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Clogging and Gel-Layer Formation during Membrane Filtration and Its Effect on Analytical Data

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Clogging and gel-layer formation during membrane filtration affect the concentration of ions in the filtrate as well as the concentration of suspended solids. The flow rate analysis and the observation of the filter surface with a scanning electron microscope show that a gel-layer is formed subsequently after the clogging. Humic acids, fulvic acids, metal hydroxides, and soft particles dispersed in natural waters cause the clogging and hence the gel-layer formation. Cross-flow filtration decreases the rate of the clogging and the gel-layer formation and gives little rise to the filtration effects on analytical results.

Membrane filters have been commonly used to separate suspended solids from natural waters.[1,2] However, it is known that the filtration by membrane filters seriously affect the analytical results in the following ways; contamination from and/or adsorption on a membrane filter; sieve effect, that is, partial permeation of the solute depending on the ratio of the pore diameter to the particle diameter; clogging and gel-layer formation on the filter.

The amounts of impurities in membrane filters,[3–5] variation of impurity levels[6] and elutions of total organic carbon(TOC), chemical oxygen demand (COD), NO_3^- from membrane filters[7] have been studied in detail. Furthermore the physical and physicochemical properties of the membrane, such as the sieve effect and the gel-layer formation on the filter, are important in relevance to filtration,[8,9] ultrafiltration,[10] and reverse osmosis.[11] However, little attention has been paid to the latter problems until now.

Seldon has reported on the size separation of marine seston by membrane filters.[12] Danielsson has studied the influence of filtration on the determined values of the colloid contents in a natural sample as a function of the sample volumes treated,[13] and Laxen et al. have reported that screen filters provide accurate size fractionation, as long as the filter is not allowed to clog.[14] Errede et al. have studied the effect of the surface modification on the flow rate of water.[15]

In this paper, the mechanism of the clogging and the gel-layer formation were studied on filtration of natural waters by various membrane filters. The possible materials which may cause the clogging and then form the gel-layer are also discussed. Cross-flow filtration was tried to minimize the influence of the membrane filtration on the analytical results.

Experimental

General Procedure for Filtration. The filters used in this study were Nuclepore 47 mm diameter filters of 0.10, 0.40, and 1.0 μm pore size (N010CPR04700, N040CPR04700, and N100CPR04700, respectively, Nuclepore Corp.) and Millipore 47 mm diameter filters of 0.45 μm pore size (HAWP04700, Millipore Corp.). A membrane filter set in a holder (FH047PL001101, Nuclepore Corp.) was washed with 200 cm³ of deionized water and then a certain volume of sample solution was filtered under a reduced pressure of 60 cm Hg (1 cm Hg=1333.22 Pa) using a handy aspirator (WP-45, Yamato Sci., Corp.). An apparatus used for cross-flow filtration is shown in Fig. 1. It was handmade using acrylic resin boards and 3 mm-thick silicone rubber sheets. For trace analysis, Teflon sheets should be used instead of the silicone rubber sheets. The sample solution was circulated and flowed on the membrane filter with a pump at a rate of 15 dm³ min⁻¹.

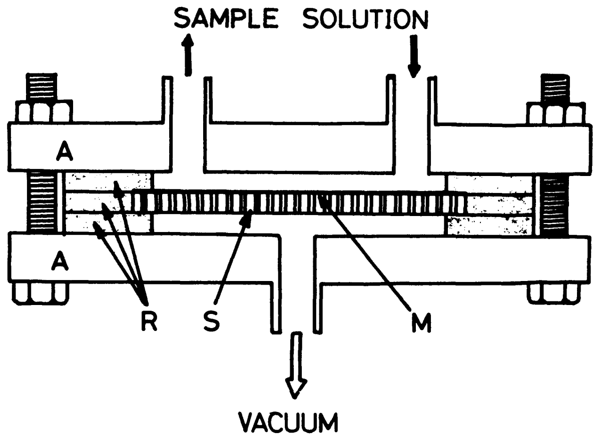

Fig. 1. Apparatus of cross-flow filtration: A, acrylic resin frame; M, membrane filter; R, silicone rubber sheet; S, membrane filter support.

Samples. The sample solutions used in this filtration experiment were river waters, a carbon black dispersion, a humic acid solution, a fulvic acid solution, and a sulfuric acid extract from a river sediment.

The river waters were sampled in 1984 and 1985 at the Kawamukoh bridge on the Tsurumi river† in Yokohama.

