

論文の内容の要旨

Removal of dissolved organic matter and phosphate by ferrihydrite for the control of bacterial regrowth potential

(微生物再増殖制御を目的としたフェリハイドライトによる溶存有機物とリンの除去)

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Dissolved organic matter (DOM) widely exists in aquatic system and affects water quality such as color, taste, odor and produce disinfection by-products (DBP). The most important is that the presence of DOM would promote bacterial regrowth that lead to biofouling on membrane surface and distribution pipes. According to the published, the biofouling potential is represented by the dissolved organic matter (DOM), microorganisms and the inorganic nutrient concentration in feed water. Among nutrient, phosphorus is an important component of bacterial cell. In addition, low phosphate concentrations can restrict biomass growth even at high organic carbon concentrations have been published. Therefore, minimizing DOM and nutrient (phosphate) availability by effective pretreatment is an effective biofouling reduction strategy.

Ferrihydrite (Fh) is a poorly crystalline iron oxide, has a large adsorption capacity for the phosphate, arsenate and organic matter present in natural systems since it presents an extremely high surface area and reactivity. The objective of this study was to investigate the effects of Fh on removal of both DOM and phosphate to control biofouling, and hybrid Fh with membrane system to separate Fh for application on practice.

The surface area and pore size of Fh was analyzed by nitrogen adsorption method. The synthesized Fh exhibited about 300 m²/g and comprised primarily mesopores. The average particle size of Fh was range 5 to 10 μm. The isotherm and kinetic adsorptions of DOM by Fh were tested with surrogate organic matters e.g. serine, glutamic acid, resorcinol and tannic acid as well as Suwannee river NOM (SRNOM) and Suwannee river fulvic acid (SRFA). Sorption increased in the order of tannic acid > glutamic acid > resorcinol ≈ serine. The results show tannic acids have high adsorption capacity, especially tannic acid was removed 81% by Fh at 10 mg Fe/L of Fh. Phenolic -OH groups of the tannin molecules were bound to Fh by hydrogen bonding, the adsorbed surfactant can become a partitioning phase on Fh which is more effective

for DOM adsorption. The adsorption of glutamic acid increased at lower pH, FT-IR spectra of treated Fh show the peak of COO^- appeared, suggested γ -carboxylate group was deprotonated and reacted with Fh by ligand exchange mechanism. Both hydrophobic and hydrophilic neutral DOM were difficult deprotonated and have low active functional groups on the surface to react with Fh. Fh more effectively remove iron DOM which contain carboxyl or hydroxyl function groups.

Adsorption of SRNOM onto Fh at different pH, Both DOC and UV_{254} removal by Fh increased as pH decreased from 11 to 6. It was constant as pH further decreased from 6 to 3. Adsorption of SRNOM by Fh was attributable to ligand exchange-surface complexation between carboxylic acids (20% of total C) of SRNOM and metal oxide surface, as well as hydrophobic interaction between aromatic moieties (23% of total C) and the oxide surfaces by FT-IR analysis. EEM spectra show that SRNOM mainly contains fulvic acid and humic acid, it was almost completely removed at pH 6 by Fh, and only very small residual of fulvic acid was observed by EEM at pH 9.

The effects of Fh adsorption were compared with powdered activated carbon (PAC) by Sanshiro Pond, coagulation, ozonation and biological activated carbon (BAC) processes by Arakawa River water. Assimilable organic carbon (AOC) and bacterial regrowth potential (BRP) were firstly used to evaluate bacterial regrowth potential after removal of both DOM and phosphate by different water treatment processes. The surface area of PAC was $956 \text{ m}^2/\text{g}$ with a highly porous when Fh was $300 \text{ m}^2/\text{g}$. Based on the pseudo second order equation, the adsorption rate of DOM by Fh was faster than that of PAC. Fh could be a better adsorbent for removing NOM within limited hydraulic residence times. Fh shows higher adsorption efficiency for DOM with MW larger than 1000Da. PAC adsorbed more DOM in a range of $800 < \text{MW} < 1000\text{Da}$. That is, PAC preferentially removed smaller MW organics than Fh. About 80% of phosphate was removed by Fh at the concentration of 50 mg/L as Fe, while PAC removed 15% of phosphate. Fh removed both DOM and phosphate in natural water.

