Korean Membrane Journal
Vol. 2, No. 1, December, 2000, 1-8

Review

Cleaner Production Option in a Food(*Kimchi*) Industry[†]

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Summary : In *Kimchi* (a salt-pickled and fermented food) manufacturing industry, the process of brining and rinsing the raw vegetable produces a vast amount of wastewater of high salinity. Instead of expensive and low-efficient conventional treatment system, brining wastewater reuse system was developed using hybrid chemical precipitation/microfiltration. In the microfiltration of chemically treated brining wastewater, comparison of flux, backwashing frequency and energy consumption was made between dead-end and crossflow filtration mode. The optimum location of neutralization step in this system was also discussed in connection with the microfiltration performance. The quality test of *Kimchi* prepared by the reuse system confirmed the new approach was successful in terms of water/raw material(salt) saving and wastewater reduction.

Introduction

Kimchi, a salt-pickled and fermented vegetable, is one of the most favored foods in Asian countries like Korea and more and more people in the world get used to its taste. There are more than two hundred *Kimchi* manufacturing industries in Korea and the annual production of *Kimchi* reached about 2,100,000 tons in 1997. In the *Kimchi* manufacturing industry, brining of raw materials (e.g., Chinese cabbage) and successive rinsing of brined raw materials generate a large amount of brining wastewater and rinsing wastewater, respectively. To comply with the effluent discharge limit the two kinds of wastewater are mixed together and passed through the conventional end-of-pipe wastewater treatment system, presented in Figure 1. However, these multiple treatment steps are not only very complicated but also unfavorable in the economic point of view. Moreover, this system suffers form some severe problems specially in the activated sludge process due to the high salinity of the brining wastewater [1]: i) difficulties in biological floc formation, ii) reduction of BOD removal efficiency, iii) poors settling characteristics of biological flocs, etc. Furthermore, loss of reusable salts and process water is inevitable in this end-of-pipe treatment system. The purpose of this study was to develop a new clean technology in

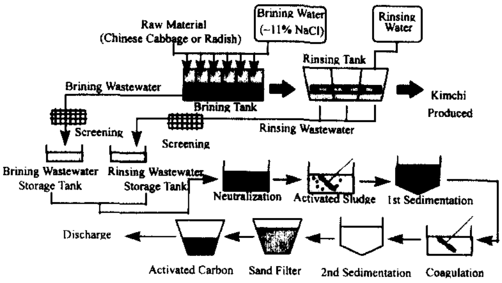

Fig. 1. Flowchart for the conventional wastewater treatment.

[†] Paper presented at the 8th membrane symposium, "Membrane Separation Processes for Recycling Technology", Seoul, April 9, 1999.

the *Kimchi* industry through the internal recycling of brining wastewater, which enables a zero-discharge system at least at the brining step as well as salt and water recovery.

Chemical Precipitation

As a first step, chemical precipitation was applied to remove the dissolved and colloidal materials that accumulated during brining steps and thus to relieve the load on the following purification step, microfiltration. Chemical precipitation was carried out in 250L of precipitation tank as well as 1L of jar. It consisted of the injection of 3M NaOH solution into the brining wastewater, 3min fast mixing, 27min slow mixing and 1hr sedimentation steps. Changes of TOC, suspended solid(SS), turbidity, retention of soluble magnesium and sediment volume were analyzed after each experiment.

Operation of Microfiltration

After chemical precipitation, the supernatant was fed to the microfiltration system. The microfiltration system(Memcor 1M1, Memtec, Australia) was used to remove cake-forming and pore-plugging foulants by high pressure air backwashing. The membrane was a polypylene hollow fiber membrane(active area; 1m^2). In operating the MF unit, both high pressure air(600kPa) and low pressure air (120kPa) were applied to control the pneumatic valves in the machine for backwashing and to remove the water filled in the lumen at backwashing, respectively. To supply high pressure clean air to the MF unit, an air compressor with 75L air tank was used, to which two air filters of 40㎛ and 5㎛ were connected in series. The crossflow microfiltration(CMF) was operated in total recycle run by recycling permeate, retentate and backwashed solution to the feed tank and the backwashing was conducted periodically during operation when the transmembrane pressure increased by 6~7kPa. As it is possible to operate the MF unit in both dead-end and crossflow filtration, the optimal operation conditions were determined by comparing permeate quality, flux, backwashing interval and energy consumption under the various operation conditions in this study. For the direct comparison of performance between dead-end and crossflow filtration, the initial condition was fixed at 1100L/hr of retentate flow rate and 180L/hr of permeate flow rate with pure water.

