization was analyzed at 77 K with a N₂ adsorption isotherm using a BELSORP (BEL Co., Ltd., Japan). Prior to each analysis, the ACFs were outgassed at 573 K for 6 h to obtain a residual pressure of less than 10⁻³ Torr. The amount of nitrogen adsorbed on the ACFs was used to calculate specific surface area and pore size distribution, which were determined using the Brunauer-Emmett-Teller (BET) equation and the Barrett-Joyner-Halenda (BJH) model, respectively. Also, the Horvath-Kawazoe (H-K) equation was applied to the experimental nitrogen isotherms for micropore size analysis.

0.05 g of the ACFs was placed in contact with a 100 mL solution of 1 mM concentrations of CuSO₄·5H₂O, NiCl₂·6H₂O, and K₂Cr₂O₇. The single bottle was sealed with paraffin film and then shaken. The adsorbed amount of heavy metal ions was measured by atomic absorption spectroscopy (SpectrAA-880; Varian, USA).

Fig. 1 shows SEM images of the oxidized, carbonized, and activated pitch fibers. The fibers were slightly contracted due to the heat treatment, but a rapid decrease in diameter was not observed.

According to the results of the EA, the pitch fibers were composed of 1.13% oxygen, 4.76% hydrogen, 92.58% carbon, and 1.38% nitrogen. The stabilized pitch fibers, however, were composed of 10.06% oxygen, 3.08% hydrogen, 85.42% carbon, and 1.01% nitrogen. As a result of stabilization, the carbon and hydrogen content decreased while the oxygen content increased. In addition, the pitch fibers that were carbonized after being stabilized were composed of 1.20% oxygen and 95.90% carbon, which was higher than those of the pitch fibers.

During steam activation, as the activation time increased, the specific surface area increased from 855 to 1693 m²/g, then decreased to 1635 m²/g, while the yield decreased from 98 to

34.5%. During CO₂ activation, as the activation time increased, the specific surface area increased slightly from 995 to 1233 m²/g, and also the yield decreased slightly from 82.3 to 70%. As the activation time increased, the yield continued to decrease. It was proven that the yield rate was greatly affected by the activation time.

In a comparison of the steam and CO₂ activation results, the steam activation produced higher specific surface area values. This corresponds to the known fact that H₂O typically reacts with pitch fibers about twice as fast as CO₂. This difference in reaction rates is due to the size difference of the molecules: CO₂ molecules (with a cross-section area of 19.5 nm²) are larger than H₂O molecules (cross-section area of 10.8 nm²), so the CO₂ molecules diffused more slowly into the carbon pores, barely reaching the micropores [12].

Fig. 2 shows the adsorption isothermal curves of the ACFs at different activation times. The curves for both the steam and the CO₂ activated pitch fibers presented typical type I shapes which have large initial adsorption amounts, thus confirming that micropores had formed in them [13].

The specific surface areas, total pore volumes, and average pore sizes of the ACFs were obtained using the BET equation, as listed in Table 1. The specific surface area tended to increase as a function of activation time at the given activation tempera-

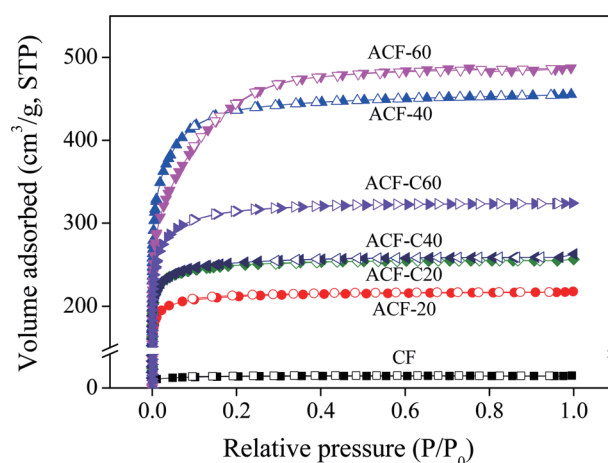


Fig. 2. N₂/77K adsorption-desorption isotherms curves of the activated carbon fibers as a function of activation time by physical activation (steam, CO₂).