The carbon black used was Thermax (Thermatomic Carbon Company), whose particle size ranges from 0.1 to 1.0 μm and the maximum was between 0.4 to 0.5 μm. The

† The Tsurumi river flows through urban regions of both Yokohama city and Kawasaki city; the total length of the river is 42.3 km, and much domestic sewage discharges into it.

surface of the carbon black particles was oxidized by H_2O_2 and a definite amount was dispersed in water by shaking in a ultrasonic bath just before the filtration.

The sediment was collected at the same sampling location. It was dried in an oven 110 °C and milled to pass through a 40 mesh screen. A 14 g sample of the dried sediment was boiled with 600 cm^3 of 0.5% NaOH solution for 30 min and centrifuged at 2000 min^{-1} for 20 min. To a 500 cm^3 portion of the supernatant, 5.0 cm^3 of concentrated H_2SO_4 was added. The solution was stirred vigorously and filtered through a Whatman glass filter GC/D. The filtrate was diluted 2-fold with pure water and used as a fulvic acid solution.[16] The precipitate on the filter was dissolved throughly with 500 cm^3 of 0.1% NaOH and the filtrate diluted 2-fold and used as a humic acid solution.[16] Another 14 g of the dried sediment was dispersed in 600 cm^3 of 0.5 mol dm^{-3} H_2SO_4 and boiled for 30 min. When cooled, the sample was centrifuged at 2000 min^{-1} for 20 min. The supernatant was diluted 2-fold and used as a sulfuric acid extract, containing much metal ions, for example, ca. 100 ppm of iron.

Detemination of Metal Ion Concentrations and Suspended Solids Contents. The metal ions in the filtrate were determined by a flame and/or flameless atomic absorption spectrophotometer (Varian AA-1275). The contents of suspended solids were determined from the difference of the weights of the membrane filter dried at 60 °C for 2 h before and after the filtration.

Observation of Membrane Surface. The surface were observed by a scanning electron microscope (JSM-35C SEM, Japan Electron Optics Laboratory Corp.) before and after the filtration. The samples were imaged with gold in vacuo.

Results and Discussion

Effect of Filtration on Analytical Results. The concentrations of metal ions in the river water sample were measured by varying the sample volume treated on one filter. It was reported by Danielsson[13] that the concentrations of heavy metal ions such as iron decreased with the increase of the volume. While, the concentrations of alkaline and alkaline earth metal ions such as sodium and calcium did not change with the increase of the volume.

By using the sample solutions, the concentration of suspended solids was examined similarly, and it was found that the amount of solids trapped on the filter varied depending on the properties of the suspended solids. Figure 2 shows the change of the suspended solids concentration against the sample volume treated. The concentrations of suspended solids in a river water sample apparently increase with the volume, but that of a carbon black dispersion in pure water remains constant as would normally be expected. The values determined by Millipore filters were different from those determined by Nuclepore filters because of the difference of the filter structures between Millipore and Nuclepore filters.[14]

Variation of Rate of Filtration. The membrane filtration influences the values of metal ions and suspended solids determines because of clogging and gel-layer formation. To clarify the mechanism of the clogging and the gel-layer formation, the following experiments were carried out: The filtration rates were measured on various types of membrane filters, the electron microscopic images of the membrane surface were compared before and after the filtration, and the permeation properties of natural waters through the filters were compared with those of the synthesized solutions containing certain components of natural waters.

A flow rate through a filter decreases on increasing the volume of the filtrate as is shown in Figs. 3(a) and

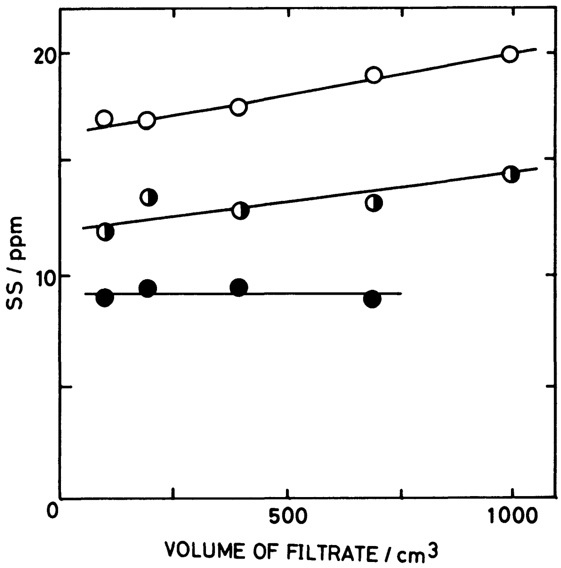

Fig. 2. Effect of volume of filtrate on measured value of suspended solids concentration: membrane filter, Nuclepore filter (0.40 μm, ●, ◑) and Millipore filter (0.45 μm, ○); sample, river water (◑, ○) and carbon black dispersion (●).

