

Elimination of hydrogen sulfide adsorbed on Cu(II)-modified hydroxyapatite by warm water

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Abstract

Elimination behavior of hydrogen sulfide (H_2S) molecules adsorbed on Cu(II)-supported hydroxyapatite (Cu-HAp) using warmed ultrapure water was investigated, and H_2S adsorption ability of Cu-HAp before and after exposure to initial H_2S gas and the subsequent water treatment was compared. Cu-HAp quickly and markedly adsorbed H_2S and its color changed from light blue to dark brown, suggesting that sulfuric component was chemically adsorbed on the surface of Cu-HAp and that it was present as a Cu(II) salt. After the water treatment of Cu-HAp at 333 K after exposure to H_2S , the solid phase kept its original crystalline structure and no sulfuric component was detected. The color of the sample gradually changed and turned back to the almost original one after immersion in water for 4 weeks. In addition, Cu-HAp treated in water recovered H_2S adsorption ability up to 76 % compared to the original Cu-HAp. Solid residue obtained by evaporation of the treated solution was mainly composed of hydrated calcium sulfate, while any Cu(II) salt was not detected. It suggests that sulfides adsorbed on Cu-HAp was oxidized and eluted into water, and that Cu(II) remained on the surface of the adsorbent. Consequently, Cu-HAp is expected to be a reusable adsorbent against gaseous H_2S .

Key words

hydroxyapatite, adsorption and desorption behavior, hydrogen sulfide, metal cation-modification, reuse of adsorbent

1. Introduction

Hydrogen sulfide (H_2S) is one of the most common compounds which are sensed as unpleasant odors in domestic environments. It is extremely toxic at high concentration and causes annoyance even at low concentration (Chen and Morris, 1972; Stita et al., 2015). Therefore, it has been required for adsorbents to remove H_2S efficiently. For example, adsorption ability for H_2S has been investigated on activated carbon, metal oxides, amine modified silica and various aluminosilicates (Feng et al., 2005; Haimour et al., 2005; Long et al., 2016; Jaiboon et al., 2014; Yaşyerli et al., 2002). In a previous research, it was found that modification of hydroxyapatite (HAp) with Cu(II) gave it dramatically enhanced adsorption ability for H_2S , in comparison to other Cu(II) salts (Nishida et al., 2017). The chemical formula of Cu(II)-modified HAp (Cu-HAp) can be estimated as $\text{Ca}_9\text{Cu}(\text{PO}_4)_6(\text{OH})_2$, according to an assumption that both phosphate and hydroxide ions were not substituted. In that study, Cu-HAp exposed to H_2S gas changed in color from light blue to dark brown (denoted as S-Cu-HAp). It suggests that an amorphous compound related to copper(II) sulfide was produced on the S-Cu-HAp due to a chemical reaction between S^{2-} and Cu^{2+} . However, it is assumed that the adsorption ability of Cu-HAp for H_2S was reduced since H_2S molecules covered its surface adsorption sites. In fact, Cu-HAp which adsorbed excess H_2S

showed lower adsorption ability for H_2S than pure Cu-HAp. In order to reuse adsorbents after the use, heat treatment and/or reduced pressure drying are generally applied. According to our preliminary trial to eliminate H_2S from S-Cu-HAp by a simple heat treatment in air, the color of S-Cu-HAp changed from brown to light blue green at 523 K. However, sulfuric component was found to remain on the sample by an X-ray photoelectron spectroscopic analysis (XPS; PHI5000 VersaProbe, ULVAC-PHI, Inc., Japan). Moreover, the adsorption ability of S-Cu-HAp after the heat treatment for H_2S was as much as that before the heat treatment. So, a warmed water treatment was attempted as an alternative way of removal of H_2S to confirm whether the adsorption ability of S-Cu-HAp is recovered for H_2S under a mild aqueous condition.

2. Materials and Methods

Synthesis of HAp was conducted by a wet method by neutralization of calcium hydroxide aqueous suspension with phosphoric acid under CO_2 -free condition. 250 cm^3 of $0.400 \text{ mol}\cdot\text{dm}^{-3}$ H_3PO_4 was dropped into 250 cm^3 of 0.167 mol $\text{Ca}(\text{OH})_2$ suspension at the rate of $5 \text{ mL}\cdot\text{min}^{-1}$ with Ca/P molar ratio of 1.67 under N_2 atmosphere, and stirred at room temperature for 6 h. The slurry was aged at room temperature for 48 h. The obtained precipitate was filtered off, washed repeatedly with ultrapure water and dried in an oven at 333 K for 24 h. The dried solid was finally ground and sieved to obtain the geometric size less than $45 \mu\text{m}$. Then, the obtained HAp was added to $0.1 \text{ mol}\cdot\text{dm}^{-3}$ $\text{Cu}(\text{NO}_3)_2$ aqueous solution and stirred at $278\pm 2 \text{ K}$ for 1 h. After stirring, Cu-HAp was collected from

the resultant slurry by filtration, washed with ultrapure water and dried at 333 K overnight. S-Cu-HAp was prepared by exposing Cu-HAp to gaseous H₂S which had been generated by a reaction of granular FeS with HCl. In order to remove H₂S adsorbed on S-Cu-HAp and attempt to recover H₂S adsorption ability for S-Cu-HAp, 0.25 g of the powder sample was added to 40 cm³ of ultrapure water warmed at 333 K.

