Neither Hollow-Fibre Membrane Filters nor Activated-Charcoal Filters Remove Fluoride from Fluoridated Tap Water
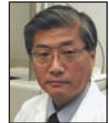
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ABSTRACT

Background and Objective: Previous reports of the reduction of fluoride concentrations in fluoridated water by domestic water treatment systems have indicated that further supplementation with fluoride is required. However, the absorption of fluoride by filters has not yet been directly identified. If these filters do not absorb fluoride, further fluoride supplementation may increase fluorosis. In this study, we determined whether filtering systems absorb fluoride ions.

Materials and Methods: We directly measured the amounts of fluoride absorbed by activated-carbon filters or hollow-fibre membrane filters using pyrohydrolysis of the filters and flow-injection analysis, the sensitivity of which is more than 100 times greater than that of conventional methods. We made fluoride solutions of pure or tap water and determined changes in fluoride concentration as a result of filtering with a fluoride electrode.

Results: Hollow-fibre membrane filters did not affect fluoride concentrations in the fluoridated water, but activated-carbon filters removed some fluoride, especially from the pure-water solution. Filtering a pure-water solution with a fluoride concentration of 0.8 mg F/L reduced the fluoride concentration until 210 L of the solution had been filtered. However, filtering a tap-water solution of 0.8 mg F/L reduced the fluoride concentration only until 8 L had been filtered. The concentration of absorbed fluoride in the filter at 10 L of filtration was 4.7 mg/kg activated carbon.

Conclusion: Further fluoride supplementation of fluoridated water should not be necessary, regardless of whether an activated-carbon or hollow-fibre membrane filter is installed on a domestic water treatment system.

Water fluoridation, a common component of public health, especially in North America, Australia and Ireland, has benefited 250 million people in over 30 countries[1-5] by providing appropriate amounts of fluoride for dental health directly through tap water.[2] However, water fluoridation must be practised with great care to prevent the excessive intake of fluoride that can occur because of concurrent use of fluoride from other sources.[6] As a consequence, treating domestic water with filters is widespread. Research studies[7-10] report that such treatment seriously reduces the fluoride concentration in drinking water and recommend that households using such filters supplement their water

with further fluoridation.[7,8] This research, however, did not verify whether filters actually absorb fluoride, nor directly detect whether they absorb fluoride.[7–10] If filters do not absorb fluoride, fluorosis may result because of excessive intake of fluoride.

In this study, we directly measured reductions in fluoride concentrations of drinking water after filtering and the amount of fluoride absorbed by the filters, using a flow-injection system after pyrohydrolysis of the filters.

Materials and Methods

Water Filters for Experiments

Simple water filters for the experiments were made with activated-carbon filters (PF-CB-S, Organo, Tokyo) and hollow-fibre membrane filters (KIF227, Organo) because these materials are most popular for the treatment of domestic water. Water (flow rate, 10 L/minute) for each filter was supplied by a pump (MDG-M2S100N, Iwaki Co Ltd, Tokyo, Japan) connected to a 100-L tank containing the test solution.

Production of Fluoride Solution

In North America, sodium silicofluoride is currently most popular for fluoridation, but because Korea has recently begun using sodium fluoride (NaF) and Japan is expected to do the same in the near future,[5] NaF (Wako Pure Chemical Industries Ltd, Tokyo, Japan) was selected for this study. Solutions of NaF in tap water (FT) and NaF in pure water (FP), each with a resistivity of 17 MΩ/cm or greater, were made by Barnstead NANO-pure (Thermo Scientific, Waltham, Mass.). Tap water with a fluoride concentration of less than 0.1 mg/L was obtained from the department of oral health at the Nippon Dental University in Tokyo, Japan. The concentration of fluoride was adjusted to create 3 solutions of fluoridated water in both tap and pure water (0.8, 5.0 and 10.0 mg/L). These solutions were then stored in a tank connected to the water filter and immediately used for the study. For each concentration, 3 independent experiments were done, and the mean values calculated.

