Coagulation characteristics of colloids indicating irreversible membrane fouling in coagulation－MF membrane filtration process

凝集－ＭＦ膜ろ過プロセスにおける不可逆的膜ファウリングを表すコロイドの凝集特性

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1. Background

Low-pressure membrane filtration (i.e., microfiltration (MF) and ultrafiltration (UF)) methods facilitate simpler and more precise solid-liquid separation than sand filtration, and their introduction is therefore being considered at many water treatment plants. Whereas, only 1% of the total water treatment plants in Japan has been installed with membrane filtration process. MF/UF membranes showed good filtration performance at the places where ground water is used as source water, but can get fouled easily when filtering surface water. It is difficult to treat surface water only using membrane filtration process. When introducing membrane filtration to surface water treatment processes, it is common to combine it with a preliminary coagulation process. The optimum coagulation condition varies based on the fluctuant and unstable surface water quality. However, conventional optimum coagulation conditions by jar tests based on the removal of turbidity or color may not be identical to optimum conditions for membrane filtration performance, which is worked and reported by studies for more than ten years.

Loss of membrane permeability or progress of trans-membrane pressure (TMP) is resulted from the progression of membrane fouling. Membrane fouling can be divided into physically reversible fouling and physically irreversible fouling. When membrane gets fouled, physical cleaning is often carried out, and reversible fouling such as accumulated cake layer could be removed. While fouling that block the membrane pores or adsorb inside membrane matrices could not be removed and is defined as irreversible fouling. The progression of irreversible fouling is a large obstacle because chemical cleaning is needed to remove irreversible fouling, which will lead to problems such as chemical waste and shortened membrane life-span. Besides, tiny particles near or small than membrane pore size (i.e., meso-particles, defined as colloids between 20 nm and 0.5 µm after coagulation in **3. Research findings**) were reported as the irreversible fouling. It is possible to find the optimum coagulation condition for alleviating irreversible fouling by paying attention to meso-particles. There have commercial equipment that can determining particle characteristics such as zeta potential (ZP) and particle number (PN) for tiny particles near or smaller than membrane pore size, but a high concentration of particles is necessary. Meso-particles after coagulation process are highly dispersed and therefore scatter light weakly, it is however extremely difficult to observe their particle characteristics underwater. And yet there is no study focusing on meso-particles regarding to coagulation－membrane filtration process. Comparing with meso-particles, submicro-particles (defined as colloids between 0.5 and 1.0 µm after coagulation in **3. Research findings**) have been studied in many researches and are reported to have relation with reversible fouling, but there is still no clear result about the relation between submicro-particles and irreversible fouling.

2. Research objectives

To develop a method to determine appropriate coagulation for MF membrane filtration, the objectives of this research were: ① to develop a way to track meso-particles near or smaller than membrane pore size after coagulation; ② to clarify difference in characteristics of submicro- and meso-particles; ③ to investigate the factor of meso-particle governing the development of irreversible fouling; ④ to clarify the organic composition of meso-particles; and ⑤ to find out the coagulants controlling the physico-chemical properties of meso-particles.

3. Research findings

① ZP and PN tracking of meso-particles

With the combination of the commercial ZP analyzer with a violet laser of high power (65 mW) and short wave length (405 nm), we succeeded in tracking meso-particles via microscopic electrophoretic image analysis. Based on the lower detection limit of this equipment and membrane pore size, tiny colloids between 20 nm and 0.5 μm after coagulation were defined as meso-partices. For comparison, colloids larger than meso-particles but smaller than 1 μm was treated as submicro-particles.

② Differences in characteristics of submicro- and meso-particles

Colloids in studies related to coagulation are always treated as a whole part, and the average ZP and PN of the measurable colloids are used for analysis. However, since it was unable to detect the meso-particles, there is no study about the difference in characteristics of particles with different sizes.

Coagulation characteristics including ZP and PN were investigated. Polyaluminium chloride (PACl) was used as coagulant. It was revealed that the ZP of the meso-particles was greatly influenced by the coagulation pH but hardly affected by PACl dose, which was totally different from that of submicro-particles. Meso-particles remained as negative charge at neutral pH, which is commonly used in water treatment plant. Besides, PN behavior of meso-particles was also different from that of submicro-particles. The neutralization point for meso-particles remained at acidic pH without influence from mixing strength, and raw water type including same river water taken in different seasons and different water categories. The PN of meso-particles was greatly influenced by the coagulation pH and PACl dose. When the pH increased, the PN became less as the PACl dose increased. From these results, it is indicated that decrease of PN of meso-particles is because of the coprecipitation with submicro-particles or sweep flocs formed by hydrolyzed PACl, not because of the growth of particles after charge neutralization. When second-stage coagulation was carried out for the purpose of removing meso-particles, the ZP hardly changed while the PN of meso-particles was reduced. This suggests that meso-particles were incorporated into the aggregated particles formed by the added PACl. Therefore, we propose to remove meso-particles by performing coagulation at low pH or over-injection of coagulant PACl.

