

Identification of chemical species of iodine and mercury on iodine-impregnated activated carbon using X-ray absorption near-edge structure analysis

Mercury (Hg) is a global pollutant, and the significant adverse impacts caused by Hg and its compounds are of great concern. The Minamata Convention came into effect in August 2017 with the aim of protecting human health and the environment from the anthropogenic emission and release of Hg. Activated carbon (AC) is often used to remove Hg from various emission and release sources, but the capacity of virgin AC (AC-virgin) is limited. Because of the high cost of AC, it is often modified to enhance its capacity and for regeneration. AC impregnated with halogens exhibits excellent Hg⁰ removal performance, and iodine-impregnated AC (I-AC) has high Hg⁰ removal efficiency, low activation energy, and low volatility of the adsorption product, HgI₂, which increases the stability of the spent sorbent, compared with AC impregnated with other halogens such as Br and Cl.

The mechanism of the adsorption of Hg⁰ by I-ACs, such as potassium iodide (KI)-impregnated AC, is via I₂, the formation of which is the key step in the chemisorption of Hg⁰, as it reacts with Hg⁰ to produce HgI₂. I₂ formation has been proposed to occur via the following reaction: $2\text{KI} + 1/2\text{O}_2 = \text{K}_2\text{O} + \text{I}_2$. However, starch-iodine tests showed that negligible I₂ is formed at temperatures lower than 300°C, and the Gibbs free energy of the proposed reaction has a positive value even at 1,000°C. Thus, whether I₂ can actually be formed in I-ACs remains unclear.

To elucidate the mechanism of Hg⁰ adsorption by I-ACs, especially with regard to the occurrence and formation of I₂, we prepared a series of I-ACs with different iodine precursors including KI, NH₄I, and KIO₃ via one-step impregnation, denoted as AC-KI, AC-NH₄I, and AC-KIO₃, respectively [1]. Comparing AC-KI with AC-NH₄I and AC-KIO₃, we analyzed the effects of the cation element and valence state of iodine on Hg⁰ removal. In an attempt to impregnate the AC with I₂ by the reaction $2\text{CuSO}_4(\text{aq}) + 4\text{KI}(\text{aq}) = 2\text{CuI}(\text{s}) + \text{I}_2(\text{s}) + 2\text{K}_2\text{SO}_4(\text{aq})$, we conducted the co-impregnation of KI followed by CuSO₄. The product is denoted as AC-KI + CuSO₄. AC-virgin without any precursors was used as the reference material for evaluating the Hg⁰ removal performance. We conducted X-ray absorption near-edge structure analysis (XANES) for iodine and Hg at SPring-8 BL01B1.

The iodine XANES spectra (Fig. 1) of AC-KI, AC-NH₄I, and AC-KI + CuSO₄ before and after the adsorption test were very similar. No similarity was detected between the sorbents and their precursors,

KI, NH₄I, and CuI. As the spectrum of I₂ contained no distinct features (Fig. 1), we could not determine whether I₂ was present in the I-AC samples from only the iodine K-edge spectra. Thus, we conducted the linear combination fitting (LCF) of the XANES data for I-ACs prior to the adsorption test, applying principal component analysis (PCA) to exclude irrelevant reference materials from the spectra. I₂ accounted for approximately 9–16% of total iodine in these sorbents. Notably, the ranking of I₂ fractions among the I-ACs was consistent with the order of Hg⁰ removal efficiency, which was as follows: AC-KI + CuSO₄ ≈ AC-NH₄I > AC-KIO₃ > AC-KI. Therefore, I₂ was confirmed to play an important role in Hg⁰ removal by I-ACs. The formation of I₂ may occur during impregnation, drying (before the adsorption test), and adsorption. However, our results indicated no I₂

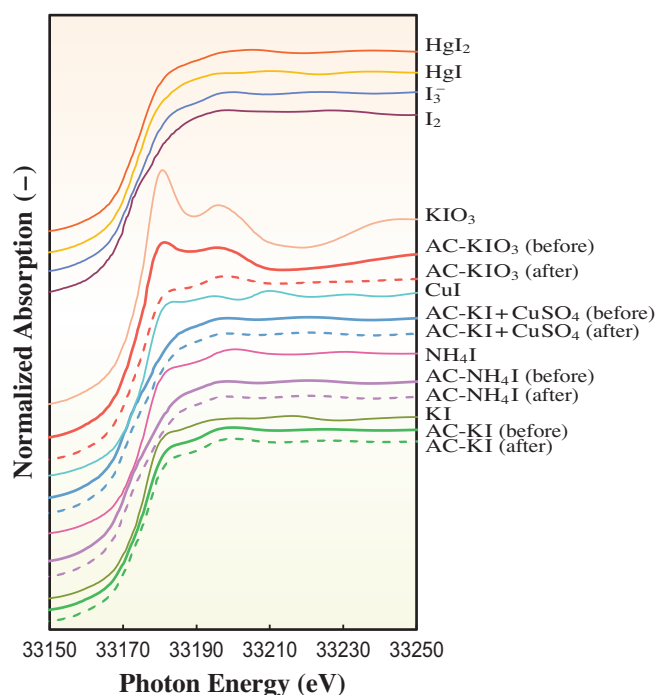


Fig. 1. Iodine K-edge X-ray absorption near-edge structure (XANES) spectra for reference materials (solid KI, solid NH₄I, solid CuI, solid KIO₃, solid I₂, I₃⁻ ion, solid HgI, and solid HgI₂) and impregnated ACs (AC-KI, AC-NH₄I, AC-KI+CuSO₄, and AC-KIO₃) before and after adsorption test (E₀ = 33,172 – 33,174 eV).