Measurement of Fluoride-Ion Concentration of the NaF Solutions

The fluoride-ion concentrations of FP and FT solutions were measured immediately before and after filtering with a fluoride-ion-selective electrode (96-09 Orion, Thermo Electron Co., Beverly, Mass.) and a
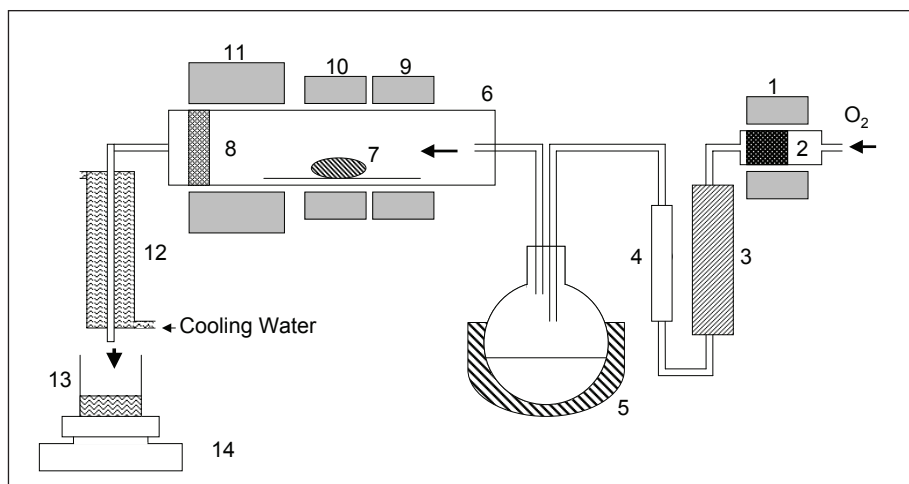

Figure 1: Fluoride-extraction system by pyrohydrolysis. A sample was placed in the middle of the thermoheater. Clean air with high humidity was carried into the thermoheater at 1050 °C. After pyrohydrolysis, the air containing the fluoride was condensed and the extract was collected in the sample bottle. 1 = heater 600 °C; 2 = cupper oxide; 3 = calcium oxide; 4 = flowmeter; 5 = boiling water; 6 = thermoheater; 7 = sample; 8 = platinum net; 9 and 10 = subheaters; 11 = main heater (1050 °C); 12 = condenser; 13 = sampling bottle; 14 = scale.

pH/ion-selective electrode meter (710A, Orion Research Inc., Boston, Mass.).

Measurement of Fluoride-Ion Concentration in the Filters

After each solution was filtered, the filters were dried at 37 °C, and the contents blended in a food processor for 3 minutes. Both the length of time required to blend the mixture completely and the food processor's ability to absorb fluoride were previously confirmed. The mixtures were divided into 1-g batches for measurement. For the analysis of the fluoride concentration, the batches were processed with a pyrohydrolysis fluoride-extraction system (FIU-1200, Daiwa Electric Industry Co. Ltd., Kyoto, Japan) (**Fig. 1**), which produced 35 mL of extract in pure water.[11–13] An extract of 0.2 mL was injected into a flow-injection analysis system (FAU-2100, Daiwa Electric Industry Co. Ltd.) (**Fig. 2**) equipped with a fluoride-ion electrode (96-09 Orion, Thermo Electron Co.) in the flow line, and the fluoride-ion concentration was measured.[11–13] The electrode was stabilized with a constant flow of buffer solution (pH 5.4, 7.5 μg F/L, 0.03 M phosphate, 0.03 M *trans*-1, 2-diaminocyclohexane-*N,N,N,N*-tetraacetic acid, monohydrate, 0.1% Triton X100) into the electrode cell at a rate of 0.5 mL/min, resulting in a detection sensitivity (0.5 mg/L) over 100 times higher than that of conventional techniques.[11–13]

