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Water-purifier filters with added hydroxyapatite

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In this study, we fabricated and evaluated the properties of water-purifier filters with added hydroxyapatite (HAp). The antibacterial property of HAp filters was assessed using the pour-plate method as per the requirements of the Korean Standards Association (KS K 0693 : 2011). The pH and calcium-ion concentration of water that was filtered through the HAp filters were measured using a pH meter and an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES), respectively. The HAp filters eliminated 99% of 3 types of bacteria (*Staphylococcus aureus* ATCC 6538, *Klebsiella pneumoniae* ATCC 4352, and *Escherichia coli* ATCC 25922), and the average pH and calcium-ion concentration were 8.0-9.0 and 17.6 ppm, respectively.

Key words: Hydroxyapatite, Water purifier, Ion exchange, pH, Antibacterial.

Introduction

Water is an essential element whose purity is of great concern. High-quality water is generally obtained by collecting unpolluted water or by purifying it. However, bacteria are detected in filtered water, which is a major problem. One of the reasons for this problem is that filtering is insufficient because regular filters that are used in water purifiers cannot remove bacteria. Thus, to remove bacteria by using water purifiers, hydroxyapatite (HAp) was added to water-purifier filters.

The chemical formula of HAp is $Ca_{10}(PO_4)_6(OH)_2$, and its chemical structure is similar to that of the material that the human bone is composed of [1, 2]. HAp has been used in bone grafts, dental implant coatings, toothpaste, and filters and is a promising candidate for application in filtration materials [3-7] because it functions as an ion exchanger and can absorb bacteria and replication-competent human viruses [8].

In this study, we fabricated and characterised a new antibacterial water filter composed of activated carbon and HAp. The pH and calcium-ion (Ca^{2+}) concentration were measured using a pH meter and an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES), respectively. Antibacterial tests were conducted using the pour-plate method and as per the requirements of the Korean Standards Association (KS K 0693 : 2011).

Experimental

Materials

We used HAp that was prepared using the hydrothermal method and activated carbon that is used in water filters. Plate-count agar (solid medium, BD Difco) was used to test the antibacterial properties of the filter. *Staphylococcus aureus* ATCC 6538, *Klebsiella pneumoniae* ATCC 4352, and *Escherichia coli* ATCC 25922 were examined in antibacterial tests.

HAp synthesis and mixing

HAp was synthesised by reacting $CaCO_3$ and H_3PO_4 by using the wet-blending method. The Ca : P ratio of the powder was determined to be 1.67. First, $CaCO_3$ (120 g) was mixed with distilled water and stirred for 5 h. Next, H_3PO_4 (54 g) added slowly to the $CaCO_3$ solution and the solution was stirred for 12 h. After mixing, the solution was dried at 100 °C, and the dried powder was sintered at 1350 °C. The sintered powder was examined using X-ray diffractometry (XRD) to observe the phases. Sintered HAp powder and activated carbon were mixed manually. A flowchart showing the process used for producing the HAp water filter is presented in Fig. 1.

HAp water filter

Sterilised acrylic tubes were filled with a mixture of HAp and activated carbon and then washed and filled with water. The new filters composed of HAp and activated carbon were sealed with silicon cork.

pH and ICP

Four samples were purified using the HAp filter and a control filter for various lengths of time. The samples used were initial cool water (20 mL), second cool water (80 mL), initial water, and second water. The pH and Ca^{2+} concentration of four kinds of samples were measured using a pH meter and an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES),

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Fig. 1. Flowchart showing the process for producing hydroxyapatite (HAp) filters.

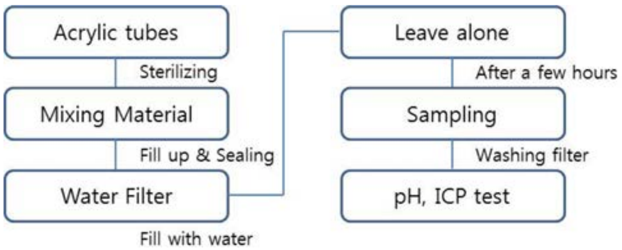

Fig. 2. Flowchart showing the water-testing process.

respectively. A flowchart showing the process used in the water filter tests is presented in Fig. 2.

Antibacterial tests

The antibacterial property of the filter was tested using the pour-plate method. The samples used were initial cool water (20 mL), second cool water (80 mL), initial water, and second water. Plate-count agar (PCA) was sterilised by autoclaving and then placed in a constant-temperature water bath at 56 °C. Liquid PCA was mixed with the samples and poured on the plates before the samples solidified. The plates were incubated for 48 h at 36.5 °C. Additional antibacterial activity tests were conducted according to the requirements of the Korean Standards Association (KS K 0693 : 2011).

Using the HAp filter in a commercial water purifier

We installed a commercial water purifier with HAp and control filters and washed for 10 min. Four samples were extracted through the HAp and control filters after 1, 5, 10, 24, and 72 h. The samples were initial cool water (20 mL), second cool water (80 mL), initial water, and second water. Antibacterial property tests were conducted using the pour-plate method.

