

# Hg Removal Characteristics of Noncarbon Sorbents in a Fixed-Bed Reactor

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**ABSTRACT:** This research targeted the development of a low-cost, high-efficiency sorbent for mercury capture in flue gas. Six non-carbon-based carriers and various impregnating substances including NaI, CuCl<sub>2</sub>, CuBr<sub>2</sub>, and FeCl<sub>3</sub> were investigated in this study. The performances of the prepared sorbents were tested in a bench-scale fixed-bed reactor at 140 °C in N<sub>2</sub> atmosphere. Some sorbents demonstrated the mercury capture capabilities similar to that of a commercial active carbon sorbent (Norit Darco LH).

## 1. BACKGROUND

The impact of Hg on human health has been a great public concern since the outbreak of Minamata disease. Hg in the environment is a long-term threat to ecosystems because of its neurotoxicity and enrichment along food chains.<sup>1</sup> With the rapid development of the power industry, Hg released from coal combustion has become one of the most important anthropogenic sources of mercury. The U.S. Environmental Protection Agency (EPA) estimated in 1997 that about one-third of the Hg released in the United States was from coal combustion.<sup>2</sup> As the world's largest coal-consuming country, China's releases of Hg from coal combustion have been estimated to increase annually. Wu et al. suggested that, from 1995 to 2003, the Hg released from coal combustion in China increased from 202 to 257 t/year.<sup>3</sup>

To reduce Hg emissions from coal-fired power plants, the U.S. EPA announced the Clean Air Mercury Rule in 2005. Although the rule was vacated by the District of Columbia Circuit Court a few years later, the U.S. EPA is now considering a new Hg control regulation under the maximum achievable control technology (MACT) scheme.<sup>4</sup> The MACT limit was set as the "average emissions of the best performing 12%" of existing sources (for which emissions data are available), corresponding to over 90% Hg reduction if applied as the regulated emission limit. A new Information Collection Request aiming to determine the MACT limit for Hg and other pollutants including dioxin is now being carried out. It is expected that the new federal Hg emissions regulations for U.S. coal-fired power plants will be issued by 2015. In the meantime, many states in the United States will have state regulations in effect before the new federal regulations become available.<sup>4</sup>

Air pollution control devices (APCDs), including the electrostatic precipitator/fabric filter (ESP/FF) hybrid precipitator and flue gas desulfurization (FGD) devices, are capable of removing part of the Hg in flue gas. To further control the Hg discharged from power plant stacks, activated carbon injection (ACI) is considered one of the most important technologies. Halogenated active carbon sorbents have high Hg capture capabilities and have been widely tested.<sup>5</sup> However, high costs and possible degradation of fly ash limit the application of

active carbon sorbents. In recent years, some researchers have suggested that modified minerals or fly ash could be attractive alternatives for Hg sorbents.<sup>6,7</sup>

The most distinctive advantage of noncarbon Hg sorbents is low cost. This type of sorbent is also friendly for the cement/concrete industry because it will not increase the carbon content in fly ash. Wendt et al. also indicated that some noncarbon sorbents can be used at elevated temperature,<sup>8</sup> which would significantly increase the sorbent residence time and therefore enhance Hg capture.

Based on existing research findings, this study attempted to develop Hg sorbents from non-carbon-based materials with high specific surface areas through active substance impregnation. Two commercial active carbon sorbents were employed in this study for comparison purposes.

## 2. EXPERIMENTAL SECTION

**2.1. Reactor System.** A schematic of the fixed-bed reactor system used for Hg adsorption experiments is shown in Figure 1. The apparatus is similar to one previously employed by Granite et al. to screen sorbents for mercury capture.<sup>9</sup> The system consists of three parts: a Hg generator, a fixed-bed reactor, and a tail-gas treatment unit. The elemental Hg (Hg<sup>0</sup>) used in experiments was generated by a PSA Cavkit 10.534 mercury generator. The Hg concentration in the gas stream was monitored with Lumex RA-915+ portable mercury vapor analyzer. Before experiments, the Hg generator and analyzer were calibrated. It was verified that the readings of Lumex RA-915+ instrument fluctuated within ±2% of the Hg<sup>0</sup> generator set values, suggesting the stabilities of both the Hg generator and analyzer.