Measurement of the Concentrations of Other Negative and Positive Ions

To investigate the reduction in fluoride-absorptive capacity, we examined the changes in the concentra-
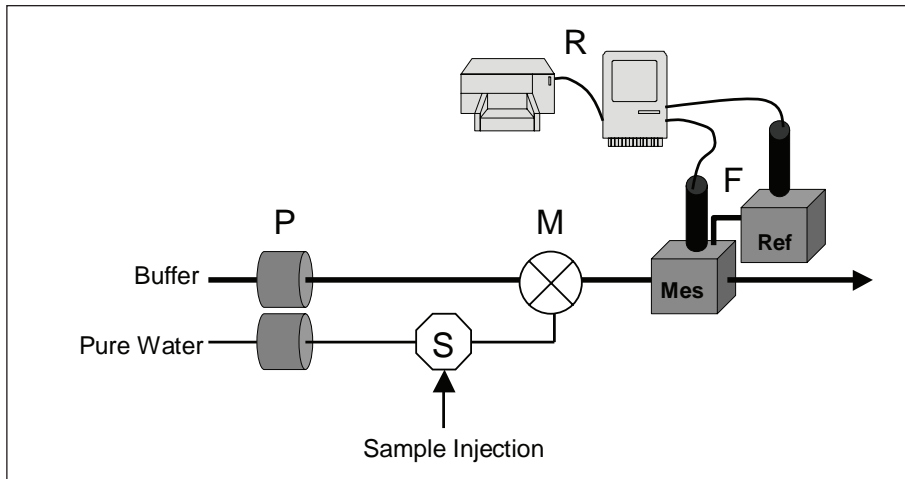
Figure 2: Flow-injection analysis. The mixing rate for both the buffer and water was 1:1. The flow rate was 0.6 mL/min for each; the total flow rate was 1.2 mL/min. A sample (0.2 mL) was injected into the sample injection port equipped with a 6-port valve and a 0.2-mL sample loop. P = pump; S = sample injection port; M = mixing coil; F = fluoride-ion-selective electrode for measuring (Mes) and reference (Ref) (Mes and Ref were connected with a salt-bridge ion-channel); R = ion meter and integrator.

tions of each ion after filtration: namely, the negative ions Cl, NO_2, Br, NO_3, PO_4 and SO_4, and the positive ions Li, NH_4, K, Mg and Ca after filtering. (We excluded Na from the determination because it was included in the carrier buffer.) For activated-carbon filters with fluoride-absorptive capacity, we measured the concentration of each ion before and after it passed through the water filter with an ion chromatograph (DX-120, Dionex Corporation, Sunnyvale, Calif.). To analyze negative ions, we used a guard column (IonPac AG4A, Dionex Corporation) in conjunction with a separation column (IonPac AS4A, Dionex Corporation) and a buffer solution of 2.7-mM sodium carbonate and 0.3-mM sodium acid carbonate at a flow rate of 1.3 mL/min at room temperature. To analyze positive ions, we used a guard column (IonPac CG12A, Dionex Corporation) and a separation column (IonPac CS12A, Dionex Corporation), in addition to a buffer fluid of 20 mM of meta-sulfonic acid at a flow rate of 1.0 mL/min at room temperature. We calculated the mean value of 3 independent measurements.

Results

Change in the Fluoride Concentration with Hollow-Fibre Membrane Filtration

Figure 3 shows the change in fluoride concentration after filtering the FP solution at initial fluoride concentrations of 0.8 mg/L, 5.0 mg/L and 10.0 mg/L with hollow-fibre membrane filters. The fluoride concentrations for each FP solution were unchanged after filtering.

Change in the Fluoride Concentration with Activated-Carbon Filters

Figure 4 shows the change in fluoride concentration after FP was filtered at initial fluoride concentrations of 0.8 mg/L, 5.0 mg/L and 10.0 mg/L with activated-carbon filters. Soon after filtration began, fluoride concentrations decreased markedly. The fluoride concentration of each solution gradually increased (**Fig. 4**). When 10 L of the 0.8-mg F/L solution was filtered, the fluoride concentration was reduced to 0.1 mg/L. When 210 L of the same 0.8-mg F/L solution had been filtered, the fluoride concentration was almost the same as it was before filtering (**Fig. 4**). Similar changes occurred in the 5.0-mg F/L and 10.0-mg F/L solutions: the fluoride concentration of the 10.0-mg /L solution matched its original concentration after 30 L or more of filtration, and the 5.0-mg F/L at 180 L or more.

Change in the Fluoride Concentration of Tap Water with Activated-Carbon Filters

Results for FT experiments at 0.8-mg F/L concentrations indicated that the activated-carbon filters used in this experiment had an absorptive capacity for volumes up to 210 L of the filtered solution. Accordingly, we examined the change in fluoride concentrations in FT solutions. After 1 L of the FT solution adjusted to 0.8 mg F/L had been filtered, the fluoride concentration was 0.4 mg/L, and the fluoride concentration increased as the volume of the filtered solution increased. When only 8 L of the solution had been filtered, the fluoride concentration was almost 0.8 mg/L (**Fig. 5**).

