博士論文（要約）

DISPERSION STABILITY OF TiO$_2$ NANOPARTICLES IN WATER AND THEIR REMOVAL BY COAGULATION AND MEMBRANE FILTRATION PROCESSES

（水中における二酸化チタンナノ粒子の分散安定性と
凝集・膜ろ過プロセスによる除去）

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In the past few decades, there has been a marked increase in the applications of nanotechnology to many industrial processes and products. Nowadays, nanotechnology has widespread application in agricultural, environmental and industrial sectors ranging from fabrication of molecular assemblies to microbial array chips.

The increasing amounts of nanoparticle production and use raised our concern about the environmental fates and ecological toxicity of nanoparticles. Among various nanoparticles produced by industries, titanium dioxide nanoparticles (TiO2 NPs) are produced by far the largest amounts for various uses including cosmetics, personal-care products, food additives, paints and coatings It was found that, although the majority of TiO2 NPs are discharged into sewerage systems, 10–100 μg/L of TiO2 remained in the secondary effluents. It was also suggested that landfills, previously assumed to be the ultimate sinks for engineered nanoparticles, may serve as continuous sources of engineered nanoparticles into aquatic environments. The objectives of this study are as follows: (1) To investigate factors affecting the dispersion stability of TiO2 NPs in synthetic and natural waters. (2) To assess the kinetics of ion adsorption onto the surface of TiO2 nanoparticles. (3) To estimate the removal efficiency of TiO2 NPs in drinking water treatment processes.

Chapter 1 is the introduction of the thesis, which includes the background and objectives of the study. Chapter 2 is the literature review that summarized the previous studies on fate and transport, as well as treatment efficiency, of nanoparticles. The fundamental theory of destabilization of nanoparticles is also described. Chapter 3 is the methodology of the experiments, and the common methods being used throughout the thesis are presented.

In Chapter 4, the effects of mixing time, cations and anions, and pH were evaluated by experimental studies, and the results were interpreted by the DLVO interaction model.

The surface charges of TiO2 NPs were different at 0.5 h and at 12 h under most of the experimental conditions, namely, destabilization at varied pH and ionic strengths. The solution pH also shifted towards the point of zero charge after 12 h. These results indicated that the ion complexation is slow especially under static condition. The slow complexation and aggregation may be explained by diffusion of ions into the aggregates and then equilibration with the bulk water, wherein ions form outer- or inner-sphere complexes with TiO2 NPs. Complexation of Na+ and Cl− alters solution pH and lessens the absolute values of the surface charge of TiO2 NPs. Hence, the combined effects of surface charge change by ion complexation and increased

ionic strength must be taken into consideration for the assessment of destabilization of TiO2 NPs by Na+ and Cl−. PO43- stabilized TiO2 NPs at low concentration below 10 mM, but destabilized at a higher concentration of 100 mM due to the limited sites for phosphate adsorption on TiO2 NPs and the increased ionic strength.

In Kasumigaura Lake water, TiO2 NPs were destabilized to become large enough to settle by gravity force due to high ionic strength (ca. 20 mM), though moderately high DOM containing fulvic acid was present in the lake water. However, it was a slow process taking about 12 h for complete aggregation and settling, which was similar to the aggregation in the synthetic waters. Despite addition of 20 mM PO43- into the Kasumigaura lake water, TiO2 nanoparticles were aggregated due to negligible effect of PO43- adsorption on the changes of the surface charge, which was overwhelmed by the effects of high ionic strength to bring the surface charge near zero, as shown in the Na and Cl complexation in pH-varied and IS-varied experiments. This result indicated that there is little effect of PO43- on stabilization of TiO2 NPs in natural waters including eutrophic, namely, PO43--rich, lake waters. The changes particles size could not elucidate the destabilization of TiO2 NPs because the particles sizes in the suspended NPs after setting could be smaller than those before destabilization and settling. The zeta potential changes were a good indicator of NP stability, but were not enough to explain the results of fairly good destabilization and settling even with high zeta potential values. The DLVO model elucidated fairly well the combined effects of ion complexation, ionic strength and the presence of multivalent counter ions in solution on stability of TiO2 NPs.

The volume-based particle size distribution showed polydispersity during the course of destabilization, which was more obvious at higher ionic strength. The number-based particle size was monodisperse, which showed an increasing trend when the. TiO2 NPs was destabilized at higher ionic strength.

In Chapter 5, the FTIR analysis showed chemisorption of carbonate species on the surface of TiO2 NPs that had been dispersed in Milli-Q water. The adsorbed carbonate species were replaced by HPO42- ions to form complexation on the surface of TiO2 NPs. Adsorption of carbonate anion onto the TiO2 NP surface at pH > pHpzc of the NP at a short contact time of 5 min probably forms ≡TiO-COCH3 and releases an OH- ion into the solution. The FTIR analysis suggests that organic and inorganic anions can form complexation on the surface of TiO2 NPs even at a short contact time of 5 min.