The fixed-bed reactor itself was made of a 30-mm (inside-diameter) quartz tube that could be electrically heated. The composition and flow rate of simulated flue gas were controlled by mass flow controllers (MFCs). Hg<sup>0</sup> carried by N<sub>2</sub> was first

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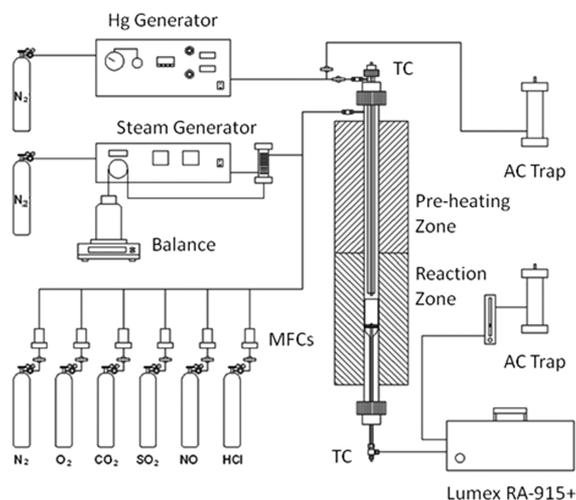


Figure 1. Schematic of the fixed-bed Hg adsorption system.

heated to 140 °C in the preheating zone of the fixed-bed reactor and then passed through the sorbent bed supported by a sintered quartz disk to complete the adsorption. A thermocouple coated with quartz was inserted into the reaction zone to monitor the reaction temperature. All tubes, joints, and valves through which Hg-containing gas passed were made of either quartz or polytetrafluoroethylene (PTFE) to avoid unnecessary Hg contamination. The tail gas was treated with an active carbon trap before being released.

**2.2. Experimental Procedures.** Before each test, the reactor tube and downstream connections were rinsed with 10% nitric acid, deionized water, and absolute ethanol in sequence (repeated three times) and then dried. A quartz fiber filter was placed on the sintered disk to prevent disk blockage by falling sorbent. In each experiment, 0.5 g of sorbent was homogeneously mixed with 5 g of quartz sand before being placed on the filter. The bed height of sorbent/sand mixture was about 6 mm. During the each test, the Hg<sup>0</sup> stream was switched on only after the reaction conditions had been attained. The Hg<sup>0</sup> concentration was set at 20 μg/Nm<sup>3</sup>, and the total flow rate was controlled at 2 L/min. Each experiment normally lasted for 1 h, during which time the Hg<sup>0</sup> concentration in the gas stream after the bed was continuously measured by Lumex RA-915+ instrument. Hg captured by sorbent (Hg<sup>p</sup>) was determined with a Milestone DMA-80 autosampler after the experiment. The oxidized Hg (Hg<sup>2+</sup>) in the gas stream after the sorbent bed was deduced by subtracting Hg<sup>p</sup> from the input Hg<sup>0</sup>. The overall experimental error was estimated as ±15%. The Hg removal rate is defined as

$$\text{removal rate} = \frac{\text{Hg}^p}{\text{total input Hg}^0} \times 100\% \quad (1)$$

**2.3. Sorbent Preparation.** Six common non-carbon-based materials with relatively large specific surface areas were selected as the carriers in this study. The characteristics of the carriers are listed in Table 1. The characteristics of two commercial active carbon sorbents compared in this study, namely, Norit Darco FGD and Norit Darco LH (brominated), are included in the same table.

For the purposes of expression simplicity hereafter, the noncarbon carriers are abbreviated as follows: kaolinite, K; bentonite, B; zeolite, Z; calcium silicate, CS; neutral alumina, NA; and silica gel, SG.