Analysis

The analytical methods from Standard Methods[2] were adopted for the measurement of TOC, SS and turbidity. Analysis of inorganic ions such as Mg^{2+} and Ca^{2+} were performed by the direct injection of aqueous samples to ion chromatograph(Dionex 4500I, USA) equipped with a sensitive conductivity detector.

Chemical Precipitation of Brining Wastewater

Given that the brining wastewater contained lots of soluble magnesium inherently, chemical precipitation to induce the precipitation of magnesium hydroxide was attempted by merely raising the pH of the wastewater through the addition of sodium hydroxide. It was conceived understanding that the precipitation of magnesium hydroxide during lime softening processes was effective for the removal of viruses [3], color [4], organic matters [5,6], and so on. Optimal dosage of sodium hydroxide was established through jar-test experiment. Taking into account the characteristics of food product, the application of polymeric or inorganic coagulants was disregarded.

Brining Wastewater Recycle through Hybrid Chemical Precipitation/Microfiltration System

The schematic diagram of brining wastewater reuse system developed in this study is shown in Figure 2, which consists of chemical precipitation and microfiltration. For the brining wastewater recycling, hybrid microfiltration with chemical precipitation was applied to remove the organics responsible for tastes and odor problems form the brining wastewater. Because sun-dried bay salt is usually used to make the brining water, about 1,800 ppm of magnesium free ion remains in the

Table 1. Water Quality of Fresh Brining Water and Brining Wastewater

Parameter	Fresh brining water	Brining wastewater
Total suspended solid(ppm)	95700	112000
Suspended solid(ppm)	negligible	160
Total organic carbon(ppm)	10	340~640
Turbidity(NTU)	6	120
Ca^{2+}(ppm)	160	142
Mg^{2+}(ppm)	1860	1880

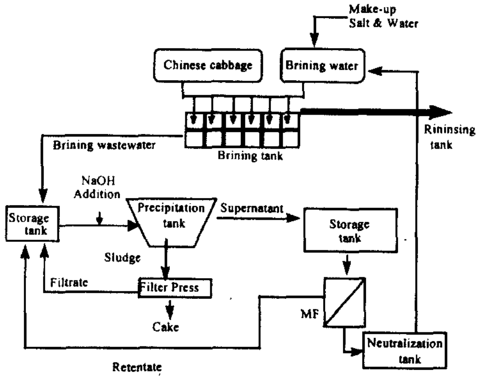

Fig. 2. Schematic of a brining wastewater recycle system.

brining wastewater. Accordingly, the addition of sodium hydroxide generates magnesium hydroxide precipitates which can easily adsorb of enmesh both the organic and colloidal impurities including microorganisms. The effluent from chemical precipitation tank was further purified by the membrane process(microfiltration) prior to the recycle to the brining process. The concentrates from microfiltration(MF) is returned to the storage tank and combined with the brining wastewater As the pH of supernatant in settling tank is more than 10, it is compulsory to neutralize the chemically treated brining wastewater prior to its reuse. In this study, it was intended to find out the optimal process option and operational condition in the MF/Precipitation hybrid system with respect to energy consumption, quality of recycled wastewater and taste of the final product, *Kimchi*.

Materials and Methods

Characteristics of Brining Wastewater

Bringing water becomes turbid and malodorous as the brining steps are repeated, because of the accumulation of debris of raw materials and growth of microorganisms. As shown in Table 1, total organic carbon(TOC) and the turbidity of the brining wastewater used 5 times were much higher than those of fresh brining water. Therefore the major components to be removed prior to the reuse of brining wastewater were thought to be the dissolved and suspended organic matters such as the debris of vegetables generated and microorganisms grown and their metabolites produced in the brining process. In this context, the brining wastewater reuse system was designed to effectively remove such organic matters. On the other hand, inorganic constituents in the brining wastewater, such as calcium and magnesium were intended to keep as much as possible even after the treatment in so much as those were known to play a key role in inducing the delicate tastes of *Kimchi*.

