Fouling performance in the filtration of water containing humic acid and/or kaolin with microporous membrane

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Abstract Acceleration tests were done using the small-scale microporous membrane (MF) module to predict the increase in transmembrane pressure at the constant flow rate dead-end filtration in a pilot plant for treating the river water or dam water. The kaolin suspension, solution of humic acid and the mixture of kaolin and humic acid were used as feed water in the acceleration tests. The conventional equations of medium blocking filtration were applied to predict the pressure increase for both pilot plant tests and small-scale ones. The experimental results are summarized as follows:

(1) The pilot plant tests: The time course of transmembrane pressure was expressed by the complete blocking filtration equation or the standard one when the unstable time at the beginning of operation was excluded.

(2) The acceleration tests using small-scale membrane module:

- (a) No increase in transmembrane pressure was observed when the kaolin suspension and the bentonite one were used as feed water,
- (b) The increasing rate of transmembrane pressure was lowered by the addition of coagulant into the humic acid solution,
- (c) The humic acid had a great influence on the increasing rate of transmembrane pressure in the filtration of water containing kaolin or no kaolin and
- (d) Similar curves of filtration time vs. transmembrane pressure were obtained in the acceleration tests as were obtained in pilot plant tests.

Keywords Microfiltration; kaolin; bentonite; humic acid; complete blocking filtration; standard blocking filtration; cake filtration

Introduction

The Japanese Ministry of Health and Welfare started the MAC21 Project (Membrane Aqua Century 21) in the fiscal year of 1991 and the New MAC21 Project (New Membrane Aqua Century 21) in the fiscal year of 1994 in order to apply membrane filtration technology to small drinking water works in Japan (Ito, 1995; Takechi *et al.*, 1995). In November 1994, "The Guidelines on Application of Membrane System to Small-scale Drinking Water Treatment Plants" was published based on the results of the demonstration experiment, conducted in the projects. In recent years, a lot of membrane filtration plants have been installed for small drinking water works, and a larger plant of 10,000 m^3/day scale is also planned.

However, one of the undesirable aspects in membrane filtration is an increase in transmembrane pressure caused by fouling. And chemical cleaning will be required in these plants when the transmembrane pressure reaches a certain level by a fouling. When the transmembrane pressure rapidly increases, an extra operation cost is required with the chemical cleaning expense and the personnel expenses. Therefore, the prediction of fouling performance is important to control the filtration condition and save the operation cost.

In this study, the acceleration tests were done using the small-scale microporous membrane(MF) module and the artificial feed water in order to predict the curves of filtration

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time versus transmembrane pressure. And the filtration models to express the curves were discussed.

Experimental

Experimental apparatus

The schematic flow diagrams of pilot plants A and B and the small-scale test apparatus are shown in Figure1. In all the experimental runs the dead-end filtration system with air backwashing was adopted. In pilot plants A and B, the backwashing drainage and the filtrate were discharged out of the system. And in the small-scale test apparatus two kinds of drainage treatment systems were taken. One was that both backwashing drainage and filtrate were discharged out of the system and another was that only backwashing drainage was discharged and filtrate was returned into the feed tank.

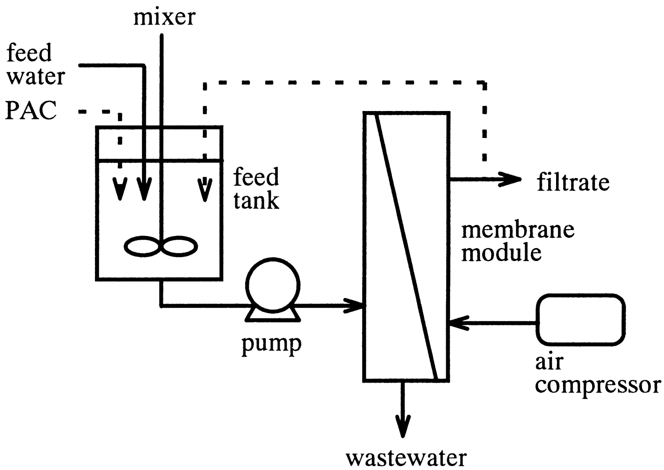

Figure 1 Schematic flow diagram of the microporous membrane pilot plants and the small-scale membrane apparatus