Table 1. Characteristics of Noncarbon Carriers and Commercial Active Carbon Sorbents

carrier	BET specific surface area (m <sup>2</sup> /g)	total pore volume (cm <sup>3</sup> /g)	BET average pore size (nm)
kaolinite	9.5	5.0 × 10 <sup>-2</sup>	21.1
bentonite	27.6	6.0 × 10 <sup>-2</sup>	8.7
zeolite	79.2	4.1 × 10 <sup>-1</sup>	20.9
calcium silicate	126.7	4.2 × 10 <sup>-1</sup>	13.3
neutral alumina	145.7	2.2 × 10 <sup>-1</sup>	6.0
silica gel	342.9	9.2 × 10 <sup>-1</sup>	10.7
Norit Darco LH	405.0	4.2 × 10 <sup>-1</sup>	4.2
Norit Darco FGD	664.8	4.9 × 10 <sup>-1</sup>	2.9

It can be seen in Table 1 that the specific surface areas of noncarbon materials are smaller than those of active carbon, especially for kaolinite and bentonite. This is mainly due to the large pore size of the materials. Low-cost activation substances as listed in Table 2 were selected to modify the carriers to

Table 2. Classifications of the Impregnated Materials and Impregnated Solution Concentrations

group	activation substance	concentration (%)
alkali metal halides	NaCl, KCl, CaCl <sub>2</sub> , KBr, NaI	10
	HCl	30
transition metal halides	CuCl <sub>2</sub> , CuBr <sub>2</sub> , FeCl <sub>3</sub> , CoCl <sub>2</sub> , NiCl <sub>2</sub> , CrCl <sub>3</sub> , MnCl <sub>2</sub> , ZnBr <sub>2</sub>	10
sulfur-containing compounds	Na <sub>2</sub> S, Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	10
oxidizers	KMnO <sub>4</sub>	5
	K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> , Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	10

produce noncarbon sorbents. To prepare low-cost sorbents, the activation substances were impregnated onto the carriers from corresponding solutions. The concentrations of the impregnation solutions are also listed in Table 2.

During impregnation, 5 g of carrier was submerged into 30 mL of solution in a 50 mL plugged conical flask, magnetically stirred for 3 h, and allowed to stand for another 3 h. The prepared sorbent was filtered and rinsed three times with deionized water. The sorbent was then dried in a 105 °C oven for 12 h. The remaining solution and the rinsed water were subsequently analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) to determine the amount of activation substances loaded onto carriers, defined as

$$\text{loading} = \frac{(M_{\text{original AS}} - M_{\text{remaining AS}}) \times 100\%}{(M_{\text{original AS}} - M_{\text{remaining AS}} + M_{\text{carrier}})} \quad (2)$$

where  $M_{\text{original AS}}$  is the original mass of activation substance,  $M_{\text{remaining AS}}$  is the mass of activation substances remained after impregnation, and  $M_{\text{carrier}}$  is the mass of carrier.

### 3. RESULTS AND DISCUSSION

**3.1. Impregnation of Activation Substances.** The loadings of different activation substances on each carrier are shown in Figure 2.

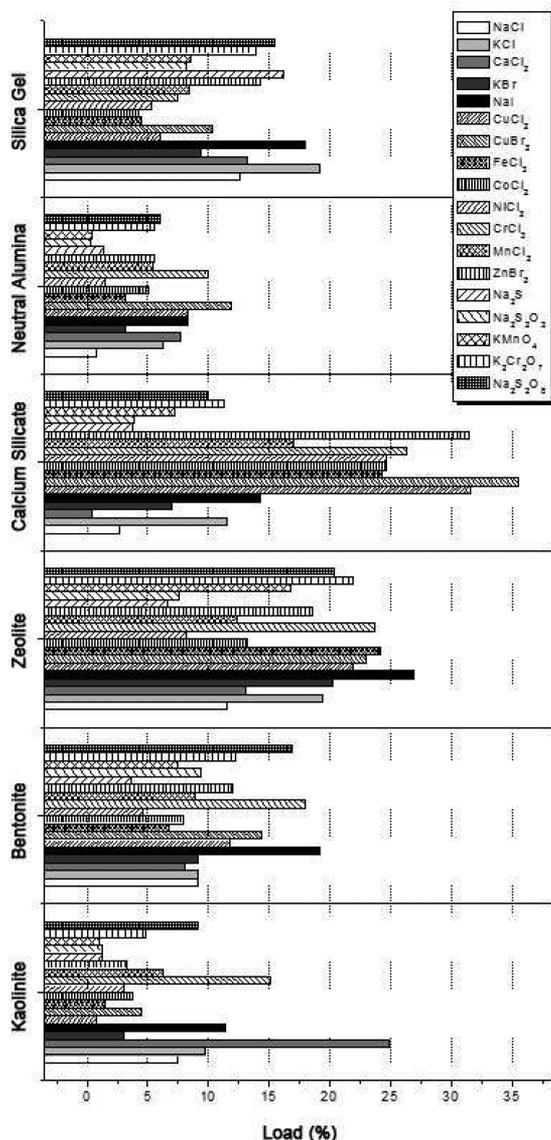


Figure 2. Loadings of activation substances on carriers.

