

# Analysis of Membrane Filtration Efficiency for the Removal of Metal Oxide Nanoparticles from Aqueous Nanoparticle Suspension with Feed Coagulation Pretreatment

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## ABSTRACT

Discharge of engineered nanoparticles (eNPs) into aquatic systems is expected to increase with the accelerated manufacturing and use of eNPs. Therefore, it is necessary to identify and evaluate efficient methods for eNPs removal from aqueous system. In this study, the effectiveness of pH adjustment and coagulation of nanoparticles to enable sedimentation in addition to removal by membrane filtration (e.g., ultrafiltration) was examined for TiO<sub>2</sub>, ZnO, and CeO<sub>2</sub> nanoparticles. A series of optimization studies revealed that pretreatment of eNP suspensions by pH adjustment toward the isoelectric pH of the eNPs combined with coagulation using typical coagulants (e.g., ACH, FeCl<sub>3</sub>, and polyDADMAC), followed by sedimentation was effective in removing a significant fraction (up to 70%) of the eNPs from suspensions of concentrations as low as 20 ppm. Subsequent ultrafiltration of the supernatant allowed nearly complete overall eNP removal.

**Keywords:** nanoparticle, removal, coagulation, membrane filtration, isoelectric pH

## 1 INTRODUCTION

The introduction of engineered nanomaterials (eNMs) into freshwater and marine ecosystems is expected to rise with increased manufacturing and use of nanoparticles. Despite accelerated production and use of eNMs, studies of their potential environmental and human health impacts are in their infancy and the information on their removal from water systems is scarce. Given concern with the potential adverse impacts of eNMs, there is a need to evaluate effective methods for nanoparticle removal from aqueous system.

Removal of ENMs from aqueous suspensions by membrane ultrafiltration filtration can lead to severe membrane fouling. Therefore, in order to reduce the potential for membrane fouling, it is essential to pre-treat

the nanoparticle feed suspension to induce particle aggregation prior to membrane filtration. Aggregation of nanoparticles can be induced by the use of coagulants as well as via destabilization by pH adjustment toward the nanoparticle isoelectric pH (IEP; pH at which there is a zero nanoparticle surface charge). Coagulation involves the addition of chemical additives to form bridges between particles [3], leading to flocculation and coagulation that results in the formation of aggregates that are significantly larger than the primary nanoparticles. Gravitational sedimentation is then feasible with subsequent filtration for the remaining suspension (Fig. 1). Accordingly, in the present study, the effectiveness of pH adjustment combined with coagulation by commercially-used coagulants, followed by flocculation, sedimentation and ultrafiltration for the removal of metal oxide nanoparticles from aqueous suspensions was examined.

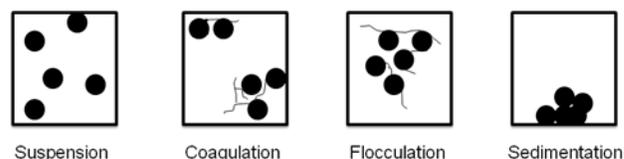


Figure 1: Mechanism of coagulation / flocculation / sedimentation process

## 2 MATERIALS AND METHODS

### 2.1 Preparation of nanoparticle suspension

Three types of commercial metal oxide nanoparticles were used in this study. Titanium dioxide (TiO<sub>2</sub>, density = 3.8 gm/cm<sup>3</sup>), Zinc oxide (ZnO, density = 5.6 gm/cm<sup>3</sup>), and cerium oxide (CeO<sub>2</sub>, density = 7.1 gm/cm<sup>3</sup>) nanoparticles with the reported primary size of 21, 10, and 10 nm in diameter and the reported IEP of 6.5, 9.5, and 7.8, respectively, in DI water. All aqueous nanoparticle suspensions were prepared at a concentration of 20 ppm via a protocol involving sonication in order to disperse the

suspension. The pH of the suspensions was adjusted to by adding 0.1 M HCl or 0.1 M NH<sub>3</sub>OH.