Table 1. Textural properties of the ACFs as a function of activation time

Samples	S _{BET} ^{a)}	V _T ^{b)}	V _{Mi} ^{c)}	V _{Me} ^{d)}	F _{Mi} ^{e)}	D _P ^{f)}
CF	1.69	0.0027	0.0002	0.0025	7.41	6.28
ACF-20	855	0.33	0.32	0.01	96.9	1.57
ACF-40	1693	0.70	0.63	0.07	90.0	1.66
ACF-60	1635	0.75	0.56	0.19	74.6	1.84
ACF-C20	995	0.39	0.37	0.02	94.8	1.59
ACF-C40	1009	0.40	0.37	0.03	92.5	1.60
ACF-C60	1233	0.50	0.46	0.04	92.0	1.62

ACF, activated carbon fiber; CF, carbon fiber.

^{a)}Specific surface area (m²/g).

^{b)}Total pore volume (cm³/g).

^{c)}Micropore volume (cm³/g).

^{d)}Mesopore volume (cm³/g).

^{e)}Fraction of micropore (%).

^{f)}Average pore diameter (nm).

ture. But, the specific surface area decreased to 1635 m²/g at the activation time of 60 min. It's possible that, as the micropore walls were destroyed due to excessive activation, the volume of micropores rapidly decreased and the oxidative reactions began to occur mainly on the surface. When there was a large quantity of mesopores, however, as in the case of the ACFs, the specific surface area and the micropore volume were not always proportionally related. This was because, while the specific surface area was greatly affected by the micropores, the micropore volume increased when there were more mesopores with large diameters.

Calculation of the pore size distribution was based on the BJH method. The result confirmed that not only micropores but also mesopores developed, because the micropore volume and the pore sizes changed as the activation time increased. ACF-60 exhibited the maximum volume, thus confirming that the micropore volume increased along with the activation time. The micropores comprised about 56% of the total area of all pores, thus confirming that many mesopores were also distributed along with the micropores. It is possible that the steam activated the existing micropores from their inside rather than developing new micropores, thereby increasing their average pore size and volume. Therefore, the number of micropores decreased while the number of mesopores increased [14].

As mentioned earlier, however, it was believed that excessive activation destroyed the micropore walls and decreased the micropore volume and pore sizes. In contrast to the steam activation, in the CO₂ activation the diameters of the pores were insignificantly affected by the activation time. The micropore size and volume increased along with the activation time, so it was assumed that new micropores formed inside the ACFs and built sufficient connection paths, through which heavy metal ions absorptions were carried out.

In this study, the adsorption characteristics of Cu(II), Ni(II), and Cr(VI) were investigated to identify how the changes in the pore structures of ACFs caused by physical activation affected the adsorption of heavy metal ions. Fig. 3 shows the adsorption of the heavy metal ions with respect to adsorption time. The

Cu(II), Ni(II), and Cr(VI) heavy metal ion solutions had initial pH values of 3, 5, and 1, respectively. The pitch fibers adsorbed very little of the heavy metal ions, and the ACFs adsorbed a greater amount than the pitch fibers.

The specific surface area of the pitch fibers as calculated based on nitrogen adsorption was 1.69 m²/g, and they failed to reach the expected adsorption capacity corresponding to the specific surface area. The low adsorption of heavy metal ions by the pitch fibers was likely caused by the scarcity of micropores in the pitch fibers and the lack of activation points on the pitch fiber surface.

For the ACFs, all of the heavy metal ions were rapidly adsorbed within the first 20 min, and had almost saturated within an hour. It's possible that this occurred because all of the micropores which had developed in the ACFs were being exposed to the surface via slit shapes, unlike the activated carbons, and had relatively small physical-transportation resistance, allowing rapid adsorption [15,16].

Following steam activation, the adsorption amounts appeared in the order of ACF-40>ACF-60>ACF-20. The adsorption amount decreased because the specific surface area was small. The adsorption of the heavy metal ions appeared greater in the ACF-40 than in the ACF-60, but ACF-40 had the largest specific surface area. This was possibly because the adsorption performance decreased as the pores were destroyed from excessive activation.

Following CO₂ activation, the adsorption amounts appeared in the order of ACF-C40≥ACF-C60>ACF-C20. The ACFs activated by CO₂ exhibited higher heavy metal ion adsorption amounts in spite of the comparatively lower specific surface areas of the ACFs activated by steam. This was attributed to the fact that new micropores were formed inside the ACFs due to the CO₂ activation, and the micropores were connected with one another. And as the contact time increased, the chromate anions likely interacted more strongly with the electron acceptor H⁺ of the surface functional groups of the ACF surfaces. Thus, the adsorption of Cr(VI) ions tended to increase as a function of contact time.