Among the different carriers, zeolite and calcium silicate had higher loadings of activation substances than did the others after impregnation. It was found that calcium silicate was capable of absorbing virtually all of the  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Cr}^{3+}$  ions in solution. This phenomenon can be explained by ion exchange between the solutions and calcium silicate. Indeed, the  $\text{Ca}^{2+}$  concentrations in the corresponding solutions after impregnation were found to be significantly increased.

Bentonite is rather special when compared with the other carriers, because of its unique layer structure formed by fine alumina silicate grains, which provides bentonite with strong adsorption and cation-exchange abilities.<sup>10</sup> It was found that bentonite loaded more cations than anions from solutions. The impregnation of activation substances onto bentonite is thus the joint effort of ion exchange and adsorption among layers.

**3.2. Hg Removal Characteristics.** **3.2.1. Carriers and Activation Substances.** To determine the Hg capture capabilities of the prepared sorbents, the Hg removals by carrier and activation substances alone were studied first, as shown in Figures 3 and 4, respectively.

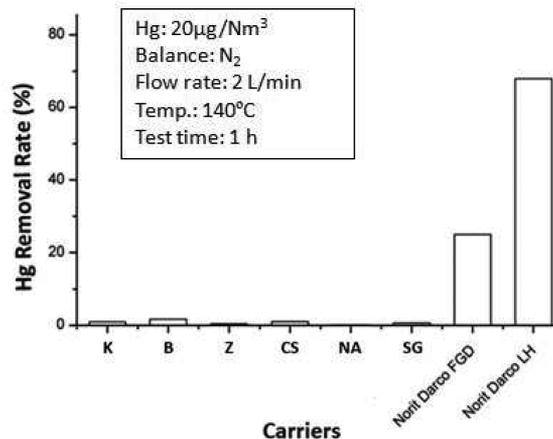


Figure 3. Hg removal by noncarbon carriers.

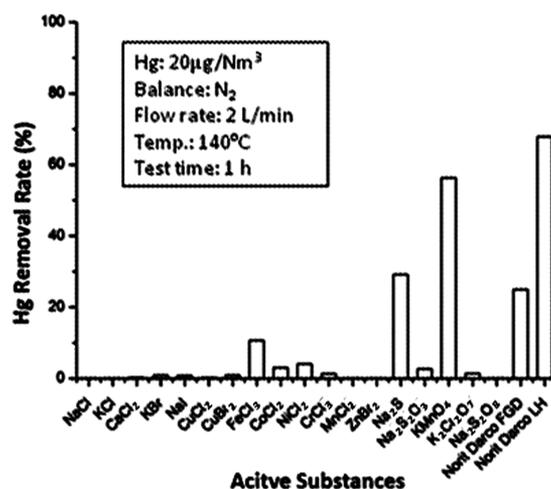
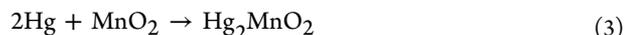


Figure 4. Hg removal by activation substances: impregnated by (a) HCl and alkali metal halides, (b) transition metal halides, (c) sulfur-containing compound, (d) oxidizers.

