Photo-Fenton reaction of composites containing iron-containing salmon bone-derived apatite and charcoal

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Abstract
Bone charcoal derived from animal bones can adsorb and remove diverse substances owing to the ion-exchange properties of hydroxyapatite and adsorption onto the charcoal pores. In this study, iron-modified bone charcoal was obtained by stirring iron(II) chloride tetrahydrate and salmon bone in an aqueous solution, followed by drying and heating in a nitrogen atmosphere. The solid state of iron in the bone charcoal and the adsorption and decomposition performance of organic substances were evaluated. Powder X-ray diffraction analysis showed a decrease in the crystallinity of hydroxyapatite and a-axis lattice constant of bone charcoal after immersion in an iron-ion solution and heat treatment, as compared to untreated bone charcoal. Mössbauer analysis revealed that the iron-modified bone charcoal contained iron in both divalent and trivalent high-spin states. To evaluate the organic adsorption capability, the modified bone charcoal was immersed in a methylene blue solution and compared with and without added H_2O_2. Under dark conditions, the decolorization rate of methylene blue was approximately 1.4 times higher with H_2O_2. Under UV irradiation and H_2O_2 presence, the decolorization performance was approximately 1.8 times better than that under dark conditions without H_2O_2. These findings indicate that the incorporation of iron within the bone charcoal leads to enhanced photo-Fenton activity.

1. Introduction
Bone charcoal derived from animal bones exhibits the capability to adsorb and remove various substances because of the ion-exchange properties of hydroxyapatite (HAp) and the adsorption onto charcoal pores[1]. However, its application in dyed wastewater treatment is limited because the adsorption saturates after prolonged use. Iron ions can be incorporated into HAp, and, in the presence of H_2O_2 and light energy, they can help decompose organic matter via photo-Fenton reactions.
In this regard, the present study aimed to develop a novel composite material that is suitable for long-term application in treating dyed wastewater. Salmon bone-derived charcoal was modified by incorporating iron. Further, the solid dissolution of iron in the bone charcoal, as well as the adsorption and decomposition performance of organic substances, was evaluated to examine the degradation of organic substances via photo-Fenton reaction. Methylene blue dye (Mb) was employed as the representative organic matter.

2. Experiment

Iron(II) chloride tetrahydrate and powdered salmon bone were added to distilled water and stirred for 1 h. The resultant mixture was dried and heat-treated at 600 °C in a nitrogen atmosphere. The bone charcoal is designated “BC” and the samples with 1.79 and 8.95 mmol/L of iron ions added during sample synthesis are designated "FeBC-1" and "FeBC-2" respectively. Each sample (0.02 g) was added to 200 mL of aqueous Mb solution (10 mg/L), and the solution was stirred for 6 h in the dark. Further, 0.02 g of each sample was added to 200 mL of aqueous Mb solution (10 mg/L) and 0.03% H_2O_2, followed by stirring for 6 h in the dark to assess the Fenton reaction. The photo-Fenton reaction was evaluated by stirring the mixture for 6 h under UV irradiation to perform the Mb decolorization experiment.

3. Results and discussion

X-ray diffraction (XRD) patterns of HAp was observed in all samples. In contrast to BC, FeBC-1 and FeBC-2 exhibited decreased crystallinity of HAp and lattice constant along the a-axis. As the ionic radius of iron (0.74 Å) is smaller than that of calcium (0.99 Å), the substitution of calcium with iron ions likely caused lattice contraction.

Mössbauer analysis showed that both samples showed of three main peaks—isomer shifts of 0.39, 0.41 and 0.96 mm/s for FeBC-1 and 0.40, 0.42 and 1.0 mm/s for FeBC-2. Therefore, the iron incorporated in the HAp in both samples is present in both divalent and trivalent high-spin states.

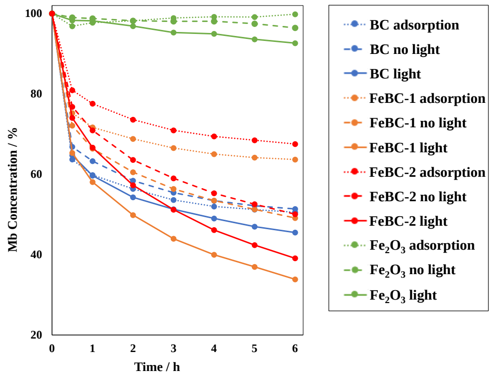

Fig. 1. Relationship between the concentration of Mb in the aqueous solution and immersion time of each sample in the Mb solution.

Fig. 1 shows the results of Mb decolorization experiments using each sample. FeBC-1 adsorbed approximately 36% of the Mb in the absence of H_2O_2 under dark conditions. Upon adding H_2O_2, Mb was decolorized by approximately 51% and 66% in the dark and under UV irradiation, respectively. The possible decolorizing factors of Mb under UV irradiation are (1) adsorption onto the sample, (2) decomposition by reactive oxygen species generated by the photo-Fenton reaction, and (3) decomposition by reactive oxygen species generated by the spontaneous decomposition of H_2O_2. In (2), the reaction proceeds via the following mechanism:

・Fe^{3+}(on the surface of FeBC-1) + H_2O + hν → Fe^{2+}(on the surface of FeBC-1) + ・OH + H^+
・Fe^{2+} (on the surface of FeBC-1) + H_2O_2 → Fe^{3+} (on the surface of FeBC-1) + ・OH +OH^-
・Organics + ・OH → Decomposed products

4. Conclusions

In this study, salmon bone-derived charcoal was modified via iron incorporation to achieve enhanced organic matter degradation capability. The solid solution state of iron, as well as the adsorption and decomposition performance of the organic matter, was examined.

The results indicate that the crystallinity of HAp and lattice constant along the a-axis decreased in FeBC-1 and FeBC-2 as compared to those in BC, suggesting the substitution of iron ions into HAp crystals. The substituted iron ions were found in both divalent and trivalent high-spin states. Furthermore, FeBC-1 and FeBC-2 exhibited high Mb decolorization rates. This suggests that FeBC-1 and FeBC-2 efficiently adsorb and decompose organic matter, leveraging the decomposition performance of the photo-Fenton reaction of iron and adsorption capacity of BC.

References

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