Result and Discussion

Water pH

When more HAp was included in the filter, the pH of the filtered water was higher. The maximal pH of HAp-filtered water was 10.19 (strongly alkaline), but

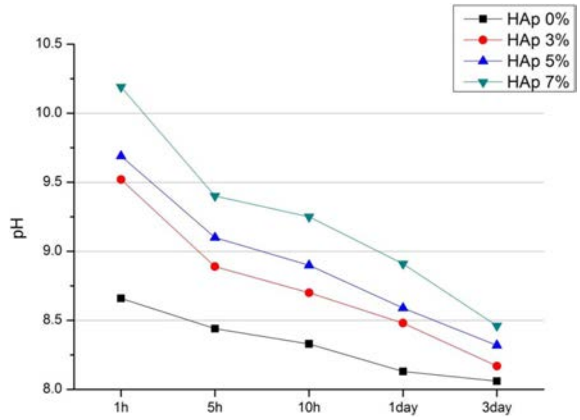

Fig. 3. Variation in the pH of HAp-filtered water over time.

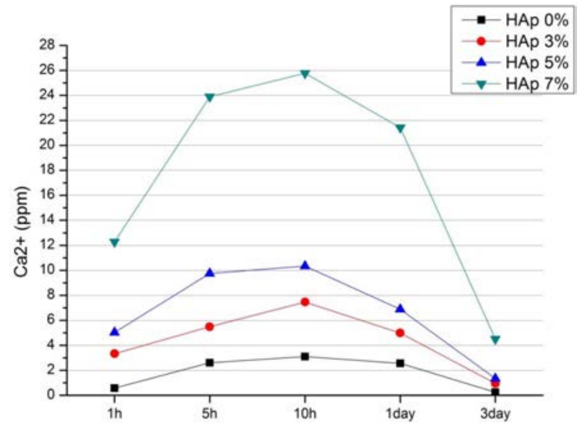

Fig. 4. Ca^{2+} concentration changes in HAp-filtered water over time.

this pH decreased over time and was approximately 8.0-9.0 after 24 h. The pH of the control-filtered water was 8.06, which was due to the activated carbon present in the filter. The pH of the control-filtered water also decreased over time and was always lower than that of the HAp-filtered water. The changes in the pH of control- and HAp-filtered water are shown in Fig. 3.

Ca^{2+} concentration

The concentration of Ca^{2+} increased gradually for 10 h and then decreased. The initial and maximal concentrations of Ca^{2+} were 12.27 ppm and 25.77 ppm when 7% HAp was present in the filter. When more HAp was included in the filter, the concentration of Ca^{2+} was higher. The control filter composed of activated carbon also increased the concentration of Ca^{2+}, but this was within the limits of experimental error. The changes of Ca^{2+} concentration are shown in Fig. 4.

Antibacterial tests

We confirmed that fewer bacteria were present in HAp-filtered water than in the control-filtered water. The number of bacteria in the control (water filtered using the activated-carbon filter) increased gradually

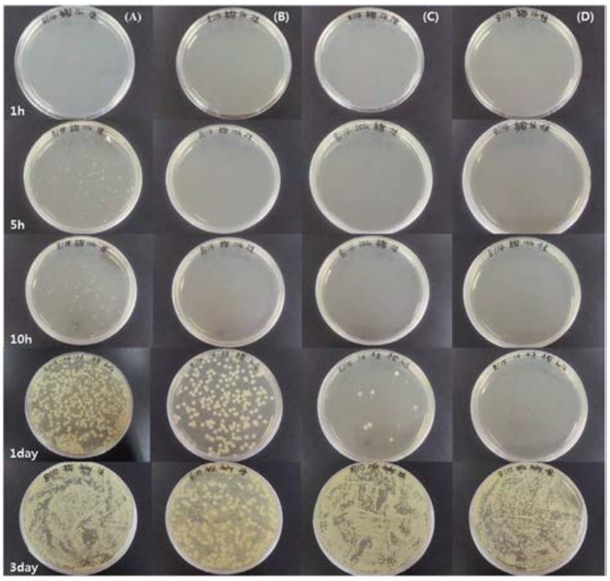

Fig. 5. Results of antibacterial tests over 3 d on HAp-filtered water. (A) 0% HAp, (B) 3% HAp, (C) 5% HAp, and (D) 7% HAp.

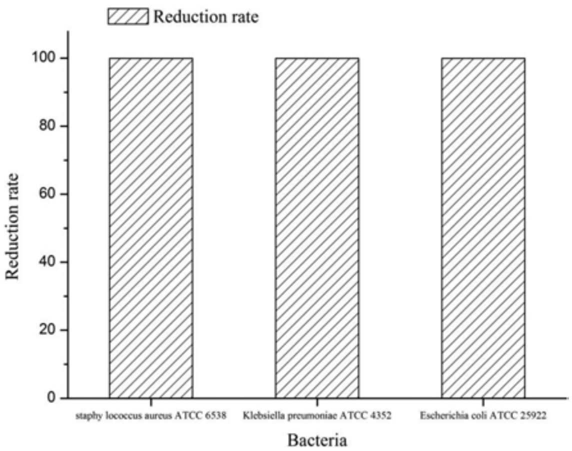

Fig. 6. Bacterial reduction tests on HAp according to the requirements of the Korean Standards Association (KS K 0693 : 2011).