The testing results revealed that the amounts of Hg captured by all of the carriers and most of the activation substances alone were very low, much lower than those of Norit Darco sorbents. However,  $\text{KMnO}_4$  demonstrated a moderate Hg removal rate of 56.3%. Previous research suggested that  $\text{KMnO}_4$  is chemically unstable and might decompose to form  $\text{MnO}_2$  during the drying process,<sup>11</sup> with which Hg could react with according to the reaction



Apart from  $\text{KMnO}_4$ ,  $\text{Na}_2\text{S}$  also exhibited some Hg capture ability, which might be caused by dissociated  $\text{S}^{2-}$  on the  $\text{Na}_2\text{S}$  surface. Although the activation substances did not show Hg capture capabilities, the Hg oxidizing capabilities of some substances (such as  $\text{FeCl}_3$  and  $\text{CuCl}_2$ ) have been confirmed by many other researchers.<sup>12,13</sup>

**3.2.2. Hg Capture by Noncarbon Sorbents in  $\text{N}_2$ .** The Hg removal rates of the noncarbon sorbents made from the materials listed in Tables 1 and 2 are illustrated in Figure 5. The Hg removal rates of the corresponding activation substances and active carbon sorbents are also included in the figure for comparison purposes.

The Hg removal rates of the prepared noncarbon sorbents varied dramatically from virtually nothing to almost 100%, but

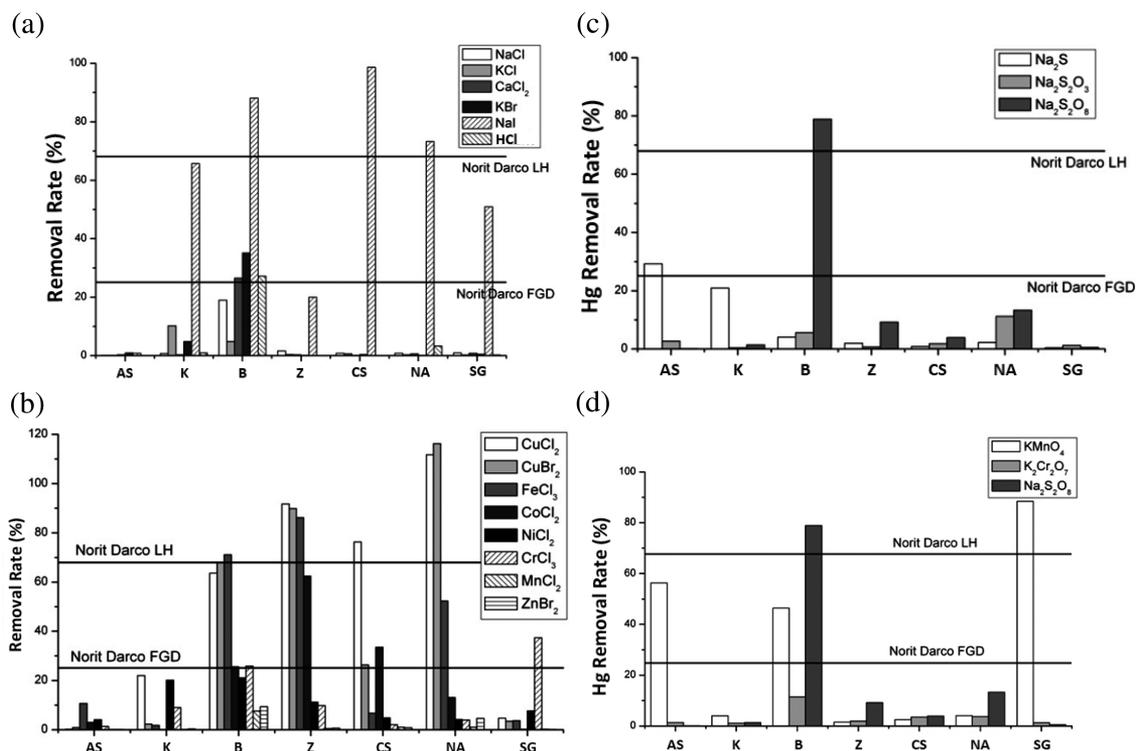


Figure 5. Hg removal by noncarbon sorbent ( $140\text{ }^{\circ}\text{C}$ ,  $20\text{ }\mu\text{g}/\text{Nm}^3\text{ Hg}^0$ ,  $2\text{ L}/\text{min}$ ,  $\text{N}_2$  balance,  $1\text{ h}$ ; AS = activation substance).

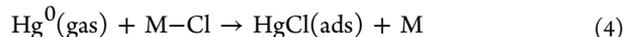
in most cases, they were much higher than the sum of the individual rates from the carrier and activation substance. It is obvious that the much improved Hg capture capabilities were contributed by the joint efforts of carrier and activation substances. The mechanisms of Hg capture by different noncarbon sorbents are discussed in detail in the following sections.