Table 1 Specifications and operational conditions of the microporous membrane plants

Specifications		
Pore size	0.2 µm	
Material	Polypropylene	
Type	Hollow fibre	
Total area	3 m^2 (1m^2×3 module)	Pilot plant A
	30 m^2 (15 m^2×2 module)	Pilot plant B
	0.1 m^2 (0.1 m^2×1 module)	Small-scale apparatus
Operational condition		
Filtration mode	Dead-end filtration	
Mode of operation	Constant flow filtration	
Flux	1.44 m^3/m^2/day	Pilot plant A
	1.3 m^3/m^2/day	Pilot plant B
	1.2 m^3/m^2/day	Small-scale apparatus
Physical washing by	Compressed air and feed water	
Interval of back washing	30 minutes	

Table 2 Qualities of the feed water and filtrate of pilot plant A (average: n=55) and pilot plant B (average: n=11)

		Pilot plant A		Pilot plant B	
		Feed water	Filtrate	Feed water	Filtrate
Turbidity	(NTU)	10.7	0	7	<1
Colour	(mg/l)	11	4.1	11	2
pH	(–)	7.8	8.1	7.4	7.5
$KMnO_4$ consumption	(mg/l)	5.8	4.0	4.4	2.4

Table 3 Media blocking filtration equations

Complete blocking	Standard blocking	Cake filtration
$\frac{p_0}{p} = 1 - \frac{K_b v}{u_0}$	$\left(\frac{p_0}{p}\right)^2 = 1 - \frac{K_s v}{2}$	$\frac{p_0}{p} = K_c u_0 v + 1$

K_b, K_s, K_c: filtration coefficient
p: filtration pressure
p_0: initial filtration pressure
v: accumulated filtrate per unit membrane area
u_0: flux

Membrane module

Table 1 shows the specifications of microporous membrane and operational conditions used in pilot plants A and B and small-scale test apparatus. The membrane was hollow fibers with pore size of 0.2 μm and made of polypropylene, which were bundled and covered by a casing. Feed water flowed from the outside into the inside of hollow fibers. The filtration system was operated at a constant flow rate filtration. In order to keep the filtration flux, physical cleaning by air backwashing was performed periodically, where the compressed air at about 600 kPa was forced to supply from the inside to the outside of hollow fibers after the inlet valve of feed water was closed (Miura *et al.*, 1995).

Feed water

Dam water was used as feed water in pilot plant A, and river water in pilot plant B. The bentonite (Wako Chemical) suspension, the kaolin (particle size 0.1–4 μm, Sigma-Aldrich) suspension with/without humic acid (sodium salt, Sigma-Aldrich) and humic acid solution were used as artificial feed water instead of actual feed water in the small-scale apparatus. And polyaluminum chloride (PAC, 10–11 wt% as Al_2O_3, Sumitomo Chemical) was used as the coagulant.

Results and discussion

Fouling performance in pilot plants A and B

The change in transmembrane pressure of pilot plants A and B are shown in Figures 2 and 3, respectively. And the qualities of feed water and filtrate for both pilot plant tests are also shown in Table 2. Although the feed water contained color materials originated from humic acid, the color value in the filtrate was reduced to a lower one in both cases by membrane treatment. The transmembrane pressure, P, increased gradually with the filtration time, t, probably owing to the accumulation of color materials. It was tried to express the experimental curves of t versus. P by the conventional filtration model of medium blocking filtration and cake using the equations shown in Table 3 (Hermans *et al.*, 1936; Grace, 1956;

