



Impact of biopolymer coating on the colloidal stability of manufactured CeO₂ nanoparticles in contrasting water conditions



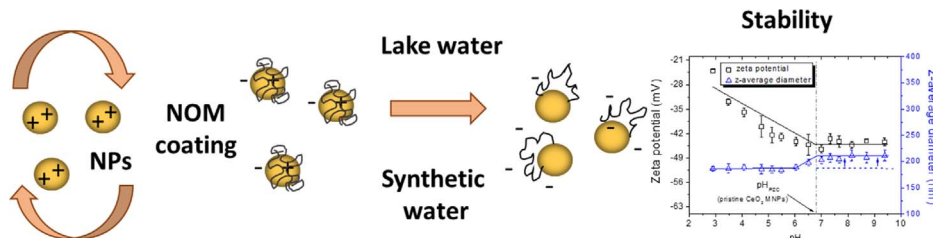
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GRAPHICAL ABSTRACT



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ABSTRACT

The use of cerium dioxide manufactured nanoparticles (CeO₂ MNPs) at a large scale in the industry, automotive and everyday products is resulting in a continuous emission and release of CeO₂ MNPs to the aquatic environments. In such complex systems, MNPs interact with water components, including biopolymers, resulting in MNP coating which give a new environmental identity to the MNPs and greatly influence their fate, transport and biological impact. MNP surface properties, aggregation, media composition such as ionic composition and pH, strongly influence the importance of natural organic matter coating and coating stability with time. In our study, we are using alginate, a relevant surrogate of natural organic polysaccharides, to coat CeO₂ MNPs under different conditions from ultrapure water to synthetic and natural waters. First, the most favourable conditions of alginate coating are defined and then the stability of this coating in changing pH condition is investigated. Then alginate coating impact, at variable alginate concentration, is studied in synthetic and natural waters and comparison is made with ultrapure water. The possible interaction mechanisms between alginate, CeO₂, dissolved ions (in particular divalent cations) and natural inorganic compounds are discussed. Our finding demonstrates that alginate concentration, solution pH and presence of divalent cations are key parameters defining the stability and effect of alginate coating and that once formed the biopolymer coating is found irreversible with time and when changing the solution chemistry.

1. Introduction

The wide application of manufactured nanoparticles (MNPs) has

increased the risk of their emission, release and environmental exposure [1–3]. Cerium dioxide (CeO₂) is one example of MNPs that are commercially used at a large scale in nano automotive products as

Abbreviations: MNPs, Manufactured nanoparticles; NOM, Natural organic matter; SEM, Scanning electron microscope; TEM, Transmission electron microscope; SI, Supporting information; IEP, Isoelectric point

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catalytic converters and diesel fuel additives to produce synthetic gas and reduce exhaust emissions, as polishing agents in chemical and mechanical polishing, planarization processes to produce transparent surfaces and as a component of compact fluorescent light tubes and interior coatings of self-cleaning ovens [4]. CeO₂ MNPs have found therefore wide applications owing to their physicochemical properties but pose a threat for the environment, for example, due to their active redox property [5–7]. Studies also demonstrate that CeO₂ MNPs have long persistence time after biological treatment in waste water treatment plants, accumulate in sludge [8,9] which results to the release of these MNPs with effluents into natural waters. After release, stability of MNPs generally depends on both nanoparticle and water properties [10,11]. One major natural water component which is expected to control the fate of MNPs is natural organic matter (NOM) [12,13]. NOM in aquatic systems is ubiquitous and mainly composed of humic substances and biopolymers (polysaccharides). In freshwaters, polysaccharide content can reach from 10 to 30% of the total amount of NOM [14].

Alginate is a polysaccharide which is commonly used as a relevant model and surrogate of natural polysaccharides [15]. Alginate is produced by some bacteria or brown algae and can be part of the algae cell walls [16]. Alginate has been used for various purposes [17,18] including applications for the improvement of water treatment processes [19,20] and for the sorption and elimination of pollutants such as heavy metals [21,22]. Alginate can have various effects on MNPs released in aquatic systems such as disaggregation or stabilization due to alginate coating [23,24]. Surface coating is expected to dominate the MNP surface properties [25,26] and often makes the surface potential of MNPs more negative in aquatic systems leading to a decrease in aggregation rate. However, coating property and stability with time is influenced by external factors such as pH, light radiation, competitive adsorption processes between water compounds and different natural organic matter fractions [27,28] implying the modification of MNP properties.

