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Оцінка поведінки наночастинок під час коагуляції з використанням SP-ICP-MS

Застосування інженерних наночастинок (ENP) викликає побоювання що до їхнього потрапляння в природні водойми через скидання стічних вод, через неправильну утилізацію виробів, що їх містять, або за допомогою вилуговування з поверхні фільтрів очищення питної води.

Потрібно мати надійний спосіб оцінювання поведінки наночастинок (ENP) при критичних процесах очищення питної води.

Коагуляція є одним з первинних процесів, використовуваних для видалення домішок і частинок з води; таким чином, розуміння долі наночастинок (ENP) під час типових процесів коагуляції потрібно для точного прогнозування їх впливу через питну воду.

Метод SP-ICP-MS є важливим досягненням в області моніторингу навколишнього середовища (ENP), який дозволяє швидко оцінити розмір, концентрацію і розчинність наночастинок металу (ENP) одночасно з мінімальною пробопідготовкою.

SP-ICP-MS методи є ефективними для виявлення і кількісного визначення наночастинок металів (ENP) Ag, Au, TiO, CeO і ZnO в воді. У даній роботі доля наночастинок цих металів під час коагуляції досліджувалася з безліччю ЄПС, які використовуються в споживчих і комерційних продуктах, ця робота зосереджена на п'яти поширених різновидах: Ag, Au, TiO₂, ZnO і CeO₂.

Доля цих частинок через процеси коагуляції в двох типах поверхневих вод оцінювалися з використанням методу SP-ICP-MS. У цих експериментах була проведена свип-флок або коагуляція в 4 зоні, коли коагулянт вводиться після точки розчинності, створюючи нерозчинні «пластівці». Інші частки в воді потрапляють в ці пластівці і видаляються під час седиментації. Це найпопулярніший режим коагуляції, який використовується як в стічних водах, так і в системах очищення питної води.

ПОСИЛАННЯ НА ДЖЕРЕЛО:

https://www.perkinelmer.com/lab-solutions/resources/docs/APP_013680_01_NexION_SP-ICP-MS_Fate_of_NPs_During_Coagulation.pdf



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За роки роботи в цій порівняно вузькій, але дуже цікавій сфері ми накопичили величезний досвід, яким хочемо ділитися. Тому проводимо кругові випробування, розробляємо нові ДСТУ, співпрацюємо з інститутами, надаючи їм обладнання для дослідницьких і освітніх цілей, беремо участь у лабораторних виставках і конференціях та організуємо їх. Тобто з ентузіазмом долучаємося до будь-якої діяльності, спрямованої на підвищення рівня контролю якості та природничих наук в Україні.

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ICP - Mass Spectrometry

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Assessing the Fate of Nanoparticles During Coagulation Using SP-ICP-MS

Introduction

The continued application of engineered nanoparticles (ENPs) raises concerns for their introduction into natural water bodies via wastewater discharge, incorrect disposal of products containing ENPs, and leaching from outdoor applications¹⁻³. If discharged into surface water collected for drinking water treatment, the

fate of ENPs during critical drinking water treatment processes used needs to be evaluated. Coagulation is one of the primary treatments used to remove particles from water for drinking use; thus, understanding the fate of ENPs during typical coagulation processes is required to accurately predict human exposure to ENPs via drinking water⁴. Single particle ICP-MS (SP-ICP-MS) is an important advancement in environmental monitoring of ENPs that has the capability to quickly evaluate ENP size, concentration, and dissolved metal concentration simultaneously with minimal sample preparation. SP-ICP-MS methods for characterization and quantification of Ag, Au, TiO₂, CeO₂, and ZnO ENPs in water have been developed recently^{5,6}.

With the multitude of ENPs utilized in consumer and commercial products, this work focused on five common varieties: Ag, Au, TiO₂, ZnO and CeO₂. The fate of these particles through coagulation processes in two surface water types were evaluated using SP-ICP-MS. More detailed information was published recently in *Chemosphere*⁷. Zone 4 coagulation, also known as sweep floc, was used for these experiments. Sweep floc occurs when coagulant is added past the point of solubility, creating insoluble “flocs” that aggregate. Other particles in the water are swept up into the coagulant flocs and are removed during sedimentation. This is the most popular mode of coagulation used in both wastewater and drinking water treatment systems due to ease of use.