Absorption of the Fluoride by Activated-Carbon Filters

To confirm the absorption of fluoride by activated-carbon filters, their fluoride concentrations after the test fluids had been filtered were measured with a 0.8-mg F/L solution. The filters examined were those that had filtered the FP solutions of 10 L and 360 L, as well as the FT of 10 L and 20 L. Three independent determinations for each filter and 3 different measurements at each determination were carried out, and the average was obtained. Unprocessed filters are shown as blank. As shown in **Table 1**, 22.61 mg F/kg activated carbon was detected in the filter when 10 L of FP at 0.8 mg F/L was filtered, and 216.43 mg F/kg was detected when 360 L was filtered, suggesting absorption of most of the
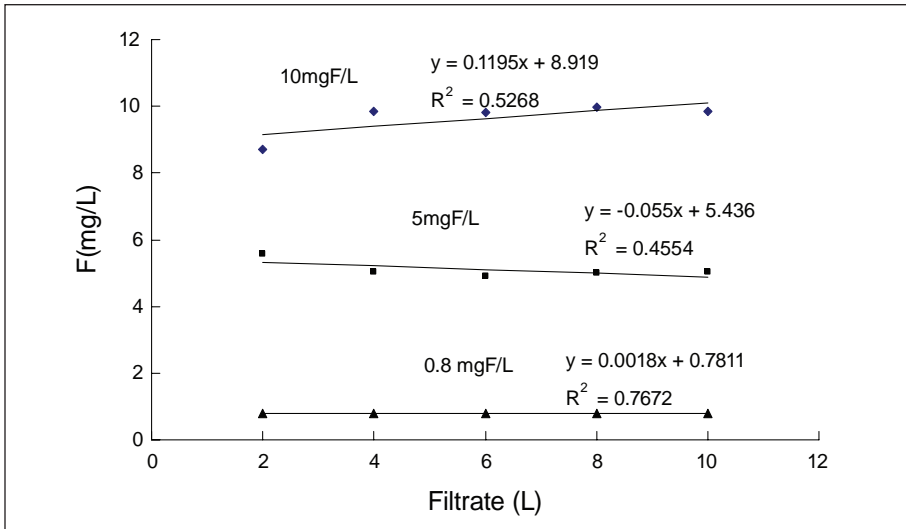
Figure 3: Change in fluoride concentrations after NaF solutions of 0.8, 5.0, and 10.0 mg F/L were filtered with hollow-fibre membrane filters.
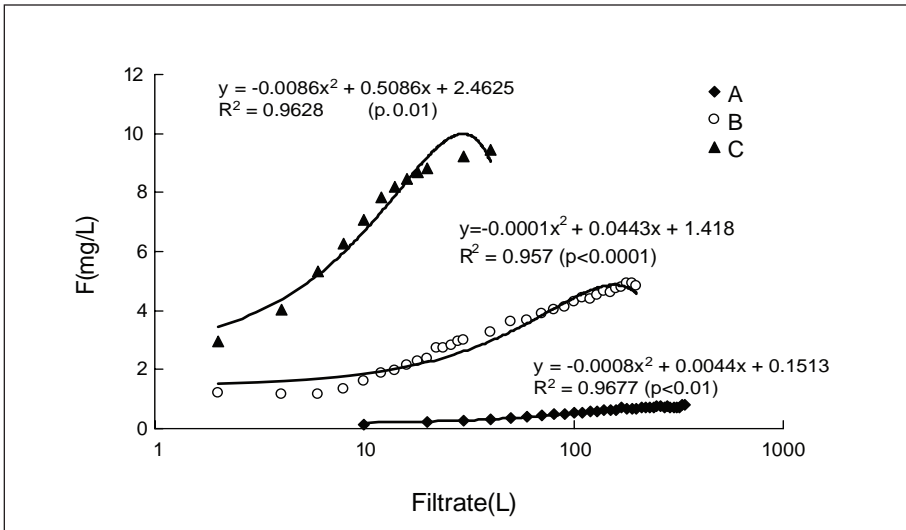

