

論文の内容の要旨

Abstract of Dissertation

Effects of Carbon Black Nanoparticles on Membrane Filtration of Surface Waters

(表流水の膜ろ過処理におけるカーボンブラック粒子の影響)

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Mesoporous aggregate of carbon black (CB) nanoparticles (referred as CB particles) was employed with the aim to reduce membrane fouling caused by organic macromolecules. Effects of CB particles on membrane filtration were evaluated in a batch filtration cell under the dead-end filtration. Membrane performance prior to and after addition of CB particle were assessed with commercially available humic acids (HA) and surface waters containing natural organic matter (NOM). Three modes of implementing an adsorption of organic matter by CB particles were used; namely, CB adding into the filtration cell prior to feeding of raw water, pre-adsorption followed by membrane filtration, and pre-adsorption followed by CB removal and membrane filtration. Resistance-in-series model was used to characterize cake filtration and determine fouling resistance in filtration of raw water and CB-added raw water.

The porous texture and size distribution of CB particles were evaluated expansively using N_2 adsorption and dynamic light scattering measurements. Mesoporous aggregate of CB particles had a total (BET) surface area of $144 \text{ m}^2/\text{g}$ and the mean pore diameter of 32.6 nm , determined by BJH method. Porosity of CB particles was derived from void space in aggregates which were composed of equal-sized spherical primary particles. The as-received CB showed a very fast adsorption kinetic with NOM in Tama River water as seen that 80% of the equilibrium adsorption capacity was attained within 10-min contact time. This revealed that mesopores of CB particles were easily accessible for organic matter. Particle size distribution of CB particles in an aqueous solution was affected strongly by the concentration of divalent ions. The calcium and magnesium ions of 1 mM , corresponding to 10 meq/g-CB , caused fast aggregation of CB particles and hence several micron aggregate was produced. This revealed that CB particles dispersed in surface waters containing significant amounts of divalent cations would rapidly coagulate.

As for membrane filtration, CB was mixed with Obitsu River water (low Ca^{2+} and Mg^{2+}) in the stirred cell prior to initiating filtration and fouling behavior was observed. Modes of initial

fouling and filtration resistances were strongly influenced by relative molecular sizes of organic matter and CB particles to the membrane pore, sorption of organic matter into CB aggregates, and concentrations of calcium ions. The presence of CB particles transformed the mode of initial fouling from internal pore adsorption by organic micromolecules to intermediate pore blocking (plugging of pore entrance). The internal pore fouling can be reduced by adsorption of the organic micromolecules by powdered activated carbon but such an effect on the initial fouling mode had no reduction in the overall flux decline. As cake filtration became the dominant mode of fouling, the resistance-in-series model was utilized to characterize filtration resistances. The presence of CB particles nullified the boundary-layer resistance by removing organic macromolecules (polysaccharide-like compound) but aggravated cake resistance, which required chemical cleaning. By adding 1mM CaCl₂ into the raw water, aggregate size was increased significantly. This resulted in a change of initial fouling from pore plugging to cake formation and reduction of cake resistance due to increased cake porosity in filtration of raw water-CB particle. At a given pH, addition of calcium increased removal of low MW organics by CB. This can be explained by calcium-enhanced intermolecular connection between negatively charged surface groups of NOM and CB particles. Reducing solution pH increased NOM rejections from 31% and 33% (pH 7.7) to 46% and 57% (pH 4.3) for DOC and UV₂₅₄ removals, respectively. This revealed the pH-dependent adsorption process. Thus calcium addition is a strategy to control particle aggregation, extent of cake resistance, and increase removal of charged organic matter.

Afterwards, CB particles were employed in the pre-adsorption step for Stockholm surface water prior to membrane filtration. Accordingly, aggregate size of CB particles was enhanced before initiating filtration. Addition of CB into raw (feed) water significantly reduced fouling resistance whereas addition of PAC exacerbated membrane fouling though the DOC removal by CB was considerably lower than that by PAC. The selective adsorption of potential foulant, a small fraction of NOM in raw water, and a change in cake structure over the course of filtration were considered as key parameters affecting the performance of these two carbonaceous materials. Preferential adsorption of potential foulant was confirmed by the lower rate of fouling resistance for filtration of CB-raw water supernatant than that of diluted raw water that had the same DOC concentration. For a cake structure, PAC cake contained large voids allowing more hydrophobic organic compound to fill in and thus the dense, less permeable cake was formed as filtration proceeded. In contrast, the potential foulant was incorporated into CB particles during pre-adsorption step and hence the membrane surface was less prone to severe fouling. Since CB was chemically treated to be hydrophilic, CB cake would allow hydrophobic organic compound to

pass through so that CB cake structure did not change over the course of filtration. Alum coagulation removed primarily hydrophobic organic matter but increased the hydrophilic organic materials. CB was then added into the unstirred cell prior to filtration of alum-coagulated raw water. As a result, CB further removed organic matter and flux decline was reduced noticeably compared to alum treatment alone.

The presence of CB particles also reduced the irreversible fouling (increased flux recovery) after membrane cleaning. With the commercial humic acid (HA), cake layer formed by CB and HA was more easily removed by hydraulic rinsing than the cake layer made by HA alone. With the surface water containing NOM, irreversible fouling was less pronounced for raw water-CB filtration than filtration of raw water alone after chemical treatment and backwashing. To confirm this advantage of CB particles, the effect of CB addition on flux recovery in several batch filtrations was investigated using Tama River water. The result clearly showed that addition of 10 mg-CB/L made flux recovered completely during four batch runs while filtration of river water alone experienced the irreversible fouling after even the second run. These results may imply that the presence of CB particles adsorbed organic matter rapidly and prevented organic matter from forming a continuous cake layer which was difficult to be removed by chemical cleaning and backwashing in this study.

Effects of CB particles on membrane fouling had been extensively investigated with surface waters containing organic matter with different characteristics (e.g. molecular weight, size distribution and hydrophobic/hydrophilic property). The result demonstrated that the presence of CB particles reduced the boundary-layer resistance but caused cake filtration. By controlling particle flocculation, the cake resistance can be lowered considerably. CB exhibited selective adsorption of organic macromolecules and adsorption capacity increasing with reducing solution pH. CB particles also made cleaning and backwashing more effective with NOM cake and thus complete flux recovery can be attained in several batch filtrations with UF membrane.