The results of jar-test experiment are summarized in Figure 3. Removal of TOC, SS, turbidity and the amount of sediment volume increased as NaOH dose increased. But the recovery of soluble magnesium, which was known to be critical component in the delicate taste of *Kimchi* and thus desired to get back as much as possible, did not change vary much, The optimal dosage of sodium hydroxide was estimated to be about 14mL of 2M NaOH per 1L of the brining wastewater though it was quite difficult to determine the precise optimal dosage.

Microfiltration of Brining Wastewater after Chemical Precipitation

Microfiltration of the effluent from the precipitation tank was necessary to further purify

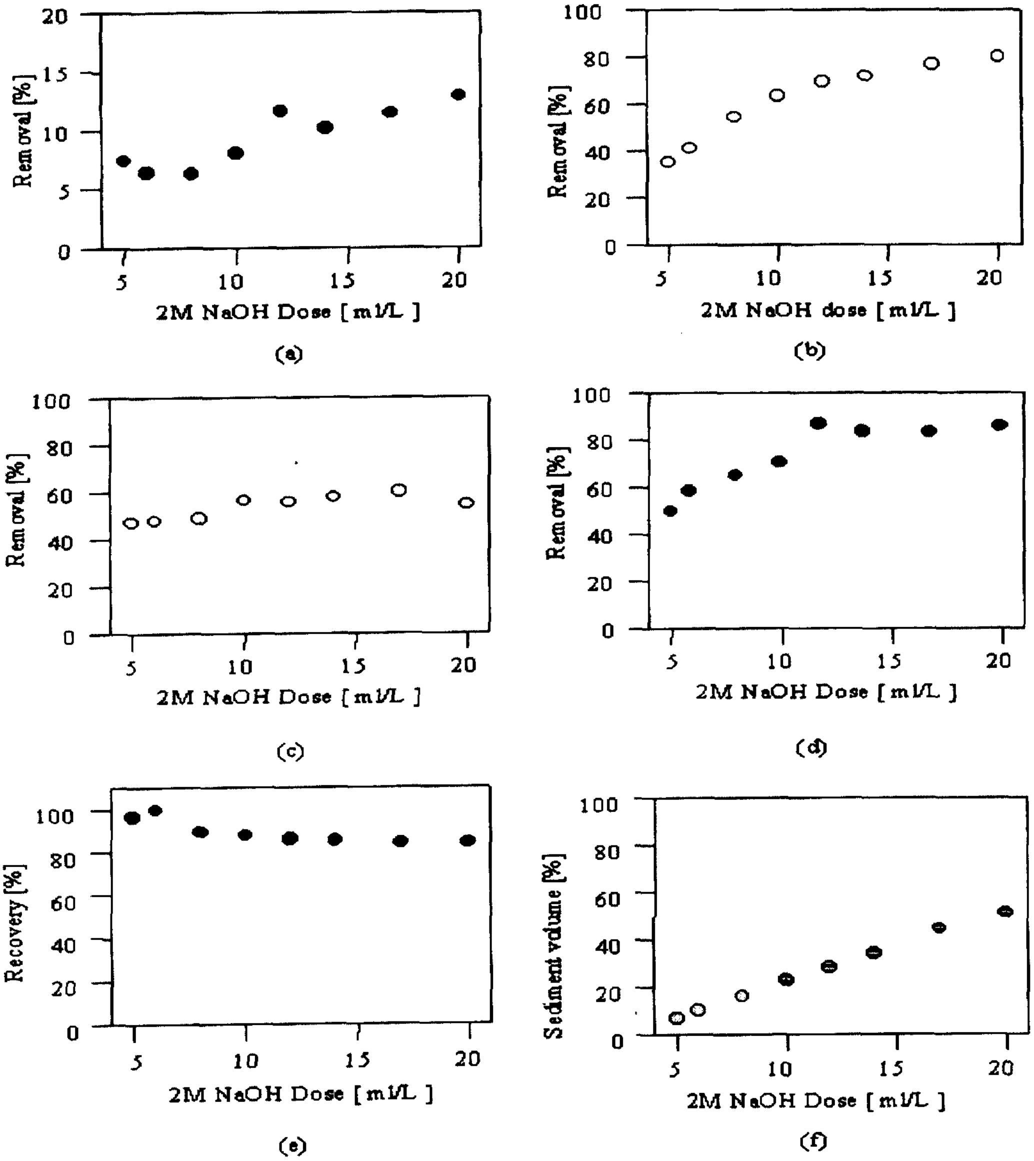

Fig. 3. Jar-test results: removal of (a) TOC, (b) turbidity, (c) SS, (d) SS after elimination of dissoved salts (e) recovery of magnesium and (f) sediment volume with respect to NaOH dose.

the chemically treated wastewater to be suitable for the reuse at the brining step. As the pH of the effluent was 10, it should also be neutralized in order to reuse. However, the selection of the neutralization point in this recycling system, e.g., before or after MF, would be closely related to the MF performance. In this context, two kinds of feeds with pH=10(non-neutralized) and pH=7 (neutralized) were applied to MF, respectively and comparison was made with respect to flux, backwashing interval and permeate quality. Figure 4 shows the results of the experiments