Experimental

Materials

Citrate-stabilized Ag (40, 70, and 100 nm diameters) and Au NPs (50, 80, and 100 nm diameters) in 2 mM sodium citrate were purchased from nanoComposix, Inc. (San Diego, California, USA). Uncoated TiO₂ (100 nm), CeO₂ (30-50 nm), and ZnO NPs (80-200 nm) were purchased from US Research Nanomaterials, Inc. (Houston, Texas, USA). Stock suspensions of the ENPs were prepared in deionized water. Dissolved Ag, Au, Ti, Ce, and Zn standards, prepared in the sample water matrix to minimize any matrix effects, were used to calibrate the instrument.

To simulate coagulation processes, the most commonly used coagulants, including aluminum sulfate (Al₂(SO₄)₃·18H₂O, alum), ferric chloride (FeCl₃·6H₂O), and ferric sulfate (Fe₂(SO₄)₃·4H₂O), were purchased from Thermo Fisher Scientific, Inc. (Pittsburgh, Pennsylvania, USA). River water samples were collected from the Missouri River, and lake water samples were collected from Schuman Lake in Rolla, MO. Samples were taken from just below the water surface approximately two feet from the bank. Pre-cleaned polypropylene bottles were used to collect samples, which were stored in the refrigerator until use. Refrigerated samples were brought to room temperature before use.

Instrumentation and SP-ICP-MS Methods

A PerkinElmer NexION® ICP-MS with Syngistix™ Nano Application software module was used for sample analysis and data processing. The instrument and method parameters are shown in Tables 1 and 2, and are described in more detail elsewhere^{8,9}. To avoid ⁴⁸Ca interferences with ⁴⁸Ti, the most abundant Ti isotope, ⁴⁷Ti was selected for analysis.

Table 2. SP-ICP-MS Method Parameters.

Parameters	Ti	Ag	Au	Zn	Ce
Isotope (amu)	47	107	197	67	140
Density (g/cm ³)	4.32	10.49	19.3	5.61	7.13
Mass-Fraction (%)	60	100	100	80.31	81.41

Coagulation Treatments

A six-gang stirrer with 2-L square beakers was used for the coagulation treatments (Phipps and Bird). Following the addition of 2 L of water into the beaker, nanoparticles, including 70 nm Au (5 µg/L as Au), 80 nm Ag (2 µg/L as Ag), 100 nm TiO₂ (6 µg/L as Ti), 30-50 nm CeO₂ (5 µg/L as Ce), and 80-200 nm ZnO (6 µg/L as Zn), were added to the beakers and dispersed by stirring at 100 rpm for 1 min. Predetermined amounts of coagulants were added to the beakers and stirred at 300 rpm for 30 seconds (rapid mix) followed by 58, 42, and 28 rpm for 10 minutes each (flocculation) and finally at 0 rpm for 3 hours (sedimentation). Samples were taken immediately after dispersion and after sedimentation to evaluate the change in particle size, concentration, and dissolved ion concentration after treatments.

For this study, one specific type of coagulation treatment is highlighted: Zone 4, which involves adding coagulant past its solubility, resulting in the formation of insoluble precipitate. Particles are caught up in the formation of the precipitate and are removed through sedimentation.

Table 1. NexION ICP-MS Operating Conditions.

Parameter	Value
Nebulizer	Concentric
Spray Chamber	Cyclonic
Sampler Cone	Platinum
Skimmer Cone	Platinum
RF Power (W)	1600
Nebulizer Gas Flow (L/min)*	1.02-1.06
Sample Flow Rate (mL/min)*	0.26-0.29
Dwell Time (µs)	100
Sample Time (s)	100
Transport Efficiency (%)*	7.5-8.5

*Parameter optimized daily.

Results

Data Collection and Interpretation

Data demonstrating the change in size distribution histograms of Ag ENPs in river water and lake water after Zone 4 coagulation with three different coagulants are provided in Figure 1. "NO TREATMENT" samples were water matrix with ENPs added and were stirred and underwent sedimentation but did not have coagulant added. "BEFORE TREATMENT" samples were collected from each beaker immediately after the ENPs were dispersed in water matrix. No obvious shift in diameter was observed after each treatment. However, the decrease in frequency indicates that the ENPs were removed after each treatment to various levels.