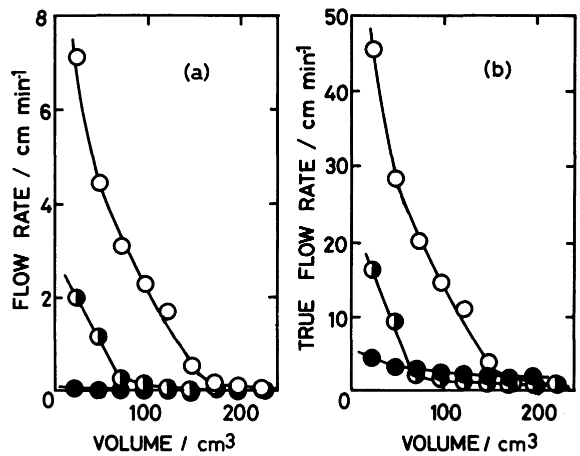

Fig. 3. (a) Flow rate vs. volume of filtrate and (b) true flow rate vs. volume of filtrate: membrane filter, Nuclepore filter; ○, 1.0 μm pore size; ◑, 0.40 μm pore size; ●, 0.10 μm pore size; sample, river water.

3(b). "Flow rates" here are defined as the volumes of filtrate obtained in unit time through unit filter area, and "true flow rates" are those obtained in unit time through unit pore area on the filter. Based on the pore density of the filter:[17] 2×10^7, 1×10^8, and $3\times10^8\,cm^{-2}$ for 1.0, 0.4, and 0.1 μm pore size filter, respectively, the ratios of the pore area to the filter area are calculated to be 16, 13, and 2.4%, respectively. In the initial period, "true flow rates" through the larger pores were faster than those through the smaller pores and this was parallel with the case of the "flow rates." As the volume of the filtrate increased, the former rate became slower than the latter. That is, at an early stage of filtration the total area of the filter pores controlled the rate, but later, the pore area remaining unclogged or unshielded by the gel-layer began to control the rate. This can be described quantitatively as follows.

It has been known that in the cake filtration process a linear relationship exists between the ratio of the filtration time to the volume of filtrate, t/V, and the volume, V.

In the standard blocking process a linear relationship also holds between t/V and the filtration time, t.[18–19] These relations can be expressed in Eqs. 1 and 2 for a given constant pressure,

$$t/V = K_C/2 \times V + 1/Q_C \quad (1)$$

$$t/V = K_S/2 \times t + 1/Q_S \quad (2)$$

where K_c, K_s, Q_c, and Q_s are constants dependent on the filter structure and the solution properties. In Fig. 4, the plots of t/V vs. V and t/V vs. t are shown for membrane filters having different pore sizes. It can be seen from the Figure that there are two processes in the filtration. The one, cooresponding to the linear relation of $t/V-t$, is observed in the early stage of filtration and is due to the development of clogging. The other corresponding to the linear relation of $t/V-V$, is due to a gel-layer formation on the surface of the membrane filter, which occurs subsequently after the clogging. As shown by curves in Fig. 4, the smaller the pore size, the earlier the gel-layer formation begins. Comparing this result with that of the filtration effect on determined values, the filtration does not have much affect on the values during the clogging process.