Then, 10 mg of each sample was exposed to H₂S diluted with 3 dm³ of pure N₂ gas for 1 h, and residual concentration of H₂S was measured by a gas detecting tube in a closed system. The initial H₂S concentration was adjusted to c.a. 150 ppm.

Concentrations of metal cations in the solid and liquid phases after immersion of S-Cu-HAp in the warm water (precipitate and eluent) were determined by X-ray fluorescence spectroscopy (XRF; EDXL300, Rigaku Co. Ltd. Japan) and inductive coupled plasma-mass spectroscopy (ICP-MS; ELAN DRC II, PerkinElmer Japan Co. Ltd.), respectively. For the precipitate, crystalline structure was determined by X-ray diffraction analysis (XRD; Ultima IV, Rigaku Co. Ltd. Japan).

3. Results and discussion

Figure 1 shows color changes of S-Cu-HAp in warm (333 K) water during 4 weeks. First, the color of S-Cu-HAp changed from dark brown to dark green just after immersion into ultrapure water (Figure 1(a)). Then, the suspension was treated at 333 K replacing the solution every 1 week. As a result, the color of S-Cu-HAp gradually changed from dark green to light blue within 4 weeks. Finally, the color of S-Cu-HAp was analogous to that of the original Cu-HAp with our naked eyes.

Figure 2 shows changes in H₂S concentration as a function of exposure period of the samples to the gas as well as a blank test, which were evaluated by a gas bag-detecting tube method. No change was found in the concentration of H₂S within 60 min in the blank test. On the other hand, the concentration of residual H₂S was drastically decreased within 10 min, and gradually decreased afterward in the case of existence of the samples in the bags. The concentrations of residual H₂S before and after the warm water treatment of S-Cu-HAp reached to 75 ppm and 41 ppm, respectively. After the warm water treatment, H₂S adsorption ability of S-Cu-HAp was recovered by 76 %, compared with the original Cu-

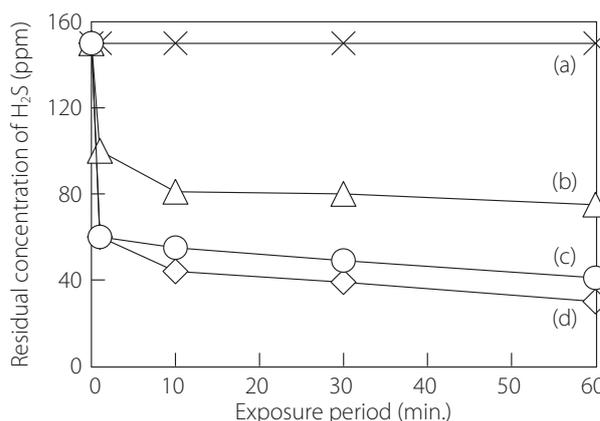


Figure 2: H₂S adsorption behavior of various samples

Note: (a) Blank, (b) S-Cu-HAp (before water treatment), (c) S-Cu-HAp (after water treatment), (d) Cu-HAp.

HAp. This result suggests that H₂S adsorbed on S-Cu-HAp was transferred into liquid phase through the warm water treatment.

Table 1 shows concentrations of metal cations in the liquid phase after immersion of S-Cu-HAp in the warm water (eluent), which were determined by ICP-MS. As a result, the concentrations of Ca(II) and Cu(II) were $9.1 \times 10^{-1} \sim 9.5 \times 10^1$ mg·L⁻¹ and $1.0 \times 10^{-3} \sim 5.7 \times 10^{-1}$ mg·L⁻¹ respectively. Metal cations eluted into the liquid phase tended to decrease with increasing the treatment frequency with the warm water. The concentrations of the metal cations in the eluent collected after treating of S-Cu-HAp for 4 weeks were almost the same as those after treating of the original Cu-HAp. Taken into ac-

Table 1: Concentrations of metal cations eluted into warm water of S-Cu-HAp and solution pH

Sample	Treatment frequency	Ca ²⁺ (mg·L ⁻¹)	Cu ²⁺ × 10 ⁻¹ (mg·L ⁻¹)	pH [-]
S-Cu-HAp	1	95.27	5.69	4.76
	2	34.32	0.88	5.47
	3	9.50	0.23	5.79
	4	3.03	0.09	6.12
	5	0.91	0.01	6.70
Cu-HAp	1	0.65	0.02	7.63