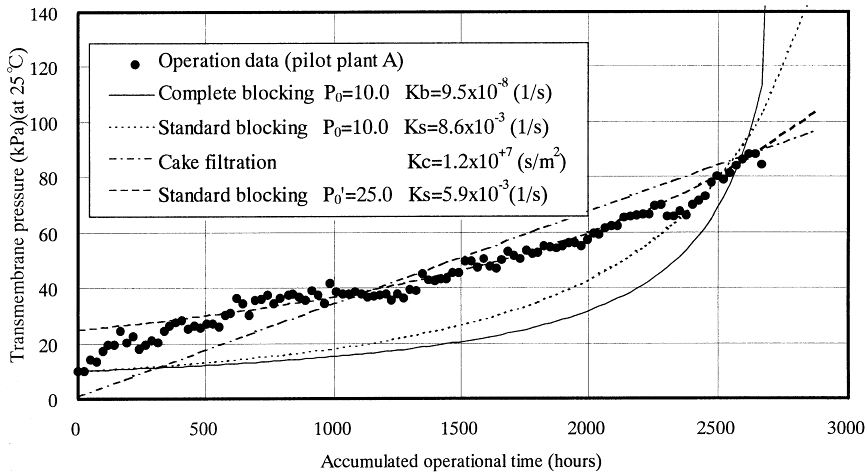

Figure 2 Changes in transmembrane pressure using dam water at pilot plant A and curve fitting by media blocking filtration equations

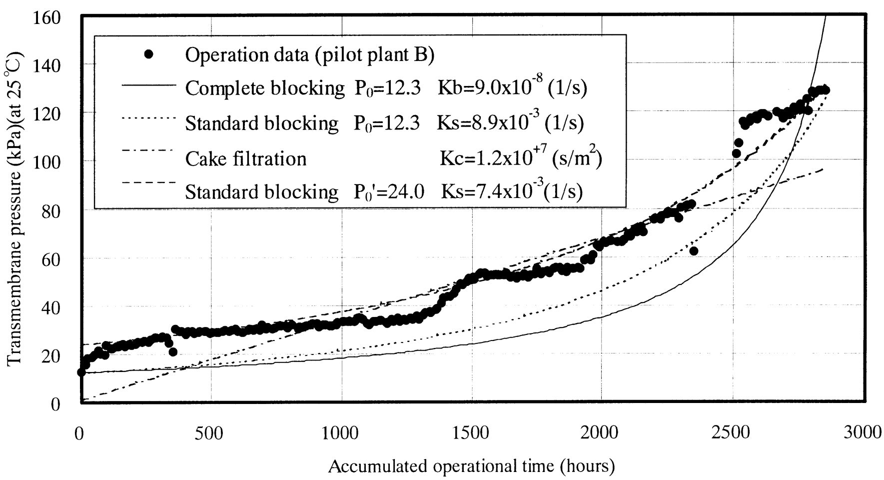

Figure 3 Changes in transmembrane pressure using river water at pilot plant B and curve fitting by media blocking filtration equations

Shirato *et al.*, 1979; Hermia, 1982; Iritani *et al.*, 1991; *Chem. Eng. Handbook Jpn.*, 1999). Two types of calculated curves were shown together in Figures 2 and 3. One curve is drawn by using the experimental value of P_0 at t=0 (i.e. P_0=10 kPa for pilot plant A and 12.3 kPa for plant B) as an initial filtration pressure P_0, and the other curve was drawn by using the extrapolated value of P'_0 at t=0 (P'_0=25 kPa for plant A and 24 kPa for plant B) from the stable filtration stage as was shown in Figure 4. Though the reason for the appearance of unstable stage (i.e. initial rapid increase in P) is not well explained, it would depend on the surface condition of the membrane. The calculated curves using the standard blocking filtration model and P'_0 are well fitted the experimental ones in both cases. And the calculated curves using the complete one and P'_0 are well fitted to the experimental ones in both cases, too. Both the standard blocking model and the complete one can express the steep increase in P of most of curves of t versus. P. However, the fouling materials, especially soluble ones, enter the membrane pore and are expected to be trapped inside the pore. In such a situation the standard one is more probable. And the steepness of the calculated curve using the complete one increases more rapidly at the end of curve. The complete one could not be applied