SEM Images of Filter Surface. The clogging and the formation of gel-layer can be visualized by the SEM technique. Figure 5(a) shows the surface of a Nuclepore filter (0.4 μm) washed with pure water running through it at $25\,cm\,min^{-1}$, and Fig. 5(b) shows the surface of the same membrane filter but filtrated with $20\,cm^3$ river water. The flow rate of the river water was calculated as $2.5\,cm\,min^{-1}$, the clogging of pores is clearly observed but not the gel-layer. Figure 5(c) is the surface of the membrane filter

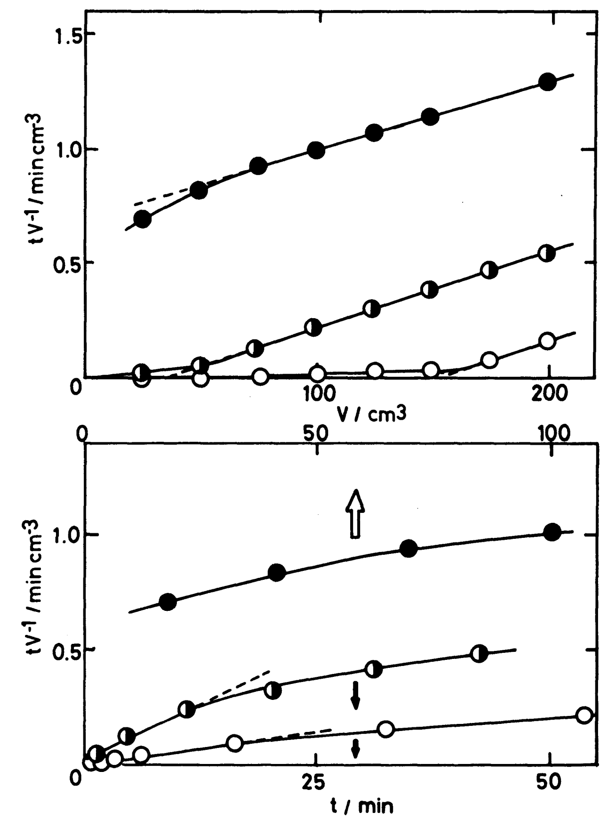

Fig. 4. t/V vs. volume of filtrate, V and t/V vs. filtration time, t: membrane filter, Nuclepore filter; ○, 1.0 μm pore size; ◑, 0.40 μm pore size; ●, 0.10 μm pore size; sample, river water.

after the filtration of $40\,cm^3$ river water with the rate of $0.41\,cm\,min^{-1}$, the whole surface of the filter is seen to be covered with a gel-layer, and no pores are observed.

Comparison of Permeabilities of Some Components in Natural Waters. In river waters, there are many kinds of colloids and particles which may cause clogging and gel-layer formation, such as humic acids, fulvic acids, metal hydroxides, bacteria suspended sediments, and so on. For the investigation of the materials which caused the clogging and the gel-layer on filters, the river water samples and the solutions of some major components of river waters, a fulvic acid, a humic acid, and surfuric acid extract were filterd at various pH and their filtration rates and suspended solids contents were compared. The pH of the samples was adjusted with HNO_3 and NaOH, and $100\,cm^3$ aliquots were filtered. The mean flow rates and the concentrations of suspended solids are shown in Fig. 6.

In the case of the river water, the flow rate was high when the pH was over 10 or under 2 and minimum in the range of pH 2 to 3. On the other hand, the suspended solids concentration was high when the pH was over 10 and low when the pH was under 2. The pH dependence of flow rate and the suspended solids