In Chapters 6, it was shown that a fraction of TiO2 NPs discharged into aquatic environment remain suspended and thus could enter into the sources of drinking water supply. Hence, the removal efficiencies of TiO2 NPs in drinking water treatment processes such as by coagulation and membrane filtration were evaluated. TiO2 NPs at different concentrations (1 mg/L and 25 mg/L) were removed by coagulation and membrane filtration. More than 90% of 25 mg/L TiO2 NPs was removed by coagulation and sedimentation when ferric chloride (FeCl3) and poly-aluminum chloride (PACl) were used as coagulants. In all coagulant dose, the energy barrier of the DLVO model diminished because of elevated ISs and surface charge changes. However, the changes of particle size were detected by NTA only when the coagulant dose was great enough, i.e. 0.2 mM FeCl3 or 0.2 mM PACl.

At the same molar concentration (0.2 mM), FeCl3 had better removal efficiency of TiO2 NPs than PACl. This was in agreement with the changes of the zeta potentials by addition of these coagulants; namely the zeta potential changed from negative to positive by addition of 0.2 mM FeCl3, while the zeta potential remained negative by addition of 0.2 mM PACl.

The particle size distribution before coagulation was unimodal with the mean diameter of 145 nm or 175 nm in the experiments with 0.2 mM FeCl3 or 0.4 mM PACl, respectively. The particle size distribution became multimodal after rapid aggregation, with three peaks greater than the original particle size before aggregation. However, after settling, the particle size of the suspended TiO2 NPs was smaller than the one before aggregation.

At 25 mg/L of TiO2 NPs, the concentration of TiO2 after 30-min gravity settling became lower by addition of NaCl and CaCl2 at 0.1 mM to 15 mM; thus it can be said that these salts enhanced coagulation of TiO2 NPs. This indicated that the background ion concentration is also important in improving the removal efficiency of TiO2 NPs. Membrane filtration of feed waters containing varied concentrations of TiO2 NPs revealed that the TiO2 concentration in the filtrate increases up to ca. 60 μg/L at the feed water TiO2 concentration of 1 mg/L, but then stabilizes at 60 μg/L up to the feed water concentration of 15 mg/L. However, the TiO2 concentration in the filtrate was twice as high at 121μg/L when the feed water TiO2 concentration was increased to 25 mg/L. After coagulation, the particle sizes of TiO2 aggregates in the supernatant became smaller than those before coagulation, thus the TiO2 concentration in the filtrate was higher after coagulation. Phosphate addition worked adversely for coagulation of TiO2 NPs, and brought about increase in the TiO2 NP concentration in the supernatant and in the filtrate of membrane filtration. However,

the removal rates, or percent removals, by 0.15μm membrane filtration increased by addition of PO_4^{3-}, while the removal rate decrease by 0.45μm membrane filtration. There was no effect of PO_4^{3-} addition to the TiO2 NP removal rates by PACl coagulation. The results given chapter 6 indicate that not only the dose (or concentration) of coagulants, we should also measure the concentration of ions such as Na^+, Ca^{2+}, and PO_4^{3-}, which might influence the removal rates of TiO2 NPs. In addition, the results indicated that the removal rates may vary in different seasons because of dilution of natural water by rainfall.

Chapter 7 describes the conclusion and recommendations. The aggregation process is slow in natural water bodies; thus we need to pay attention to the hydraulic retention time in estimating the fate of TiO2 NPs. Other factors that need to be taken into consideration in destabilization of TiO2 NPs are; the concentration of ions including Na^+ and Cl^-, which have been considered to be inert. Ions The DLVO model was effective in predicting the destabilization of TiO2 NPs in both synthetic and natural lake waters.

The coagulation and membrane filtration processes were effective in removing TiO2 NPs; however, up to 121 μg/L of TiO2 NPs remained in the filtrate. Since the particle size of residual TiO2 NPs was smaller than the initial one, aggregation of TiO2 NPs made it more difficult to remove TiO2 NPs by membrane filtration.

As it was found that, after coagulation, it would be more difficult to remove the residual particles having smaller mean sizes by microfiltration, it is recommended to look into the processes of aggregation more in detail so that we can understand why the smaller particles remain in the supernatant. Thus, we can explore the methods to control aggregation process of TiO2 NPs. Other types of membrane filtration should be also explored for the better removal of TiO2 NPs. Different processes other than aggregation and microfiltration are also to be evaluated for the better removal of TiO2 NPs.