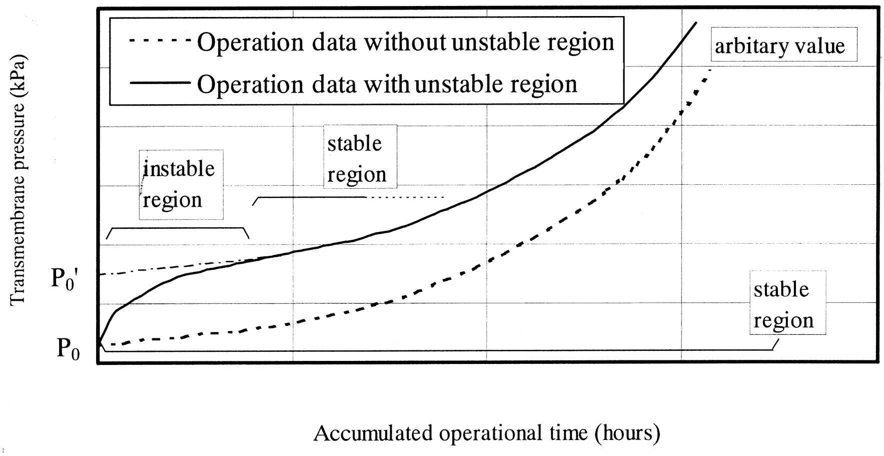

Figure 4 Schematic curves of change in transmembrane pressure with/without unstable region

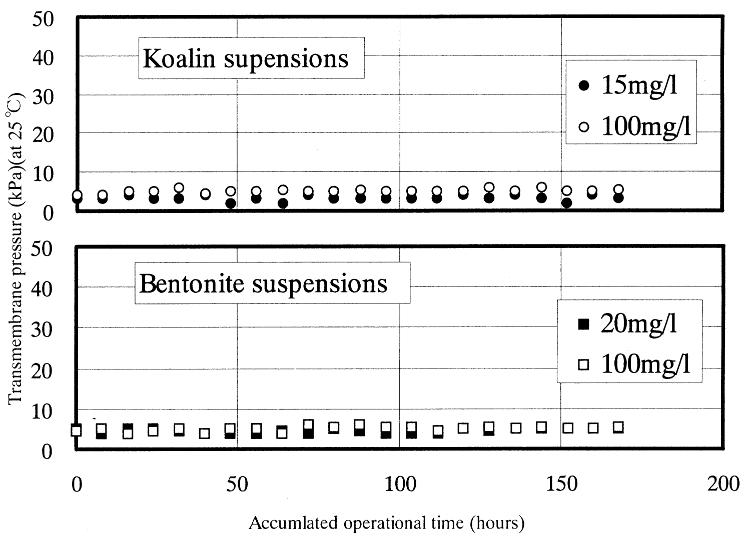

Figure 5 Changes in transmembrane pressure with filtration time using kaolin suspensions and bentonite suspensions

to the changes in P when the solution is of high concentration similar to the acceleration tests described later in this study. For these reasons mentioned above, the standard one was only applied. The steepness of increase in P is evaluated by the value of filtration constant, K_S. That is, K_S becomes larger, the transmembrane pressure increases more rapidly.

Fouling performance in the small-scale test apparatus

Fouling performance in the filtration of kaolin or bentonite suspension. The change in P of kaolin suspension (kaolin concentration:15 mg/l, 100 mg/l) or bentonite suspension (bentonite concentration: 20 mg/l, 100 mg/l) with the filtration time is shown in Figure 5. No increase in P was observed when these particles are suspended. And the rejection rate of kaolin or bentonite was 100%.