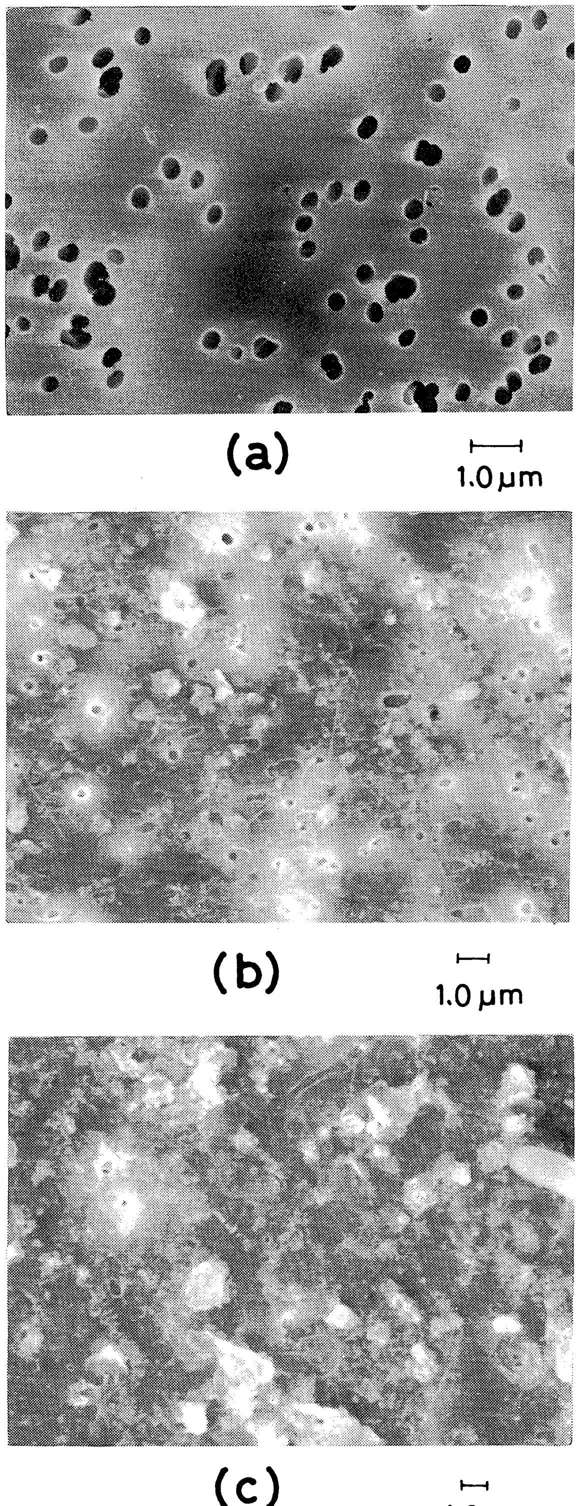

Fig. 5. Observation by scanning electron microscope on surface of Nuclepore filter. (a) Before filtration. (b) After filtration of 20 cm^3 river water. (c) After filtration of 40 cm^3 river water: membrane filter, Nuclepore filter (0.4 μm).

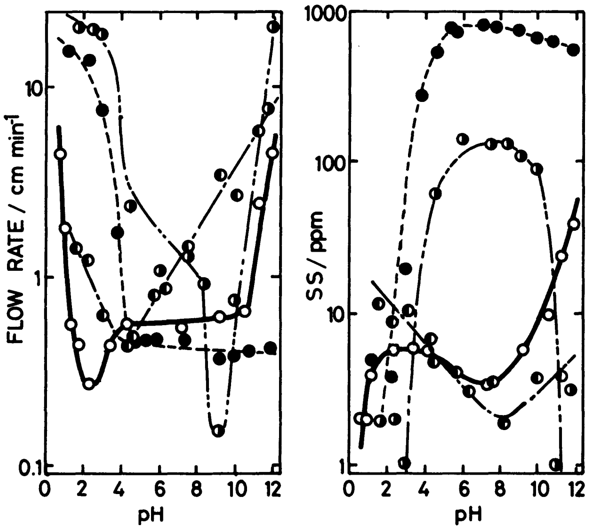

Fig. 6. Flow rate and suspended solids concentration, SS vs. pH: membrane filter, Nuclepore filter (0.40 μm); ○, river water; ◐, humic acid solution; ◑, fulvic acid solution; ●, acid extracted solution; volume of each solution, 100 cm^3.

concentration of the river water were not the same as those of the solutions of the fulvic acid, the humic acid, and the sulfuric acid extract. However some points were commonly observed in them; the minimum flow rate and minimum suspended solids concentration in intermediated pH range for the humic acid; the high flow late and the low suspended solids concentration in low pH range for the fulvic acid and the sulfuric acid extract.

These pH dependences are due to the change of the surface charge of the colloids in the solutions.[20] In a high pH range, they are negatively charged, whereas they are positively charged in a low pH range. The filtration rates are high at low or high pH, because the causing materials in the river water are highly charged and repel each other at the pH and a gel-layer with loose structure is formed on the filter. The high concentration of suspended solids at high pH is due to the precipitation of metal hydroxide. In the intermediate pH range, the charge on the colloids became low and they coagulate at their isoelectric points. Then, a layer with high density was formed on the filter as a result of van der Waals forces of attraction and the filtration rate was low.[21] The flow rate was constant in a wide pH range, because there are many kinds of materials causing the clogging and the gel-layer and their isoelectric points vary widely. It is also reported that humic acids and fulvic acids are coagulated with polyvalent metal ions in a neutral pH range,[22] while iron by itself is coagulated mostly at pH 6.5.[11]

Consequently, in the filtration of river waters, humic acids, fulvic acids, and metal ions or