over time. However, with HAp-filtered water, we were unable to detect bacteria initially. Although bacteria grew in the HAp-filtered water after 24 h, the number of bacteria was lower than in the control-filtered water. When more HAp was included in the filter, the antibacterial effect was stronger. Results of antibacterial tests over 3 d on Hap filtered water were shown in Fig. 5. The results of additional antibacterial tests that were performed at the FITI Testing & Research Institute showed that the HAp filter eliminated 99% of *Staphylococcus aureus* ATCC 6538, *Klebsiella pneumoniae* ATCC 4352, and *Escherichia coli* ATCC 25922. Bacteria reduction tests on Hap according to the requirements of the Korean Standards Association (KS K 0693 : 2011) were shown in Fig. 6.

Use of the HAp filter in a commercial water purifier

With a commercial water purifier, bacteria appeared in the water that was filtered using the control filter after 1 h and increased steadily in number. However, in water that was purified through the HAp filter installed in the purifier, bacteria were not detected for 72 h. The results of the antibacterial tests on water filtered through a water purifier installed with the HAp filter are shown in Fig. 7. Bacterial colony forming units (CFUs) over time for water filtered through Hap filters and control filters shown in Fig. 8.

Conclusions

In this study, we fabricated a water filter with HAp by mixing HAp and activated carbon [9, 10], and investigated the HAp filter's chemical and antibacterial properties. The pH and Ca^{2+} concentration of HAp-filtered water depended on the ratio of HAp and activated carbon, with both pH and Ca^{2+} concentration increasing with an increase in the amount of HAp

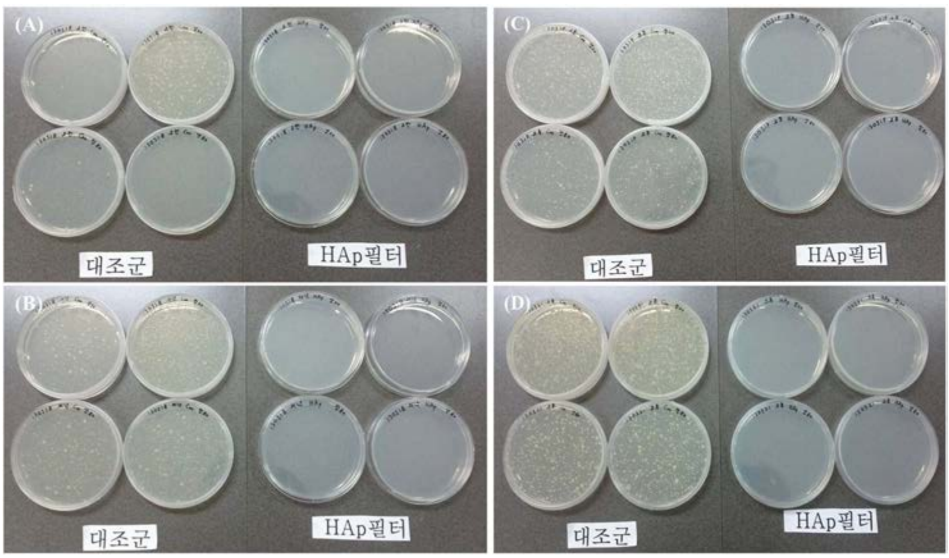

Fig. 7. Antibacterial tests (by the pour-plate method) on HAp filters installed in a water purifier: (A) 1 h, (B) 5 h, (C) 10 h, and (D) 24 h.

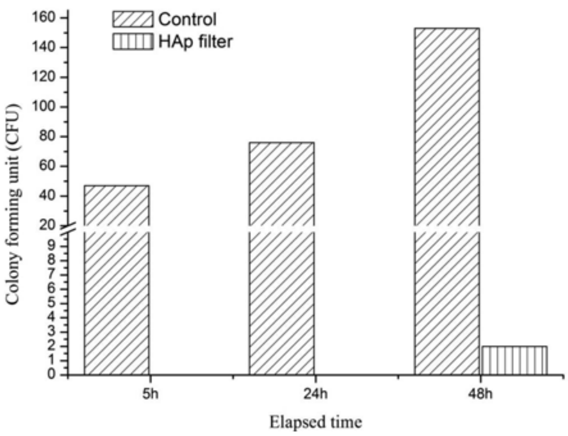

Fig. 8. Bacterial colony forming units (CFUs) over time for water filtered through HAp filters and control filters.

added. The antibacterial properties of the filter were investigated using the pour-plate method and by the FITI Testing & Research Institute. Bacteria were removed effectively by the HAp filter: 99% of bacteria were eliminated. We also confirmed the changes in pH and Ca^{2+} concentration of water that was filtered using a HAp filter installed in a commercial water purifier, and the antibacterial effects of the HAp filter installed in a commercial water purifier. In conclusion, HAp can be used to develop water filters for installation in commercial water purifiers.

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