In order to evaluate the feasibility of coagulation to destabilize nanoparticles, three types of coagulants - Aluminum chlorohydrate (ACH), ferric chloride (FeCl<sub>3</sub>), and polydiallyldimethylammonium chloride (polyDADMAC) were utilized. Coagulant dose was maintained at 2 ppm for the three different antiscalants. After allowing the nanoparticle aggregates to settle the remaining suspension was filtered via cross flow ultrafiltration using a polysulfone UF membrane (MW cutoff of 77,000 g/mol).

The concentration of metal oxide nanoparticles before and after each removal step was measured by the Induced-Coupled Plasma Microscopy (ICP-MS) post acid digestion of the nanoparticles. The size distributions of the nanoparticle suspensions were determined via both dynamic light scattering (DLS) and static light scattering (SLS). The removal efficiency was for each removal step calculated as

$$\% \text{ removal of NPs} = (1 - C_{\text{final}}/C_{\text{initial}}) \times 100 \quad (1)$$

where  $C_{\text{initial}}$  and  $C_{\text{final}}$  are the initial and final nanoparticle concentrations, respectively.

### 3 RESULTS AND DISCUSSION

The aggregation behavior of TiO<sub>2</sub> nanoparticles was affected by the pH as shown in Figure 2. The largest nanoparticle aggregates were detected at pH 7, which is near the IEP of TiO<sub>2</sub> (6.5), while the aggregates were smaller at the pH removed from the IEP (pH 4 and 9, in this case). The above behavior is consistent with the removal efficiency as determined via ICP-MS, as illustrated in Figures 3 for TiO<sub>2</sub>. The highest removal (78% and 98%) was attained at pH 7 for TiO<sub>2</sub> nanoparticles and at pH 10 for ZnO nanoparticles (IEP 9.5), respectively. For the CeO<sub>2</sub> nanoparticles, pH did not significantly impact the removal efficiency of these nanoparticles which was high (>87%) for at the pH range of 7-10. The above results indicated that pH adjustment toward the IEP coupled with coagulation was capable of inducing nanoparticle aggregation and thus significant sedimentation removal.

The optimal condition for coagulation generally depends on the nature of the suspended solids to be destabilized, the water chemistry, and chemical cost [3]. In this study, a series of screening experiments were initially performed to select the optimal coagulant type and dose that would yield the highest degree of nanoparticles removal. Each type of coagulants was individually added to the nanoparticle suspension after pH adjustment and the efficiency of

removal determined as described previously. As illustrated in Figure 3, for example, the coagulant type did not have a measurable impact on the removal of TiO<sub>2</sub> nanoparticles. On the other hand, coagulant type did impact the removal efficiency of ZnO and CeO<sub>2</sub> nanoparticles; for the tested pH range (7-10), coagulation with ACH yielded high removal efficiency (>60%) of ZnO nanoparticles, while coagulation with FeCl<sub>3</sub> yielded the highest removal of CeO<sub>2</sub>. Studies at different coagulant doses demonstrated that at a relatively low coagulant dose (2 mg/L) was sufficient to remove 20 mg/L of the metal oxide nanoparticles from aqueous suspensions. Higher coagulant dose did not result in a higher degree of removal.

Enhanced removal of nanoparticles by ultrafiltration was evaluated in cross-flow filtration mode of operation. The supernatant of the suspension, after coagulation and sedimentation yielded removal efficiency up to nearly 100%. The study demonstrated that the combined approach of pH adjustment, coagulation and UF removal were effective with respect to removal efficiency. However, UF studies under extended operational periods in order to assess long-term operational stability with respect to nanoparticle fouling and possible impact on the membrane surface integrity.