Adsorption kinetics of DOC and phosphate were investigated in Arakawa River water. Adsorption was fast and instantly reached equilibrium in less than 5 min, the k_2 value for phosphate adsorption was higher than that for DOC. Phosphate forms a very strong surface complex with hydroxyl groups and has a higher affinity with Fh than DOC. The adsorption of DOM and UV_{254} decreased as pH was lowered from 11 to 3 in river water and consistent with synthetic water. Fh present negative charge at pH was larger than 8, which electrostatic repulsion with negative charged DOM. Comparison of different water treatments, removal of DOC and UV_{254} by Fh were higher than those after coagulation–sand filtration, which indicated

that Fh effectively removed both DOM and aromatic organic matter. Ozonation was more effective than Fh adsorption in reduction of UV_{254} and SUVA, which indicated that ozonation decomposed aromatic organic matter and produced more hydrophilic smaller molecules.

The AOC of Arakawa River water were ranged from 100 to 218 $\mu\text{g}\cdot\text{acetate}\cdot\text{C/L}$ during one year analysis. The value was slightly decreased after coagulation and increased again after ozonation treatment. Coagulation-sedimentation-sand filtration process removed 30% of DOC and 50%-60% of phosphate from raw water, resulting in higher reduction of BRP than AOC. This result showed that higher phosphate removal may effectively decrease BRP. In all the results of Fh treated water, the AOC level was nearly same with coagulated water. The concentration of phosphate was removed by Fh as low as 0.3 mg/L. It can effectively control the bacteria regeneration and provide low BRP value.

For application of Fh, a bench-scale unit was used for microfiltration (MF) and ultrafiltration (UF) to separate Fh and some parts of DOM in the feed water. On SRNOM solution, the flux decline of RC membrane not very different after addition of Fh in the existence of DOM and phosphate. After Fh reacted with DOM and phosphate, the particle size and characteristics of Fh were changed and formed loose cake larer on membrane surface which increased the permeability. During all processes, Fh hybrid membrane system shows the 90% removal efficiency for phosphate when membrane alone almost does not remove phosphate. Different with RC hybrid system, the flux of Fh-PES system reduced 50%. Since, the PES membrane existence of large negative charge which has strong attraction with positive charged Fh. Then, the Fh coated and deposited on the membrane surface, reduce the permeability of PES membrane. MF membrane alone practically did not reject DOM from water sample due to the large pore size. However, more than 90% of UV_{254} and 70% of DOC were removed after addition of Fh. Therefore, the Fh combined RC and MF membrane system show the high permeability and removal efficiency for DOM and phosphate.

Arakawa River water and Hanoi ground water were used to evaluate the effects of Fh-RC and Fh-MF systems. The flux sharply declined in all processes for filtration of Arakawa River water. Even though, the DOC and UV removal rates by Fh-membrane system also reached to 30% and 50%, respectively. The phosphate removal rate was higher than 60%. In order to determine the membrane fouling mechanisms on these two kinds of water, fouling models were used to distinguish the fouling type. The fouling of RC and MF membrane were pore blocking and pore constriction mechanism, respectively. However, very little fouling took place in filtering Hanoi water. The intramolecular binding of Ca^{2+} of Mg^{2+} decreased the DOM

molecular volume, and then the DOM size distribution became smaller to pass through the membrane. The DOM rejection and flux decline were lower than filtration of Arakawa River water. After addition of Fh, the flux was very stable and the removal rates of DOC, UV254, and arsenic reached 35%, 56% and 90%, respectively. Therefore, Fh hybrid membrane system exhibited higher removal rate for DOM, phosphate and arsenate in natural water. More importantly, the Fh not reduce membrane flux in combination system. Fh may combined with membrane system for application of raw water which contain DOM, phosphate or arsenate to control biofouling.