in AC-KI; instead, I_3^- and KI were detected. The LCF results revealed larger proportions of I_3^- in all I-ACs. Notably, sorbents with greater Hg^0 removal efficiency, namely, AC-KI + $CuSO_4$ and AC- NH_4I , contained larger fractions of I_3^- than did the other sorbents. Thus, in addition to I_2 , I_3^- may serve as an I_2 donor and play an essential role in Hg^0 removal by I-ACs. Moreover, as the reaction of I_3^- with starch produces a black-blue color, I_3^- formation may have improved the Hg^0 removal performance in previous studies, in which KI was used as the impregnation precursor and the starch test was employed for I_2 detection.

We investigated the Hg species present after I-AC adsorption, which was assumed to be HgI_2 in previous research. The Hg L_{III} -edge XANES analysis of sorbents was conducted after the Hg^0 adsorption test to determine the chemical species of Hg (Fig. 2). Two references, $HgCl_2$ and $HgSO_4$, produced a marked shoulder peak at 12,282 eV; this shoulder peak was also produced by AC-virgin, which contains Cl and S, but not by the I-ACs. Therefore, $HgCl_2$ and $HgSO_4$ may have been present in AC-virgin, not adsorption products of I-ACs. LCF was conducted after PCA and target transformation to confirm the species of Hg in the spent sorbents and their ratios. The main species of Hg in I-ACs in this study were HgI_2 and HgI , with a higher proportion of HgI_2 than of HgI . The mechanism of HgI_2 generation in I-ACs, according to the adsorption test results, can be explained as follows. In I-ACs, HgI is more readily formed than $HgCl$ because of its lower activation energy. This HgI can be further oxidized into HgI_2 by I_2 , which is released from I_3^- . HgI_2 can also be formed via the direct oxidation of Hg^0 by I_2 . Furthermore, HgI_2 is more stable than $HgCl_2$, which is in accord with our finding that HgI_2 , rather than $HgCl_2$, dominates the I-AC samples.

In this study, the main Hg removal mechanism was clear from both the I-K and Hg- L_{III} -edge XANES spectra. The results were supported by those of other analyses such as X-ray diffraction and X-ray photoelectron spectroscopy. Future research should focus on the stability and regeneration of the spent sorbents.

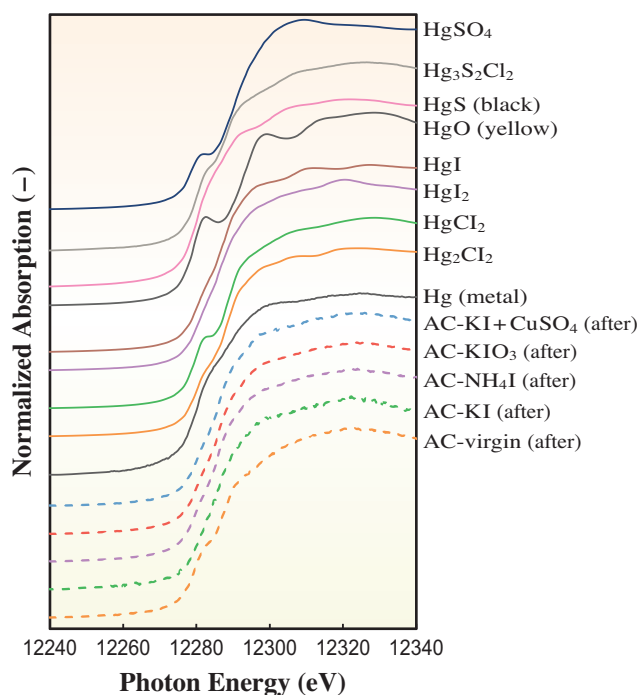


Fig. 2. Mercury L_{III} -edge XANES spectra for reference materials (metallic mercury, solid Hg_2Cl_2 , solid $HgCl_2$, solid HgI_2 , solid HgI , solid HgO [yellow], solid HgS [black], solid $Hg_3S_2Cl_2$, and solid $HgSO_4$), AC-virgin, and impregnated ACs (AC-KI, AC- NH_4I , AC- KIO_3 , and AC-KI + $CuSO_4$) after adsorption test ($E_0 = 12,284$ eV).

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References

[1] Y. Cheng, K. Shiota, T. Kusakabe, K. Oshita, M. Takaoka: *Chem. Eng. J.* **402** (2020)126225.