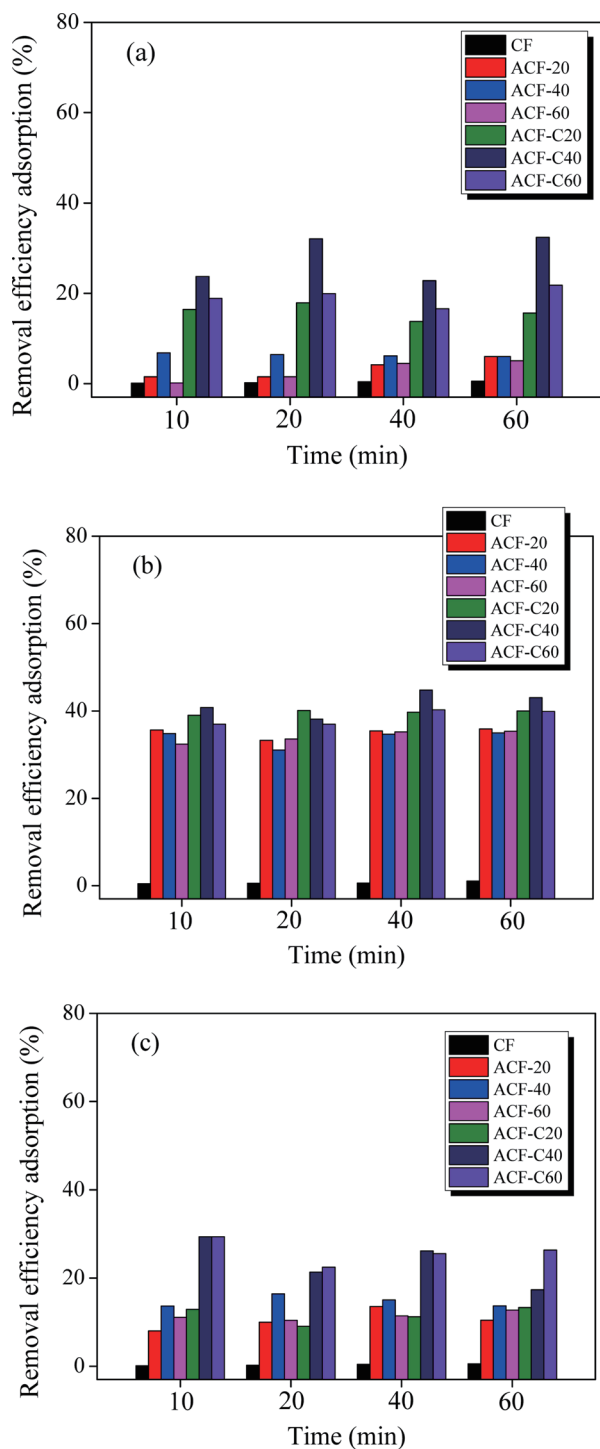


Fig. 3. Heavy metal ion adsorptions of the activated carbon fibers (ACFs) as a function of contact time; (a) Cu(II), (b) Ni(II), and (c) Cr(VI). CF, carbon fiber.

Based on these results, it was proved that the development of micropores with large specific surface areas could be controlled by the proper activation conditions, and was demonstrated to be an effective method for the synthesis of coal tar pitch-based ACFs.

In this study, ACFs were prepared from coal tar pitch fibers by physical activation with steam and CO₂. The specific surface area, the amount of heavy metal ion adsorption, and pore size distribution of the ACFs were investigated. In ACF-40, a micropore volume/total pore volume proportion of 90%, specific surface area of 1693 m²/g, and average pore diameter of 1.66 nm was obtained. And the Cu(II), Ni(II), and Cr(VI) adsorption capacities were 6.03%, 34.99%, and 13.68%, respectively. ACF-C40 had a micropore volume/total pore volume proportion of 92.5%, specific surface area of 1009 m²/g, and average pore diameter of 1.60 nm, respectively. And the Cu(II), Ni(II), and Cr(VI) adsorption capacities were 32.41%, 43.03%, and 17.31%, respectively. The heavy metal ion adsorption capacity of the CO₂ activated ACFs was higher than that of the steam activated ACFs.

By increasing the specific surface area and developing micropores in ACFs, it was confirmed that the structural properties of the adsorbents affected the adsorption of heavy metal ions.

Conflict of Interest

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

Acknowledgements

This work was supported by the “Energy Technology Program” of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) granted financial resource from the Ministry of Trade, Industry & Energy, Republic of Korea (No. 20153030031710).