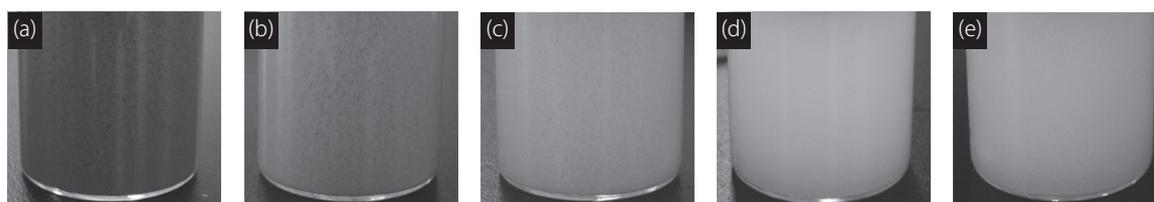


Figure 1: Color changes of S-Cu-HAp in warm water at 333 K during 4 weeks
Note: (a) just after immersion, (b) 1 week, (c) 2 weeks, (d) 3 weeks, (e) 4 weeks immersion.

count of all the eluent collected, total amounts of Ca(II) and Cu(II) eluted into the liquid phase were calculated to be 6.8 % and 0.2 %, respectively. This indicates that elution of Cu(II) was markedly suppressed than that of Ca(II). On the other hand, pH of the eluent changed from 4.76 (1 week) to 6.70 (4 weeks). The pH of the eluent for Cu-HAp was 7.63, which is closer to the latter liquid than the former. It suggests that the treatment of S-Cu-HAp by warm water caused dissolution of H₂S leading to an increase of acidity of the liquid, and that thus solubility of S-Cu-HAp got higher for the initial eluent. Finally, no signal attributed to sulfur was detected by XRF for S-Cu-HAp after the warm water treatment for 4 weeks.

To clarify the mechanism of desorption of H₂S already adsorbed on S-Cu-HAp, solid residue was collected by evaporation from the eluent. Analysis using Scanning electron microscopy-Energy dispersive X-ray analyzer (SEM-EDX; JSM-7600F, Jeol Ltd., Japan) revealed that the obtained solid residue was composed of elementary O, Ca, P, S and Cl. Figure 3 shows XRD patterns of S-Cu-HAp and the solid residue obtained from the eluent by evaporation after the warm water treatment. Diffraction peaks assigned only to hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂, #09-0432) were detected for the S-Cu-HAp. On the other hand, peaks attributed to calcium sulfate 0.53 hydrate (CaSO₄·0.53H₂O, #41-0225), calcium hydrogen phosphate (CaHPO₄, #09-0080) and monocalcium chlorophosphate monohydrate (CaClH₂PO₄·H₂O, #44-0746) were detected for the solid residue.

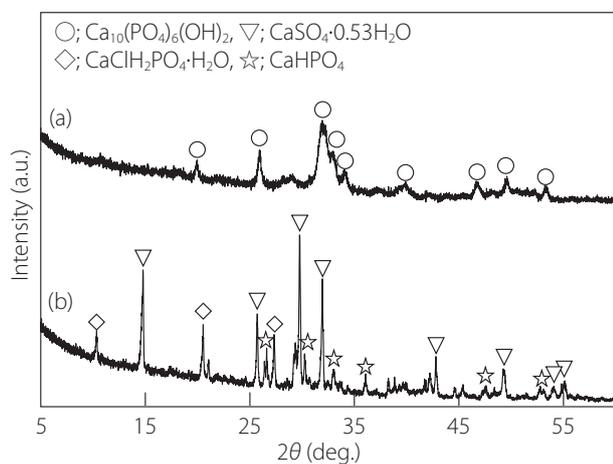


Figure 3: XRD patterns of (a) S-Cu-HAp after warm water treatment and (b) solid residue obtained by evaporation of treated solution

Consequently, the warm water containing dissolved oxygen used in this study might have acted as an oxidant for sulfide ion to produce sulfate ion (Chen and Morris, 1972; Sharma and Yuan, 2010). However, oxidation of sulfide ion might have occurred during the evaporation process. Therefore, it is necessary to clarify the detailed mechanism including timing

of oxidation. Nevertheless, it is rather important in this study that Cu(II) was retained on the surface of the sample and that the adsorption ability for H₂S was recovered by a simple warm water treatment. Thus, this Cu-HAp is expected to be used for a reusable deodorant material against H₂S.

4. Conclusion

Change of adsorption ability and mass transfer behavior of Cu(II)-modified hydroxyapatite (Cu-HAp) on which hydrogen sulfide (H₂S) gas was adsorbed was investigated through a warmed water treatment. The solid phase collected after the water treatment did not change its original crystalline structure, while its color gradually shifted to the original one during 4 weeks. Moreover, H₂S adsorption ability of Cu-HAp was recovered up to 76 % by 4 weeks immersion in warm water. Solid phase collected by evaporation of the treated solution consisted mainly of hydrated calcium sulfate, but any copper(II) salt did not remain. Consequently, sulfides adsorbed on Cu-HAp was released into the aqueous phase, and Cu(II) was kept staying on the surface of Cu-HAp. So, this material may be useful adsorbent for continuous catching and releasing of H₂S molecules.

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