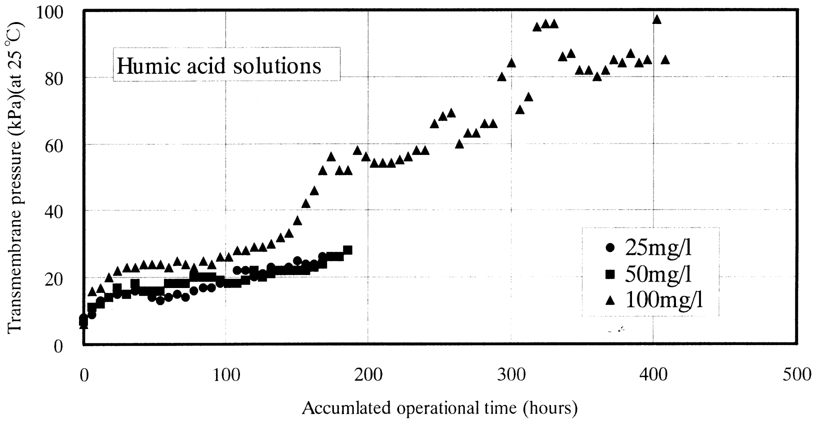

Figure 6 Changes in transmembrane pressure using humic acid solutions

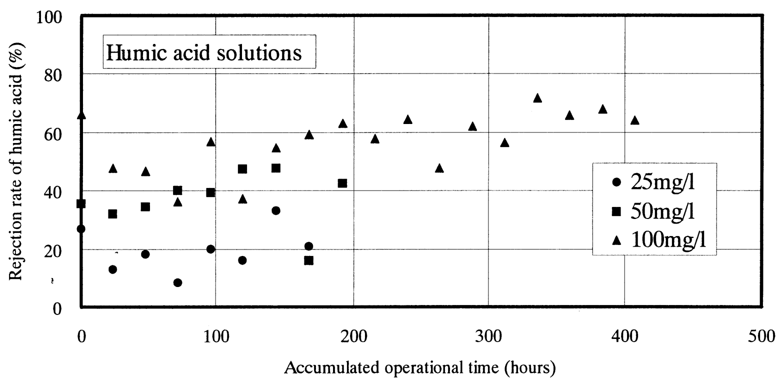

Figure 7 Changes in rejection rate of humic acid using humic acid solutions

Fouling performance in the filtration of humic acid solution. The effect of humic acid concentration (25 mg/l, 50 mg/l, 100 mg/l) on the change in P with the filtration time is shown in Figure 6. In the humic acid solution the transmembrane pressure increased with the increase in humic acid concentration. The increasing rate of P was much larger than the case in pilot plant A or B. This rapid increase is due to the excess concentration of humic acid. And the rejection rate of humic acid with the filtration time is shown in Figure 7. The rejection rate of humic acid at the concentrations of 25 mg/l, 50 mg/l and 100 mg/l were in the range of 10–30%, 30–50% and 40–70%, respectively. It was seen that the rejection rate was roughly proportional to the humic acid concentration, and that it increased gradually with the filtration time. It is concluded from Figures 6 and 7 that the increase in P is due to adhesion of humic acid on the membrane surface or membrane pore.

Fouling performance in the filtration of a mixture of kaolin and humic acid. The change in P of a mixture of kaolin (kaolin concentration: 50 mg/l) and humic acid (humic acid concentration: 25 mg/l, 50 mg/l, 100 mg/l) is shown in Figure 8. The higher increase of P at the humic acid concentration of 50 mg/l comparing with the other concentrations was observed. Though its reason was not clear, the reproducibility was obtained. And the rejection rate of humic acid is shown in Figure 9. The rejection rates at the humic acid concentrations of 50 mg/l, 75 mg/l and 100 mg/l were 10–40%, 5–40% and 20–40%, respectively.