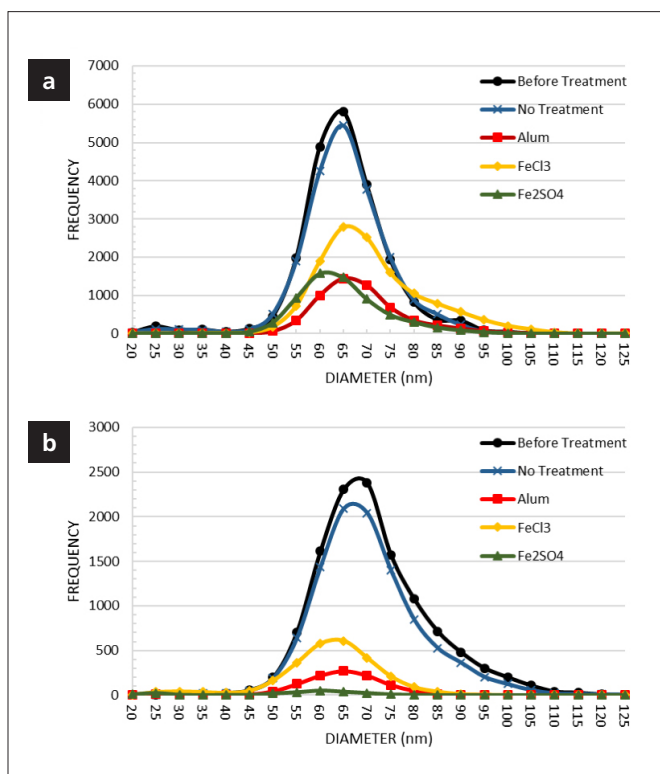


Figure 1. Change in size distribution histograms for Ag ENPs during various coagulation treatments in (a) river water and (b) lake water.

ENP Fate During Various Coagulation Treatments

The change in ENP particle concentration after various coagulation treatments was studied in river water and lake water. Particle-size-distribution histograms were generated for each treatment and each particle type. Combined distributions after each treatment for each type of particle are shown in Figures 2 and 3

for river water and lake water, respectively. Particle concentrations decreased after each treatment for all ENPs. The water matrix impacted size distributions, likely due to differences in dissolved organic carbon (DOC). CeO₂ ENPs showed greater stability in high DOC lake water compared to lower DOC river water, as indicated by a mean particle size closer to that of the primary particles in the standard. ZnO is known to be highly soluble in water, thus particle size will vary based on water chemistry. In this case, particles aggregated more in lake water compared to river water. In control samples ("NO TREATMENT"), where coagulant was not added to samples, the particle size and concentration was similar before and after treatment for most particles, showing stability between the time of ENP addition and final sampling. ZnO ENPs exhibited dissolution over time when no treatment was applied due to its known solubility in water.

For all types of coagulants, total ENP removal was improved when polymer was added as a coagulant aid. This result was expected due to the cross-linking nature of the polymer during floc formation. Compared to citrate-stabilized ENPs, uncoated TiO₂, CeO₂, and ZnO ENPs were more efficiently removed across all treatments in river water, likely due to the lower average surface charge resulting in more charge neutralization and aggregation. Contradictory results were observed in lake water, where removal decreased when the polymer coagulant aid was added. This result indicates that the polymer is less effective in waters with higher dissolved organic carbon (DOC), of which comparable results have been reported⁸⁻¹⁰. Alum with polymer addition resulted in the highest Ag and Au ENP, and uncoated ENP removal was similar among all treatments in river water. Ferric sulfate with polymer removed Ag and Au ENPs the best in lake water with ferric sulfate alone removing the most uncoated ENPs. These results are likely a product of water chemistry, dependent on pH, ionic strength, and DOC content.