Figure 4: Change in fluoride concentrations after NaF solutions were filtered with activated-carbon filters. A = 0.8 mg F/L; B = 5.0 mg F/L; C = 10.0 mg F/L
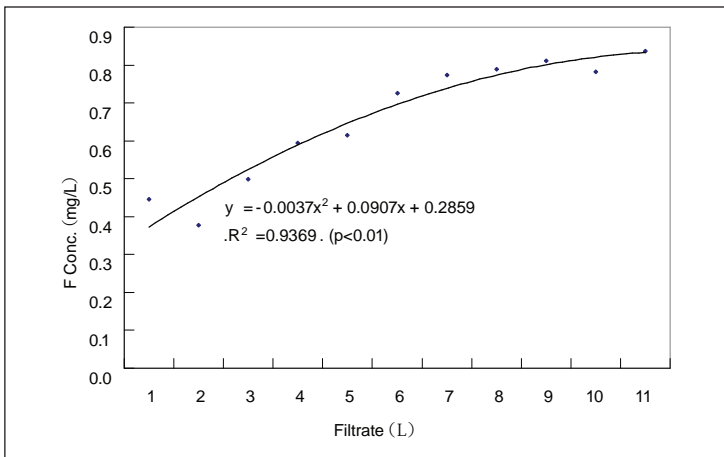

Figure 5: Change in fluoride concentrations (F Conc.) after an NaF tap-water solution adjusted to 0.8 mg F/L was filtered with activated-carbon filters.

fluoride. The concentration was 4.68 mg or 4.93 mg F/kg when 10 L or 20 L of FT at 0.8 mg F/L, respectively, was filtered.

Effect of Activated-Carbon Filters on Other Negative and Positive Ions

Because the fluoride absorptive capacity of activated-carbon filters decreased remarkably when FT solutions were used, the effects of these filters on other ions were examined. First, for 340 L of FP solution at 0.8 mg F/L filtered with activated-carbon filters, the ions shown in **Table 2** could not be detected before filtering because the solution was made with pure water. Concentrations of Cl (8.75 ppm), K (4.07 ppm), Mg (1.69 ppm) and Ca (6.91 ppm) were detected when 1 L of the solution was filtered. Concentrations of these ions decreased to 0.02 ppm, 0.21 ppm, 0.00 ppm and 0.05 ppm, respectively, after 340 L of the solution was filtered. Other ions could not be detected. Consequently, Cl, K, Mg and Ca were thought to originate from the filters (**Table 2**). Before the FT solution was filtered, concentrations of Cl (9.89 ppm), NO_3 (6.03 ppm), SO_4 (19.51 ppm), NH_4 (1.37 ppm), K (0.31 ppm), Mg (0.07 ppm) and Ca (13.07 ppm) were found. After filtration of 1 L of the solution, the concentrations of NO_3, SO_4 and NH_4 were reduced and the others, elevated: Cl, 17.69 ppm; NO_3, 1.47 ppm; SO_4, 12.84 ppm; NH_4, 0.00 ppm; K, 1.07 ppm; Mg, 0.68 ppm; Ca, 14.40 ppm. At the end of the filtration, the concentrations of NO_3 and SO_4 had increased to their original levels (6.30 ppm and 21.34 ppm, respectively); NH_4 was not detectable. The concentrations of NO_3, SO_4 and NH_4 were reduced during

Table 1 Absorption of fluoride by activated-carbon filter

Solution	F⁻ conc (mg/L)	Total volume of filtered solution (L)	F⁻ conc in the filters (µg/g)
Pure water	0.8	360	216.43
	0.8	10	22.61
Tap water	0.8	10	4.68
	0.8	20	4.93
Blank	–	–	1.24

Note: F conc. = fluoride ion concentration; Blank = fluoride ion concentration in the unused filter was determined.

Table 2 Changes in ion concentrations after filtration with activated-carbon filters

F conc. (mg/L)	Litres of filtration	Concentration of ions										
		Cl	NO₂	Br	NO₃	PO₄	SO₄	Li	NH₄	K	Mg	Ca
0.8 (PW)	340	↓	ND	ND	↓	ND	ND	ND	ND	↓	↓	↓
0.8 (TW)	10	↓	↓	ND	↓	↑	↑	↑	↓	↓	↑	↑

The concentrations of ions were determined before filtration at 1 L flow out and at the end of filtering. Changes in the average of 3 measurements are expressed as arrows (↓ = decreased; ↑ = increased). Before filtration, concentrations of all ions were undetectable in the solutions with pure water (PW). Before the solution with tap water (TW) was filtered, these concentrations (mg/L) of ions were found: Cl, 9.89; NO₃, 6.03; SO₄, 19.51; NH₄, 1.37; K, 0.31; Mg, 0.07; Ca, 13.07. Note: F conc. = fluoride concentration; ND = not detected.

filtration until 340 L or more of solution had been filtered (**Table 2**).