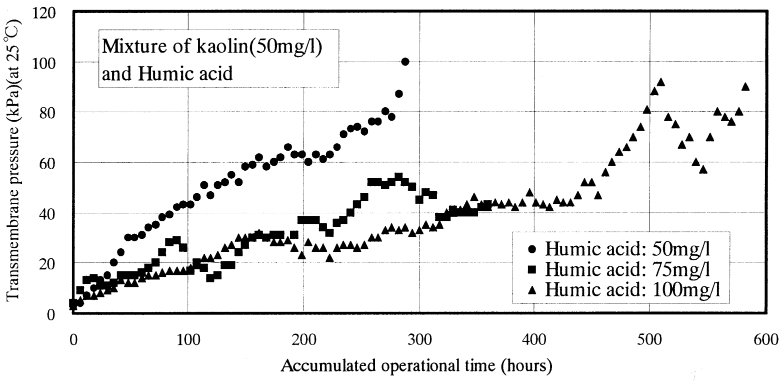

Figure 8 Changes in transmembrane pressure using mixture of kaolin (50 mg/l) and humic acid

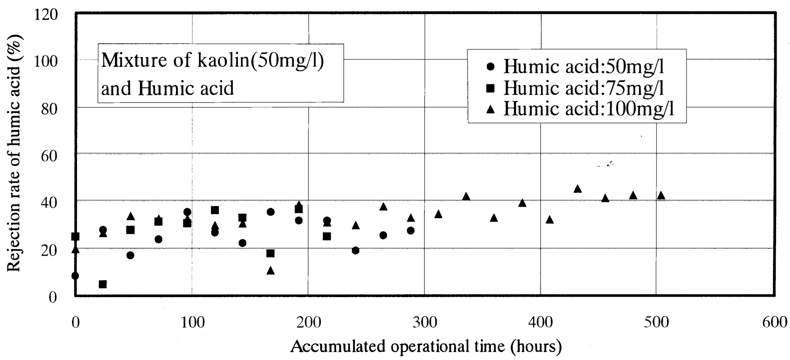

Figure 9 Changes in rejection rate of humic acid using mixture of kaolin (50 mg/l) and humic acid

The rejection rate for the kaolin suspension with humic acid did not depend so much on the humic acid concentration compared with the case of humic acid solution.

Effect of coagulant addition. The change in P of humic acid solution (humic acid concentration:30 mg/l) with/without coagulant addition (PAC concentration:36 mg/l) is shown in Figure10. The increasing rates of P was reduced by coagulant addition. And the rejection rates is shown in Figure 11. The rejection rate of humic acid with/without coagulant addition were 50–85%/20–40%. The lower increasing rate of P by the addition of PAC was probably caused by the intake of humic acid into the aluminum hydroxide flocs and lower adhesion of humic acid on membrane surface or membrane pore. The high rejection of humic acid with coagulant is explained by the removal of humic acid with floc formation in the feed solution. The time dependence of P with/without coagulant are also estimated by standard blocking filtration model.

Comparison of pilot plant test and small-scale test. In the small-scale test it was clear that the humic acid was the main fouling material and that the acceleration effect of fouling formation was observed using a high concentration solution of humic acid, though it did not always follow the concentration of humic acid in the feed water of the mixture. Concerning the relationship between t versus P in small-scale tests, in most cases the curves of similar shape to those in pilot plant tests were obtained, although some of them were quite different from the shape of curves in pilot plant tests. This irregular increase in P would be due to the acceleration test of high humic concentration. The curves of t versus P were roughly

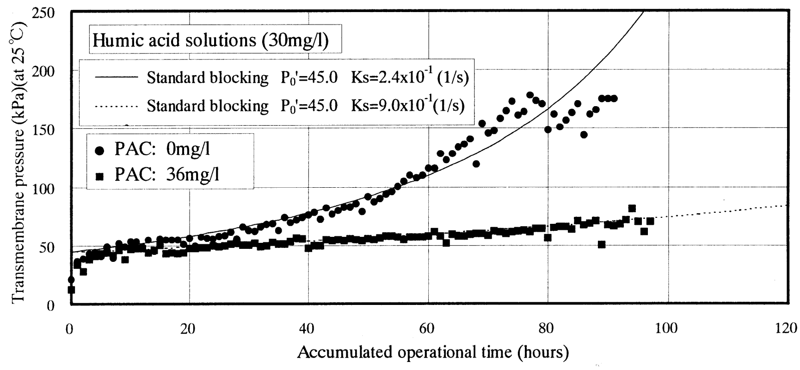

Figure 10 Change s intransmembrane pressure using humic acid solutions (30 mg/l) with/without PAC and curve fitting by media blocking filtration equations