③ Factor of particle characteristics governing the irreversible fouling development

The principle factors governing the degree of irreversible MF membrane fouling were identified based on the repeated membrane filtration experiment using both polyvinylidene difluoride (PVDF) and ceramic membranes under various coagulation conditions. As the result, irreversible membrane fouling in both PVDF and ceramic MF membrane was best controlled while meso-particle ZP approached zero. ZP of submicro-particles had some relation with the progression of irreversible fouling potential, but lower than that of meso-particles. While PN of submicro- and meso-particles had no relation with irreversible membrane fouling regardless of membrane type and source water.

④ The organic composition of meso-particles

Regarding the size range of defined meso-particles, there has another factor called biopolymer (BP) having similar size with meso-particles. BPs are defined as macromolecular organic matters in water. Therefore, it is possible to predict the organic composition from that of BPs. We found that BP removal depends on the type of source water, while nearly identical processes for removing humic substances. This result demonstrates the complexity of optimization for BP coagulation. Fractionation of BP by excitation–emission matrix-parallel factor analysis (EEM-PARAFAC) showed that at least three organic component groups (C1, C2 and C3) constitute BP. C1 is tryptophan-like organic matter that is often found in wastewater effluent, C2 is tyrosine-like organic matter that has a phenolic chemical structure, and C3 is a humic-like substance. C1 was removed thoroughly at acidic pH but not at neutral pH, while the removal of C2 was inefficient even with a significant change in pH or dose, indicating similar difficulties in a coagulation process. The difference in components C1 and C2 may partly explain the difference in efficiencies of removal of BP in water from different sources. Therefore, the complex organic composition of BPs indicates that meso-particles are consisted of different organic constituents with varied coagulation characteristics. It is difficult to select the pre-coagulation condition based on the BP removal rate. While this results on the other hand emphasized the importance of meso-particle ZP in selection of pre-coagulation conditions.

⑤ Coagulants controlling the physico-chemical properties of meso-particles

Optimum pre-coagulation condition for the prevention of irreversible membrane fouling, or acidic pH, is not suitable for actual operation, as considering residual aluminum concentration, pipe corrosion, and chlorination efficiency. It is therefore necessary to investigate coagulants or other methods for the appropriate modification of meso-particle characteristics so as to achieve the efficient pre-coagulation from the view point of both water quality and fouling prevention. It is therefore three coagulants (i.e., PACl 50, PACl 70, and aluminium chlorohydrate (ACH)) were tested. Comparing the zero charge line when using PACl 50 and PACl 70, the influence of basicity of PACl on neutralization of meso-particles was small. Charge neutralization of meso-particles near neutral pH was only achieved when using ACH as coagulant. Based on the filtration results, we propose to use ACH to neutralize meso-particles at neutral pH which is applicable in water treatment plant.

4. Conclusion

In this research, with the purpose to develop a method to determine appropriate coagulation for MF membrane filtration, the particle characteristics during coagulation was focused on. Firstly, effort was made to develop a new equipment to track meso-particles after coagulation; then, differences in characteristics of submicro- and meso-colloids were clarified; and then, the relations between irreversible fouling potential with particle characteristics were compared to investigate the factor of meso-particle governing the development of irreversible fouling. Then, the organic composition of meso-particles were investigated. At last, considering the operational condition at water treatment plant, coagulants controlling the physico-chemical properties of meso-particles were studied.

The main results obtained are shown below:

① Identification of ZP of meso-particles remaining after coagulation was succeeded with the use of the new developed ZP analyzer.

② The neutralization points (ZP = 0) were found to be different depending on the size of particle. Under same PACl dose, the neutralization point of meso-particles was lower in pH than that of micro-particles.
Under the traditional coagulation condition where submicro-particles were neutralized, meso-particles tended to remain as negatively charged particles, and it was still difficult to neutralize them even when the PACl dose was increased to 3.0 mg Al/L.
The neutralization point for meso-particles remained at acidic pH without influence from mixing strength, and raw water type including same river water taken in different seasons and different water categories. Thus ZP could only get neutralized at acidic pH by PACl is considered as a principle nature for meso-particles.

③ Irreversible membrane fouling in both PVDF and ceramic MF membrane was best controlled while meso-particle ZP approached zero.
PN of submicro- and meso-particles had no relation with irreversible membrane fouling regardless of membrane type and source water.

④ BPs in natural water were categorized into three PARAFAC components: C1 and C2 (protein-like substances) and C3 (humic-like substances). Removal of C1 was strongly affected by pH, but that of C2 was influenced less by coagulation. This difference may partly explain the different efficiencies of BP coagulation in various raw water samples.
It is difficult to select the pre-coagulation condition based on the BP removal rate. While this results on the other hand emphasized the importance of meso-particle ZP in selection of pre-coagulation conditions.

⑤ There exists coagulant appropriate for coagulation－MF membrane filtration process such as ACH which can control the physico-chemical properties of meso-particles. We propose to use ACH to neutralize meso-particles at neutral pH which is applicable in water treatment plant.

These findings are expected to contribute to expand conventional coagulation theory to ‘nm’ range.

By neutralizing meso-particles during coagulation process, the progress of irreversible fouling could be alleviated. This will extend the chemical cleaning interval and membrane life-span, which will lead to the reduction of the operation cost including cost for membrane cleaning and membrane module replacement. The further application of coagulation－MF membrane filtration process in water purification plant along with cheaper and safe water could be expected. Neutralization of meso-particles at neutral pH might become a principle property for either selection or development of coagulants for coagulation－MF membrane filtration process.