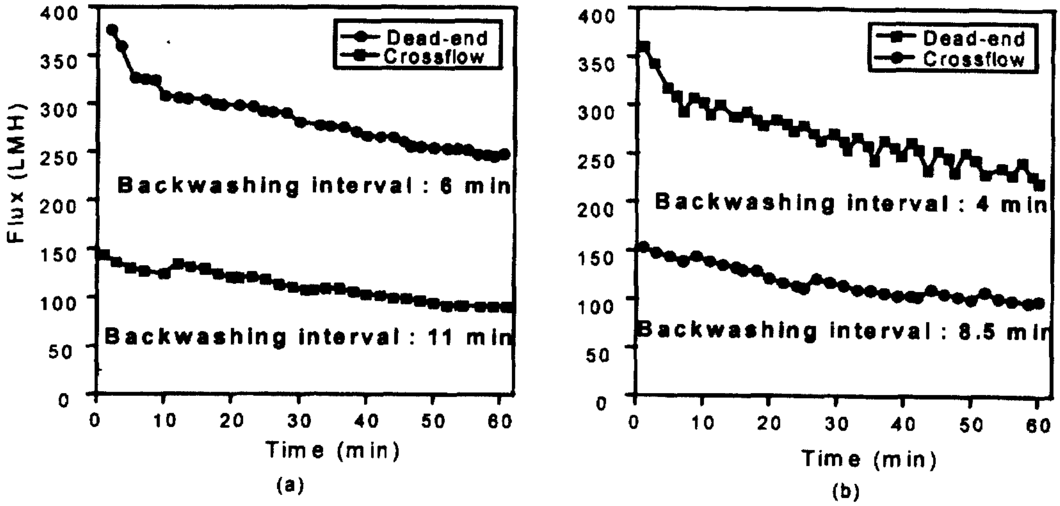

Fig. 4. Comparison of flux according to the operation mode (a) nonneutralized feed (pH-10), (b) neutralized feed (pH=7).

Table 2. Comparison of Permeate Quality according to the Operation Mode

Item		TOC(ppm)	Turbidity(NTU)
Feed		629.4	10.0
Permeate	Dead-end	418.1	0.08
	Crossflow	419.5	0.22

with the two feeds in both dead-end and crossflow filtration modes. With the dead-end filtration the flux was about two times larger but the backwashing interval was shorter than those with the crossflow filtration regardless of the feed pH. The difference of flux between dead-end and crossflow filtration was attributed to the difference of transmembrane pressure. As the pump equipped in CMF unit was a centrifugal type the retentate flow rate was controlled only with the back-pressure valve. Therefore, as the retentate flow rate(or feeding rate in the dead-end mode) decreased, the trans-membrane pressure increased and thus higher flux was obtained. However, the shorter backwashing interval was observed in the dead-end mode due to the thicker cake layer formed on the membrane. In summary, the lower the retentate flow rate, the higher the trans-membrane pressure, the higher the flux but the shorter the backwashing interval.

