

論文概要
[Abstract of Thesis]

論文題目 [Thesis Title] * Effects of Humic Substances on the Initial Stage of Colloidal Flocculation Induced by Cationic Flocculants [陽イオン性高分子凝集剤によるコロイド凝集の初期過程に対する腐植物質の作用]

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The concurrent removal of dissolved organic matter and colloidal particles from water bodies is constantly required in the water treatment process. For this purpose, polymer flocculation is one of the most fundamental technologies with satisfying purification efficiency due to their strong affinity to the oppositely charged surfaces. Notably, anionic humic substances (HS) are one of the major groups of dissolved organic matter that commonly coexists with negatively charged particles in the water bodies. Although the presence of HS in water bodies is known to increase the dosage of cationic flocculants in flocculating colloidal particles, the underlying mechanisms are not well understood. In the absence of HS, many works have reported that the cationic flocculants enhance the colloidal flocculation by forming a thick adsorbed layer thickness on the particle. Subsequently, it improves the effective collision between particles and facilitates bridging flocculation. Thus, investigating flocculation at the early stage is necessary to understand how HS affects the flocculation mechanisms of cationic flocculants.

Herein, we studied how HS reduces the efficiency of cationic flocculants in the initial stage of flocculation. For the materials, a monodispersed polystyrene sulfate latex (PSL) particle was used as a model of suspended solids, five cationic polyelectrolytes differing in charge densities and branching degrees were employed as standard flocculants, and four polyanions differing in origins (synthetic or natural), molecular weights, and charge densities were used as model HS. First, all the samples were mixed using an end-over-end rotation apparatus for standardized turbulent mixing for the experiments. Then, the rate of flocculation, electrophoretic mobility of polymer-coated particles and polyion complex (PIC), and the adsorbed layer thickness of polymer on the particle were measured and used for analysis. Additionally, the characterization of polyelectrolytes was performed through viscometry, colloidal titration, and dynamic light scattering experiments.

Firstly, the influence of small oppositely charged polyanion, polyacrylic acid (PAA), on the flocculation induced by a highly cationic linear flocculant (PCMA) was investigated. In the absence of PAA, colloidal flocculation was remarkably enhanced by PCMA compared to salt-induced rapid coagulation. However, the presence of PAA inhibited the large enhancement in all tested conditions. The results suggest that the PAA regulated the cationic charge of PCMA, which induced shrinkage of PCMA. Consequently, it reduced the adsorbed layer thickness of polymer on the particle, which reduced the initial rate of flocculation. To confirm such an effect occurs in the real HS, PAA was replaced by fulvic acid (SRFA), and humic acid (SRHA) originated from the Suwannee River. Flocculation experiments demonstrated that all adopted polyanions inhibited the flocculation

enhancement. Additionally, the electrophoretic mobility experiments revealed that these polyanions increased the dosage of polycations required for particles to reach the isoelectric point. At the same polycation to polyanion charge ratio, the degree of inhibitory is arranged in PAA > SRHA > SRFA, corresponding to their affinity toward the polycations and particles. The results suggested that the inhibitory mechanism of polyanion on polycation-induced flocculation is mainly driven by the electrostatic attractions between polyanions and cationic flocculant, and this mechanism involves three stages. Apart from electrostatic attraction, the inhibitory degree of the polyanions on the flocculation rate depended on the polyanions adopted and is evidence of non-electrostatic inhibitory effects.

Following that, a low-charged density cationic flocculant (PTMC) was used to flocculate water containing the PSL particles and polyanions to reveal the non-electrostatic inhibitory effects of HS. Four polyanions differing in origins, molecular weights, and charge densities were employed. Electrophoretic mobility results revealed that the charging behavior of polymer-coated particles remained the same with and without polyanions. However, flocculation results revealed that the presence of all tested polyanions reduced the flocculation enhancement induced by PTMC. Furthermore, the degree of inhibitory of polyanions directly corresponds to their molecular weights. Moreover, electrophoretic titration confirmed that high molecular weight polyanions have a stronger affinity towards PTMC to form PIC. Accordingly, the non-electrostatic inhibitory mechanisms of HS on the polycation-induced flocculation, determined by their affinity towards other surfaces, are illustrated.

To further unravel the effect of HS in the polycation-induced flocculation, cationic flocculants differing in their branching degrees with similar charge density were studied. Although many works have reported the better flocculating abilities of branched flocculants, the reasons remained unclear. Hence, these flocculants are firstly used to flocculate water containing only particles. Flocculation results showed that linear flocculant induced patch flocculation, forming charge patches on the oppositely charged particle surface under the optimum dosage. Meanwhile, the branched flocculant enhanced the flocculation through patch flocculation accompanied by bridging effects. In excess dosage, the flocculation rate increased with the degree of branching, corresponding to their hydrodynamic adsorbed layer thickness. Such findings implied the importance of the relaxation behavior of the adsorbed polymer and were further investigated through the particle tracking analysis method. From the results, the branched polymer consistently showed thick adsorbed layer thickness than the linear ones. Branched polymer tends to retain its shape upon being adsorbed onto the particle due to their branched chains that are less susceptible to relaxation effect. Meanwhile, a flexible linear polyelectrolyte adopts a flat conformation upon adsorbed onto the particle.

Next, these flocculants were added into the water containing both particles and HS. Flocculation experiments revealed that colloidal flocculation is enhanced as it corresponded to the degrees of branching of flocculant. The results suggested that before approaching the particle surface, the flocculants firstly interact with the free polyanions in the bulk solution and/or polyanions adsorbed onto the particle to form PIC. Since all the PIC formed has a comparable charge, the difference between the flocculation enhancement is due to their adsorbed layer thickness on the particle. In contrast to the linear-polyanion PIC that adopted a flat conformation upon adsorbing onto the particle, branched-polyanion PIC maintains their shape upon adsorbing onto the particle. Subsequently, it increases the overall size of particle that improves the effective collision between particles and facilitates bridging flocculation.

Lastly, the flocculation mechanisms of all adopted flocculants in their optimum and excess dosage to flocculate particles and HS are compared. The critical findings of this work are then concluded with recommendations for future works.