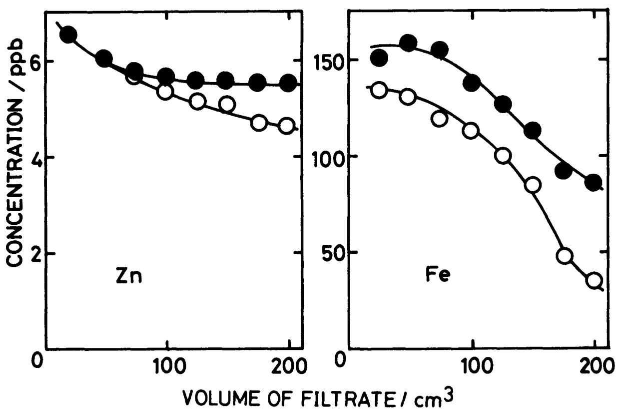

Fig. 7. Concentration change with volume of filtrate: Membrane filter, Nuclepore filter (0.40 μm); O, usual filtration; ●, cross-flow filtration; sample, river water.

hydroxides cause the clogging and the gel-layer formation independently or in combination with each other. Furthermore, as it is known that soft particles readily plug the pores of the membrane filter,[23] soft and fine particles dispersed in river waters such as bacteria also cause clogging and gel-layer formation. The pH range of 2 to 3 where the flow rate of the river water was minimum may be related to the isoelectric points of most of the bacteria and colloidal silica particles (pH 2 to 3 and pH 2, respectively[20]) which are also major components of river waters.

The effect of the ionic strength on the filtration behavior was also studied by adding NaCl to river waters. The flow rate decreased and the suspended solids concentration increased gradually with NaCl concentration.

Cross-Flow Filtration. Cross-flow filtration is commonly applied to prevent gel-layer formation in reverse osmosis and ultrafiltration. For the improvement of the filtration behaviors, the cross-flow filtration was developed. The apparent changes of solute concentration with the volume of filtrate was observed on cross-flow filtration, and the results were compared with those of the usual filtration. As shown in Fig. 7, the decrease of the concentrations in the cross-flow filtration was less significant than in the usual filtration.

Figure 8 shows the plots of t/V vs. t and V observed in the cross-flow filtration. As is obvious from the comparison with those of the usual filtration, the filtration is much facilitated in the cross-flow filtration because the clogging and the gel-layer formation grows much more slowly. By cross-flow filtration, a large quantity of sample solution can be treated without a significant decrease of the filtration rate and a large deposition of metal hydroxides on the filter. To further improve filtration, more filter material is necessary to weaken the interaction between the colloidal particles and the filter matrix.

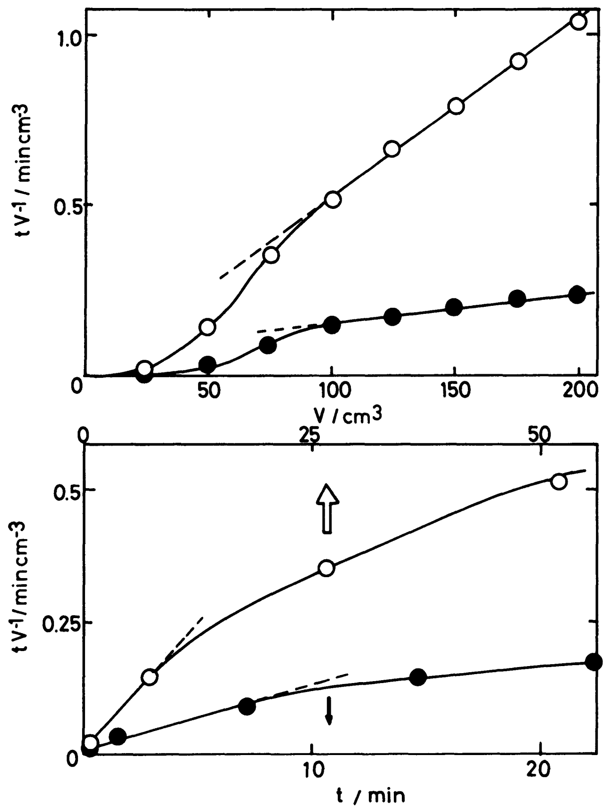

Fig. 8. Relationships between t/V and V, and t/V and t in usual filtration and in cross-flow filtration: Membrane filter, Nuclepore filter (0.40 μm); O, usual filtration; ●, cross-flow filtration; sample, river water.

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