The quality of permeate was monitored and shown in Table 2. The suspended solid was removed completely and turbidity removal was over 99.8% while TOC removal was around 30%. The permeate TOC and turbidity were almost similar in both two operation modes, but the dead-end mode was a little better than the crossflow one in terms of turbidity.

As the magnesium concentration in brining water was known to affect the taste of the final product (*Kimchi*), the lower magnesium removal, the better the brining wastewater reuse system. Through the hybrid MF/chemical precipitation, the loss of magnesium was only 10~15% resulting in no significant difference in the taste of *Kimchi*.

Particle Size Distributions in Various MF Feeds

Suspended solids concentrations of non-neutralized feed and neutralized one are 37.5 and 27.5 ppm while turbidities are 10.0 and 9.1 NTU, respectively. Therefore it was expected that the non-neutralized feed would result in greater membrane fouling than the neutralized one. As seen in the backwashing intervals(Figure 4), however,

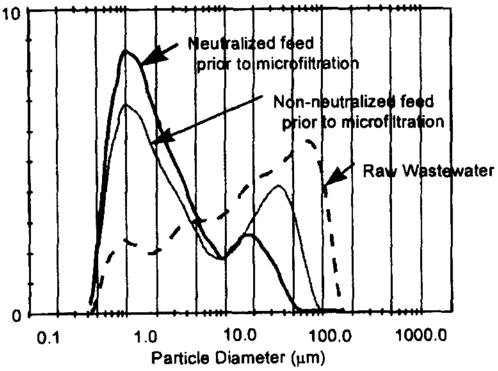

Fig. 5. Particle size distributions of various feeds for microfiltration.

the neutralized feed showed worse filtration performance than the non-neutralized one in both MF modes. A reasonable interpretation of these unexpected results was possible by analyzing particle size distributions of the two feeds, presented in Figure 5. As shown in Figure 5, most of the particles whose sizes are over 10㎛ in raw brining wastewater were removed through the chemical precipitation. After the chemical precipitation, the neutralization of the supernatant still caused the fraction of larger particles(30-40㎛) to decrease while the fraction of the smaller particles(around 1㎛) to increase. This is because the suspended magnesium hydroxide crystals that had not settled in the precipitation tank might be redissolved after being neutralized. During this process, the adsorbed organic matters on the magnesium hydroxide crystals that had not settled in the precipitation tank might be redissolved after being neutralized. During this process, the adsorbed organic matters on the magnesium hydroxide crystals would also be desorbed. It is well known that smaller particles curse more serious membrane fouling than the larger particles in the membrane process according to the Carman-Kozeny equation shown in equation (1).

$$J=\frac{\varepsilon^3 d_p^2 \triangle P}{180(1-\varepsilon)^3 \eta} \tag{1}$$

In this equation, the flux(J) is proportional to the square of the particle size(d_p). Therefore, the reason why the neutralized feed demanded more frequent backwashing in order to maintain a certain range of trans-membrane pressure than the non-neutralized one is that neutralization made the particles smaller in MF feed.

Comparison of Energy Consumption

As previously described, the dead-end filtration model had the highest flux but the shorter backwashing interval than the crossflow mode. As an alternative criteria for selecting the better MF mode, the energy supplied to pump and compressor to produce the unit volume permeate was evaluated according to the MF mode and crossflow rate.

The power(P) that pushes the incompressible fluid from the pump can be expressed by multiplying the feeding flow rate(v) by the pressure drop(ΔP). In this study, the feeding flow rate and the trans-membrane pressure changed as the flux declined and thus the power changed with the operation time. The energy used can be obtained by integrating the power with respect to time and the amount of total permeate can also be obtained by integrating the flux(J) with respect to time. Considering time required for backwashing(t_b) conducted during operation, the net time fraction, $(t_t-t_b)/t_t$, was applied where t_t is the total operation time. Then the amount of work(W) done by the pump to produce the unit volume of permeate can be evaluated by using equation (3). Dividing the work by the energy efficiency of the pump (0.3) gives the energy consumption.

$$P(kW)=v(m^3/\mathrm{sec})\times\triangle P(kPa) \tag{2}$$

$$W(J/m^3)=\frac{\int v(t)\times\triangle P(t)dt\times\frac{t_t-t_b}{t_t}}{\int J(t)dt\times\frac{t_t-t_b}{t_t}} \tag{3}$$

In an air compressor, a piston compresses the air in a closed space instantaneously, so it could be considered to be an adiabatic compression.