Aggregation of pristine and citrate coated CeO₂ nanoparticles was investigated in Volvic® water and in a mesocosm [27]. After one week 81% of the cerium from pristine nanoparticles was found in the sediment. However, for coated particles the concentration of cerium in the sediments was found to increase gradually and reach a maximum after four weeks. Such behavior was attributed to the degradation of the citrate coating because of dilution effects and light radiation. The authors assumed that in mesocosm experiments both homoaggregation and heteroaggregation were occurring due to surface charge changes and presence of natural colloids. It was shown that citrate coating of cerium dioxide nanocomposite was degraded during a long term aging under artificial daylight inducing surface changes and molecular reorganization of initial nanocomposite [28] and that the coating properties could change with time and have an impact on the final MNP properties, behavior in the environment [29,30] and therefore on living organisms [5,30,31].

Despite such findings, several key questions about aging and stability of natural organic coating around MNPs in aquatic systems are still not clear and need to be elucidated. In particular, the effect of pH on the coating properties is not well understood as well as the role of surface charge change and its implication in the mechanism of aggregation in complex environmental matrix. In addition, detailed mechanistic investigations in realistic environmental conditions such as in natural waters or at least in synthetic waters are also needed.

In the work presented here, we used alginate as a model of natural polysaccharide to form an organic coating around CeO₂ MNPs and alginate adsorption on CeO₂ in changing alginate concentration condition was studied. Two different electrostatic scenarios at pH > pHPZC and pH < pHPZC to investigate the effect of particle surface charge on the coating were considered. Then after formation of CeO₂/alginate complexes the stability of alginate coating in changing pH conditions was investigated. The effect of alginate coating in synthetic and natural

waters and the possible interaction mechanisms were also investigated by considering surface charge and z-average changes. SEM and TEM analysis were used to gain an insight into the homo- and hetero-aggregate structures in various environmental and coating conditions.

2. Materials and methods

2.1. Methods

2.1.1. Zeta potential and size distribution analysis

Z-average hydrodynamic diameters of pristine (uncoated) CeO₂ MNPs and mixtures of CeO₂ in presence of alginate as well as MNPs in synthetic and natural waters were measured with a Malvern Zetasizer Nano ZS (Malvern Instruments Ltd, UK). The autocorrelation function accumulated at least ten runs for each samples for five parallel measurements with time delay of 5 s. The hydrodynamic diameter d_H was calculated from the transitional diffusion coefficient D using the Stokes-Einstein equation. The polydispersity index was found less than 0.6 in all our measurements. To obtain information on the surface charge and changes via the zeta potential, the electrophoretic mobility was measured using the Doppler technique with the Malvern Zetasizer Nano ZS and the Smoluchowski approximation model was applied [32].

2.1.2. SEM image analysis

A JSM-7001FA (JEOL) scanning electron microscope (SEM) was used to obtain images of pristine CeO₂ MNPs and mixtures of CeO₂ with alginate. For each samples, 10 µL of the MNPs dispersion were placed on one aluminum stub covered with a 5 × 5 mm silica wafer Agar Scientific (G3390) and wrapped with 3–5 nm of Pt/Pd coating.

2.1.3. TEM image analysis

A Hitachi A7650 Transmission electron microscope (TEM) was used for imaging the texture, size, distribution, and morphology of the CeO₂ MNPs and also to precise the agglomeration-dispersion trends between non-coated and coated MNPs in ultrapure, synthetic and lake waters. The TEM configuration allows both high contrast (low Z element can be imaged) and high resolution (better than 5 Å). Thus, a condenser 2 with a large aperture (100 µm apparent diameter), associated with a diaphragm objective (20 µm apparent diameter) under an 80 keV accelerating voltage have been used. The samples were prepared directly onto the copper grid covered by an amorphous carbon thin film with a thickness around 50 nm (Delta MICROSCOPIES, France). Direct sample deposition of a 2 µm³ volume droplet using a dedicated syringe (Mettler-Toledo SAS, France) followed by several washing steps by ultrapure water, to minimize the formation of artefacts, especially for organic colloids or NOM associated with nanometric metallic trace elements [33].

2.1.4. pH measurement

The control of pH, by direct immersion of electrode in the solution, was done during all experiments with a Hach Lange HQ40d portable meter and one pH probe PHC101 (Hach Lange, Switzerland).

2.2. Materials

Uncoated CeO₂ MNPs as a powder (NM-212, JRC nanomaterial repository, Ispra, Italy) with a nominal particle diameter 28 ± 10 nm and a specific surface area equal to 27.2 ± 0.9 m²/g [34] was used. The powder was weighed and diluted in ultrapure water (R > 18 MΩ cm, Millipore, Switzerland) and the pH was adjusted to 3.0 to obtain a 1 g/L CeO₂ stable stock suspension. After sonication, aliquots of the stock suspension were used to prepare diluted suspensions for further experiments. A 50 mg/L CeO₂ suspension was used in all experiments unless indicated. Such a concentration was considered to optimize the signal during the dynamic light scattering and electrophoretic measurements. A detailed protocol for suspension preparation is provided

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