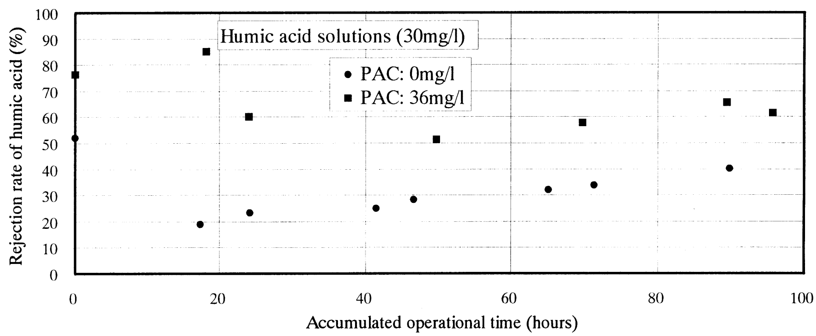

Figure 11 Change s inrejectino rate using humic acid solutions (30 mg/l) with/without PAC

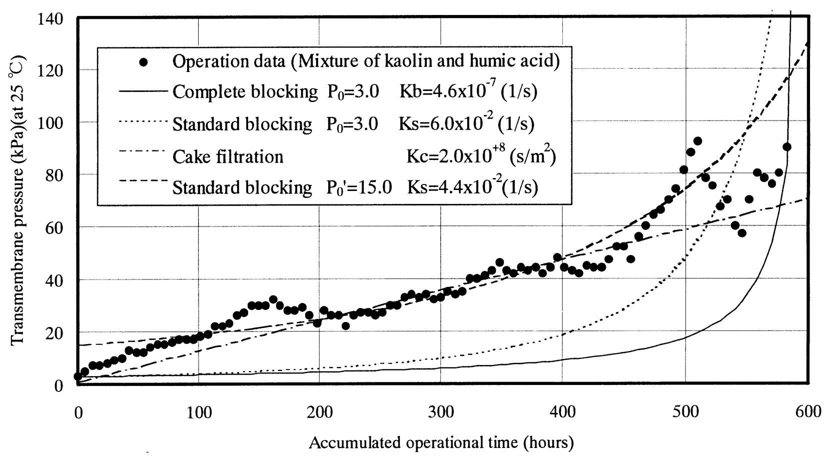

Figure 12 Change s intransmembrane pressure using mixture of kaolin (50 mg/l) and humic acid (100 mg/l) and curve fitting by media blocking filtration equations

expressed by the standard blocking filtration model (see Figures 10 and 12) by using the extrapolated value of P_0, i.e.P_0' as shown in pilot plant tests (see Figures 2 and 4). The values of Ks in small-scale tests were about ten times larger than those in pilot plant tests, that is, the filtration time required to reach the same pressure is by ten times faster at the acceleration tests of small-scale than in the pilot plant tests when P_0 or P_0' is the same in both test plants.

Conclusions

The following results were obtained in the acceleration tests of fouling using the small scale MF membrane module and the artificial feed water prepared with kaolin, bentonite and humic acid to predict the increase in transmembrane pressure, P, in the pilot plant test for treating the river water or dam water: (1) No increase in P was observed when using the kaolin or bentonite suspension, (2) The increasing rate of P was higher in the feed water of higher humic acid concentration, (3) The addition of coagulant in the humic acid solution retarded the increase in P and (4) The standard blocking filtration module was well fitted to express the relationship between filtration time and P at the constant flow rate filtration by using the extrapolated value of P_0' as an initial transmembrane pressure at t=0 at both pilot plant tests and small-scale acceleration tests.

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