Table 3. Energy Consumption of MF Unit to Product the Unit Volume pf Permeate

Operation Mode	Pump kJ/m^3	Air compressor kJ/m^3	Total kJ/m^3
Dead-end	115.3	1274.0	1389.3
Cross-flow(0.6m^3/hr)	348.5	1289.8	1638.3
Cross-flow(1.1m^3/hr)	624.4	1241.4	1865.4
Cross-flow(1.3m^3/hr)	730.3	1246.6	1946.9

Table 4. Quality Test of *Bak-Kimchi* Brined with Regenerated Brining Water

Number of brining	Before fermentation		After fermentation	
	Taste	Odor	Taste	Odor
1st	N.R.[a]	N.R.	N.R.	N.R.
2nd	N.R.	N.R.	N.R.	N.R.
3rd	N.R.	N.R.	N.R.	N.R.
4th	N.R.	N.R.	N.R.	N.R.

[a] No Response by connoisseur, which means no differences in taste and odor between *Bak-Kimchi* brined in fresh brining water and brined in the recycled brining wastewater.

The power of the piston action is given in equation (4) [7] and the energy yield defined by the fraction of energy supplied to the air compressor to the actual piston action is 0.66 [8]

$$P(kW) = \frac{k}{k-1} \times \frac{ZRT_1}{9806} \times \left[\left(\frac{P_2}{P_1} \right)^{(k-1)/k} - 1 \right] \quad (4)$$

where, P_1: inlet pressure, P_2: outlet pressure, Z: mass flow rate of air, T_1: inlet air temperature, R: ideal gas constant, k: constant reflecting the difference from ideality of gas(for air k is 1.395).

All of the results involved in calculating the energy consumption is shown in Table 3. The energy consumption for pumping varied considerably with the operation conditions, but the energy supplied to the air compressor was almost constant regardless of operational conditions and made up 60-90% of the total energy consumption in this study. The total energy consumed to produce the unit volume of permeate in the dead-end filtration was less than that in the crossflow filtration but this difference was brought about entirely by the energy consumption for the pump. If the energy supplied to the air compressor were reduced comparatively, the difference in the total energy consumption would be much larger according to the operation conditions.

Quality Test of Bak-Kimchi Prepared with Recycled Brining Wastewater

The effect of the recycling system on the product quality was tested by brining raw materials with the recycled brining wastewater and manufacturing *Bak-Kimchi*, a kind of *Kimchi* whose taste and odor were known to be the most sensitive to the quality of a brining solution. Taste and odor tests by professional connoisseurs of *Kimchi* proved the recycling system was successful as shown in Table 4.

Conclusions

In this study, the hybrid MF/chemical precipitation was developed for the brining wastewater recycle in a food(*Kimchi*) industry. The following conclusions could be drawn:

(1) The addition of NaOH into the brining wastewater generated magnesium hydroxide precipitates which effectively removed the soluble organics and colloidal particles, but the recovery of valuable magnesium inducing the peculiar taste of *Kimchi* reached more than 85%.

(2) In MF of the effluent from the precipitation tank, the non-neutralized feed was better than the neutralized one in both dead-end

and crossflow modes in terms of backwashing interval. It was attributed to the shift of the larger particles to the small ones due to the redissolution of magnesium hydroxide precipitates during neutralization. The dead-end mode was superior to the crossflow one with respect to flux and energy consumption.

(3) The quality test of the product(*Kimchi*) prepared with the recycled brining wastewater confirmed that the hybrid MF/Chemical precipitation system was so successful that it could add another example to the worldwide cleaner production cases.

Acknowledgement

This work was supported from the Ministry of the Environment, Korea. The authors with to thank Doosan Food Industry, Korea for supplying raw brining wastewater and the quality test of *Kimchi*. The authors also thank J. S. Yeom and H. S. Lee for their assistance in the analysis of samples at the Institute of Environmental Science and Engineering, Seoul National University.

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