References

- [1] Park SJ, Jang YS. Pore structure and surface properties of chemically modified activated carbons for adsorption mechanism rate of Cr(VI). *J Colloid Interface Sci*, **249**, 458 (2002). <https://doi.org/10.1006/jcis.2002.8269>.
- [2] Chiang YC, Chen TC. Surface characterization and adsorption performance of electrochemically oxidized activated carbon fibers. *Sustain Environ Res*, **20**, 387 (2010).
- [3] Kim BJ, Bae KM, Park SJ. Elemental mercury vapor adsorption of copper-coated porous carbonaceous materials. *Microporous Mesoporous Mater*, **163**, 270 (2012). <https://doi.org/10.1016/j.micromeso.2012.05.038>.
- [4] Lee SY, Park SJ. Determination of the optimal pore size for improved CO₂ adsorption in activated carbon fibers. *J Colloid Interface Sci*, **389**, 230 (2013). <https://doi.org/10.1016/j.jcis.2012.09.018>.
- [5] Moon HS, Kim IS, Kang SJ, Ryu SK. Adsorption of volatile organic compounds using activated carbon fiber filter in the automobiles. *Carbon Lett*, **15**, 203 (2014). <https://doi.org/10.5714/CL.2014.15.3.203>.
- [6] Tekinalp HL, Cervo EG, Fathollahi B, Thies MC. The effect of molecular composition and structure on the development of porosity in pitch-based activated carbon fibers. *Carbon*, **52**, 267 (2013). <https://doi.org/10.1016/j.carbon.2012.09.028>.

- [7] Bai BC, Kim JG, Naik M, Im JS, Lee YS. The hydrogen storage capacity of metal-containing polyacrylonitrile-based electrospon carbon nanofibers. *Carbon Lett*, **12**, 171 (2011). <https://doi.org/10.5714/CL.2011.12.3.171>.
- [8] Heo GY, Park SJ. Effects of structure of heat-treated pitch precursors on electrochemical properties of pitch-based activated carbon. *Powder Technol*, **239**, 94 (2013). <https://doi.org/10.1016/j.powtec.2013.01.049>.
- [9] Basova YV, Edie DD, Lee YS, Reid LK, Ryu SK. Effect of precursor composition on the activation of pitch based carbon fibers. *Carbon*, **42**, 485 (2004). <https://doi.org/10.1016/j.carbon.2003.12.070>.
- [10] Maciá-Agulló JA, Moore BC, Cazorla-Amorós D, Linares-Solano A. Activation of coal tar pitch carbon fibres: physical activation vs. chemical activation. *Carbon*, **42**, 1367 (2004). <https://doi.org/10.1016/j.carbon.2004.01.013>.
- [11] Park SJ, Kim YM. Adsorption behaviors of heavy metal ions onto electrochemically oxidized activated carbon fibers. *Mater Sci Eng A*, **391**, 121 (2005). <https://doi.org/10.1016/j.msea.2004.08.074>.
- [12] Rudnicki P, Hubicki Z, Kołodyńska D. Evaluation of heavy metal ions removal from acidic waste water streams. *Chem Eng J*, **252**, 362 (2014). <https://doi.org/10.1016/j.cej.2014.04.035>.
- [13] Huh JH, Seo MK, Kim HY, Kim IJ, Park SJ. Influence of KOH activation on electrochemical performance of coal tar pitch-based activated carbons for supercapacitor. *Polymer(Korea)*, **36**, 756 (2012). <https://doi.org/10.7317/pk.2012.36.6.756>.
- [14] Roh JS. Microstructural changes during activation process of isotopic carbon fibers using CO₂ gas(I)-XRD study. *Korean J Mater Res*, **13**, 742 (2003). <https://doi.org/10.3740/MRSK.2003.13.11.742>.
- [15] Machida M, Fotoohi B, Amamo Y, Ohba T, Kanoh H, Mercier L. Cadmium(II) adsorption using functional mesoporous silica and activated carbon. *J Hazard Mater*, **221-222**, 220 (2012). <https://doi.org/10.1016/j.jhazmat.2012.04.039>.
- [16] Yanagisawa H, Matsumoto Y, Machida M. Adsorption of Zn(II) and Cd(II) ions onto magnesium and activated carbon composite in aqueous solution. *Appl Surf Sci*, **256**, 1619 (2010). <https://doi.org/10.1016/j.apsusc.2009.10.010>.