**3.2.2.1. Alkali Metal Halides.** HCl and alkali metal halides are often used to modify active carbon sorbents. Existing research<sup>12–14</sup> has shown that the Hg capture capability of active carbon can be significantly improved by Cl, Br, and I ions on the sorbent surface.  $\text{Hg}^0$  could react with these ions to form  $\text{Hg}^{2+}$ , which would be more likely to be adsorbed. Potassium iodide and other halide-promoted sorbents were studied previously, and several potential mechanisms for mercury capture were suggested.<sup>9</sup>

For noncarbon carriers modified by alkali metal halides, NaI performed much better than any other activation substances (Figure 5a). NaI-modified bentonite and calcium silicate achieved 88.1% and 98.6%  $\text{Hg}^0$  removals, respectively. NaI-modified kaolinite and neutral alumina also removed more than 60%  $\text{Hg}^0$ , comparable to the removal achieved with Norit Darco LH. It was noticed that NaI-modified sorbent became slightly brownish after impregnation. A starch test confirmed that  $\text{I}_2$  dissociated during sorbent preparation.  $\text{I}_2$  on the sorbent surface would chemically absorb  $\text{Hg}^0$  to form  $\text{HgI}_2$ , which resulted in the high Hg removal rates by NaI-modified sorbents.

From the carrier's point of view, bentonite seemed to be more adapted than others, as all of the halides improved its Hg removal after modification (Figure 5a). It might be worthwhile to point out that the chemical bonds between alkali metals and halogens are relatively strong, so that halogen– $\text{Hg}^0$  reactions under these conditions are difficult. Bentonite, however, exhibiting good ion exchange and adsorption abilities because of its unique layer structure,<sup>10</sup> might assist the release of  $\text{Cl}^-$

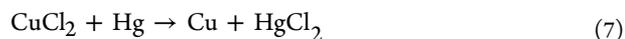
and  $\text{Br}^-$ . These halogen ions could oxidize  $\text{Hg}^0$  to achieve chemical capture. The captured  $\text{Hg}^{2+}$  might also be released in gas form. This type of reaction can be described by the Mars–Maessen mechanism, as follows



**3.2.2.2. Transition Metal Halides.** Among the transition metal halides,  $\text{CuCl}_2$  and  $\text{CuBr}_2$  seemed to be very effective, especially when modifying neutral alumina (Figure 5b).  $\text{FeCl}_3$ -modified sorbent also demonstrated a decent Hg removal rate (except for silica gel). Other active substances, such as  $\text{CoCl}_2$  and  $\text{ZnBr}_2$ , seemed to be inadequate for modifying the carriers to achieve acceptable Hg removal rates.

Lee et al. investigated the performance of  $\text{CuCl}_2$ -modified active carbon and bentonite in both fixed-bed and entrained-flow reactors.<sup>15,16</sup> Their studies suggested that the Hg removal rate is directly linked to the characteristics of the carrier.  $\text{CuCl}_2$  could enhance Hg oxidation and adsorption to a great extent. Their sorbent consisting of 90%  $\text{CuCl}_2$ -modified bentonite and 10% Norit Darco FGD could achieve a Hg removal rate as high as 98%.

Although  $\text{CuCl}_2$  and  $\text{CuBr}_2$  themselves have little capability for Hg capture, their impregnation on the selected carriers resulted in high Hg removals. The findings in this study agree with the results from Lee et al.<sup>15,16</sup>  $\text{CuCl}_2$  and  $\text{CuBr}_2$  could considerably oxidize  $\text{Hg}^0$ ; however, the fixation of  $\text{Hg}^{2+}$  on the sorbent surface is largely determined by the sorbent morphology and chemical bond strength. The reaction between  $\text{CuCl}_2$  and Hg can be expressed as







substances have been identified as potential sorbents in realistic simulated flue gas. Low production costs could be an important advantage for noncarbon sorbents.

This article describes some promising mercury removal sorbents. As the research has just begun, many of the reaction mechanisms require in-depth study. Moreover, secondary pollution problems caused by such removal methods need to be verified.

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### Notes

The authors declare no competing financial interest.

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