Conclusions

Monitoring ENPs during drinking water treatment processes is important as their use in consumer and commercial products continues to rise. This work has demonstrated SP-ICP-MS to be a good technique to monitor the particle size and concentration of ENPs in surface waters. This study also demonstrated the efficacy of coagulation processes to remove ENPs from surface waters, an important parameter to consider for risk assessments.

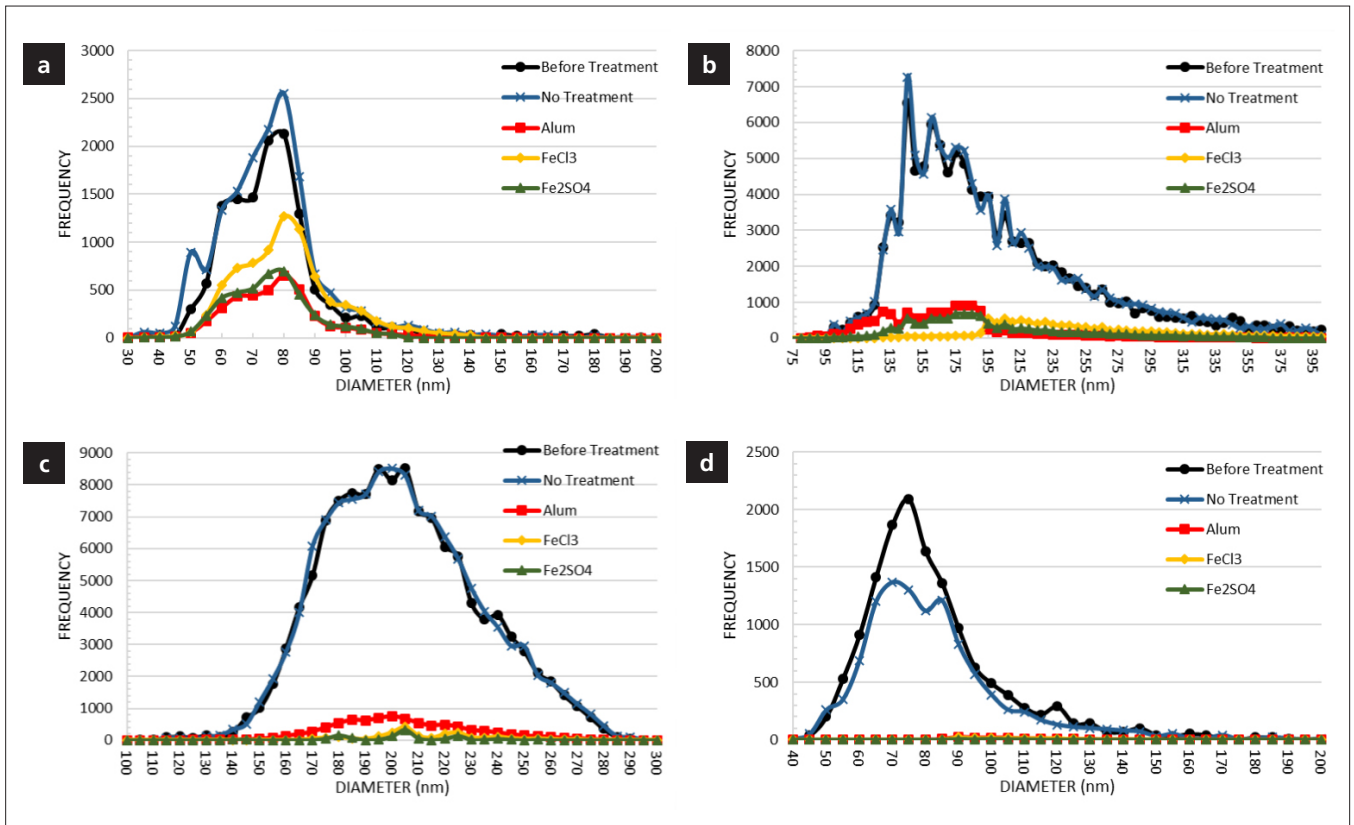


Figure 2. Size distribution histograms for (a) Au, (b) TiO₂, (c) CeO₂, and (d) ZnO ENPs after Zone 4 coagulation treatments using various coagulants in river water.