Discussion

Although fluoridated dentifrice and other fluoride applications are highly effective for preventing tooth decay,[14] water fluoridation is considered more beneficial for preventing tooth decay.[1] Browne and others,[6] Robinson and others,[7] and Jobson and others[15] reported that water filters negate the effects of water fluoridation, and suggested that further fluoride supplementation might be required. Some domestic water filters are reported not to absorb fluoride.[16] No consensus about the circumstances under which fluorosis may be induced when fluoride supplementations are applied in addition to water fluoridation has been reached.

Although the most scientific way to resolve this disagreement is to directly confirm whether filters themselves absorb fluoride, previous studies[6–9] have examined the change in the fluoride concentration of the water before and after filtration. This study examined not only the fluoride concentration of the filtrate, but also the filter materials' absorption of fluoride with pyrohydrolysis and supersensitive flow-injection analysis.[11–13] In this study, the filter materials hollow-fibre membrane and activated carbon were examined. Because reverse osmosis is capable of removing up to 70% or more of fluoride[10] and is used for desalination, we had no doubts about the ability of reverse osmosis to remove fluoride. However, because reverse osmosis is not used in popular domestic water filters, we excluded it from this investigation.

Hollow-fibre membrane filters used to treat water with fluoride concentrations of 0.8–10.0 mg/L do not change the fluoride concentration of the water, which implies that domestic water systems equipped with hollow-fibre membrane filters do not affect the fluoride concentration of water, as previously reported.[8]

Activated charcoal has a large surface area and a strong ability to absorb various substances. Bone charcoal, one form of activated charcoal, is mainly used to remove fluoride from water with high fluoride concentrations.[17,18] The activated-carbon filters used in this study were filled with granular coconut-shell charcoal. When they were used to filter NaF solutions with fluoride concentrations ranging from 0.8 to 10.0 mg/L, the fluoride concentrations of all test solutions decreased. Based on our result that the amount of fluoride absorbed by activated charcoal increased with the fluoride concentration or the volume of filtered solutions, activated-carbon filters were confirmed to absorb fluoride. Nevertheless, little absorption was detected in this study after 210 L of the solution was filtered. In the tests involving tap water to which NaF had been added, the absorptive capacity disappeared when as little as 8 L of the solution was filtered. Although activated-carbon filters are able to absorb fluoride to some extent, their effectiveness was extremely limited. Brown and Aaron[8] reported an 81% reduction in fluoride concentration in the filtrate of an activated-charcoal filter. However, because they did not clarify the amount of water filtered, the reduction of fluoride concentrations in their study may have been observed in the low amount of filtrate. No report demonstrates

the fluoride-absorptive capacity of the filter materials. Because all studies examined the plausible absorptive capacity indirectly, we determined the fluoride concentration bound to the filters in this study.[7–10]

Determining a very low concentration of fluoride in a solid compound, such as filter material, is difficult. Such fluoride concentrations must be extracted in water and are so low that they are not detectable by conventional means. Consequently, we used pyrohydrolysis to extract the fluoride from activated carbon, followed by flow-injection analysis with a fluoride-ion-selective electrode.[11–13] Itai and his group[11–13] demonstrated that the constant flow of the buffer used in this study keeps contact with the surface of the electrode, increasing its sensitivity by a factor of more than 100. These procedures would be very effective for fluoride research in the dental field.

On investigating why fluoride-absorptive capacity was reduced by examining the changes in the concentrations of each ion after filtration, we found that only NO_3, SO_4 and NH_4 ions were reduced by activated-carbon filters. It is not clear whether ions other than fluoride affected the reduction in the fluoride-absorptive capacity of the activated carbon filters.

Activated-carbon filters had a low absorptive capacity for fluoride ions and the absorptive capacity of coconut-shell charcoal in domestic water filters for fluoride ions differs from that of activated bone charcoal, possibly because the component of bone charcoal is hydroxylapatite, which imparts a high fluoride-absorptive capacity.[17,18]
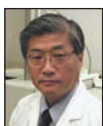
Conclusion

Hollow-fibre membrane filters or activated-carbon filters used for domestic water filtration preserve water fluoridation and additional fluoride supplementations should not be necessary.[19,20] We recommend that dentists warn people whose drinking water contains more than 1.5 mg/L fluoride that their children are at risk of developing fluorosis and that the filters studied in this paper are useless for removing fluoride. ❧

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The authors have no declared financial interests in any company manufacturing the types of products mentioned in this article.

This article has been peer reviewed.

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