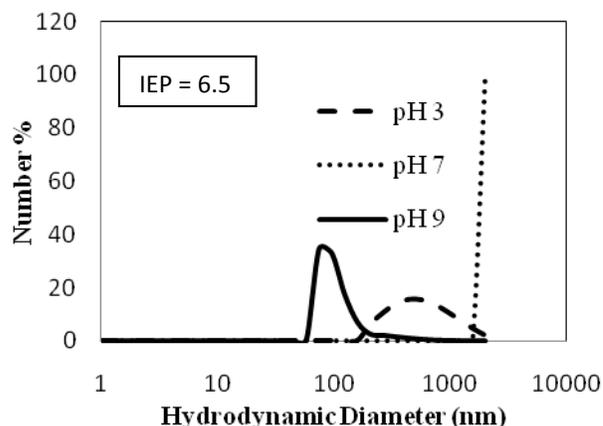


Figure 2: Particle size distribution showing the impact of pH on aggregation behaviors of 20 ppm TiO<sub>2</sub> nanoparticles in DI water

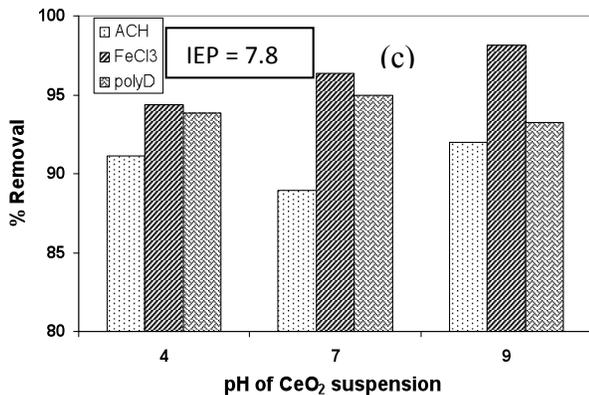
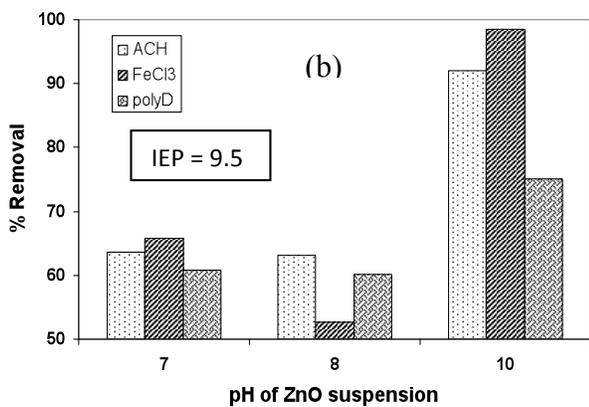
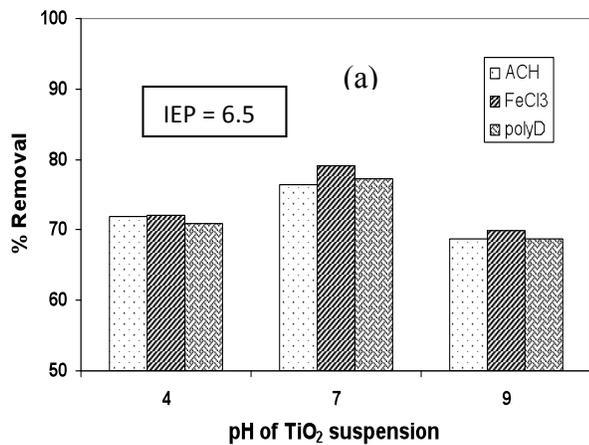


Figure 3: Effect of suspension pH and types of coagulants on removal efficiency of (a) TiO<sub>2</sub> (b) ZnO, and (c) CeO<sub>2</sub> nanoparticles

## 4 CONCLUSIONS

The efficiency of pH adjustment and coagulation treatment followed by sedimentation and integration with membrane ultrafiltration to remove metal oxide nanoparticles from aqueous suspension were evaluated experimentally. pH adjustment toward the IEP combined with coagulation at a coagulant dose of 2 mg/L enabled significant removal of nanoparticles (in excess of 70%) from suspensions of concentration as low as 20 mg/L. Subsequent ultrafiltration enhanced the overall percent removal of nanoparticles to essentially 100%.

## 5 REFERENCES

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