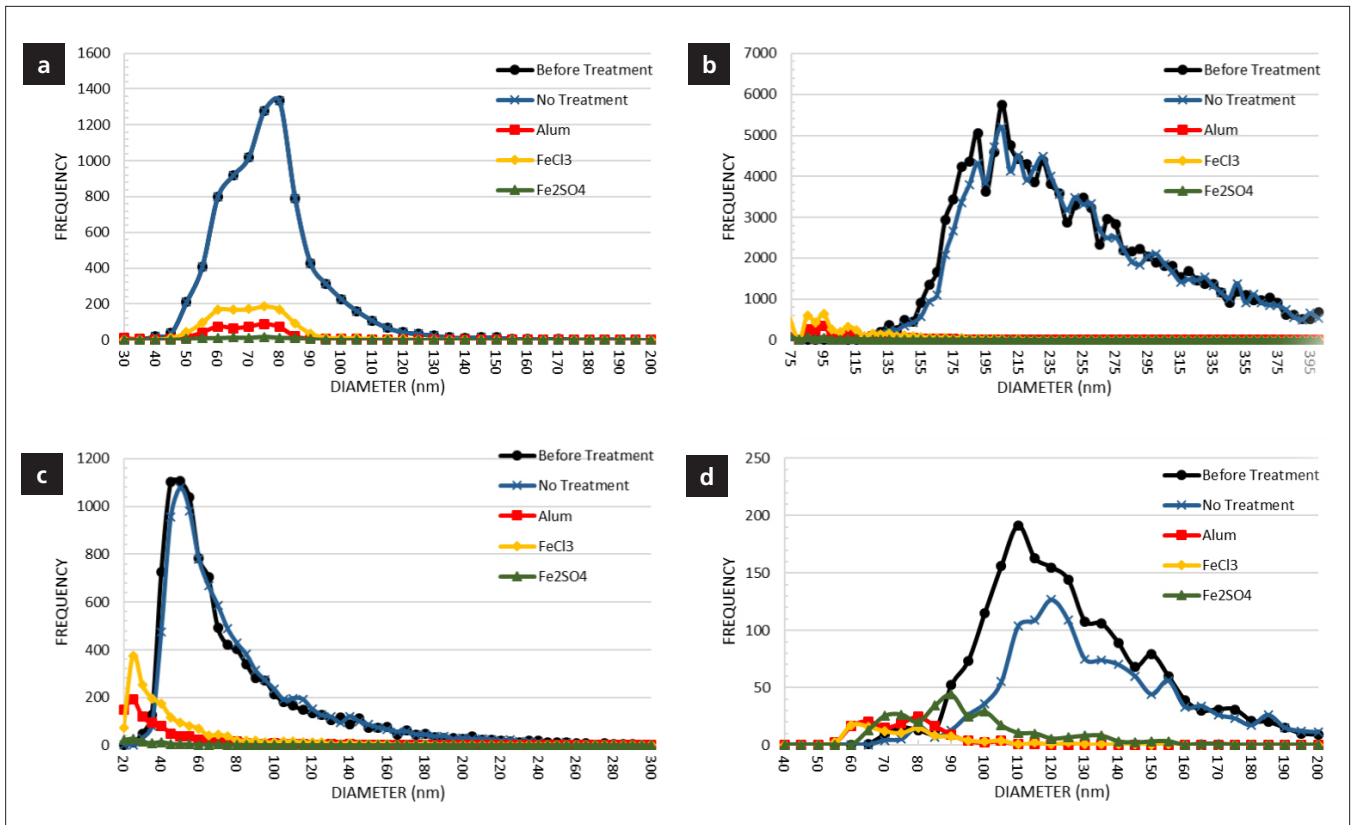


Figure 3. Size distribution histograms for (a) Au, (b) TiO₂, (c) CeO₂, and (d) ZnO ENPs after Zone 4 coagulation treatments using various coagulants in lake water.

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Consumables Used

Component	Part Number
Green/Orange (0.38 mm id) PVC Sample Uptake Tubing	N0777110
Gray/Gray (1.30 mm id) Santoprene Drain Tubing	N0777444
Sample Tubes	B0193233 (15 mL)
	B0193234 (50 mL)