



# Aggregation behaviour of engineered nanoparticles in natural waters: Characterising aggregate structure using on-line laser light scattering



L. Chekli<sup>a,b</sup>, Y.X. Zhao<sup>a,c</sup>, L.D. Tijning<sup>a</sup>, S. Phuntsho<sup>a</sup>, E. Donner<sup>b,d</sup>, E. Lombi<sup>d</sup>, B.Y. Gao<sup>c</sup>, H.K. Shon<sup>a,b,\*</sup>

<sup>a</sup> School of Civil and Environmental Engineering, University of Technology, Post Box 129, Broadway, Sydney, NSW 2007, Australia

<sup>b</sup> CRC CARE, PO Box 486, Salisbury, SA 5106, Australia

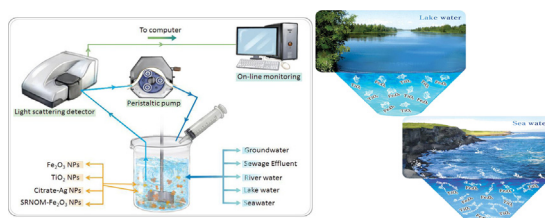
<sup>c</sup> Shandong Key Laboratory of Water Pollution Control and Resource Reuse, School of Environmental Science and Engineering, Shandong University, 27 Shanda South Road, Jinan 250100, People's Republic of China

<sup>d</sup> Centre for Environmental Risk Assessment and Remediation, University of South Australia, Building X, Mawson Lakes Campus, SA 5095, Australia

## HIGHLIGHTS

- We propose a novel method to study the aggregation of ENPs in natural waters.
- Aggregation and DOM adsorption were correlated to the initial TOC concentration.
- Aggregate structure were closely related to the amount of DOM adsorbed by the ENPs.
- Aggregate strength factor and fractal dimension were strongly correlated.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 15 August 2014

Received in revised form 22 October 2014

Accepted 4 November 2014

Available online 8 November 2014

### Keywords:

Engineered nanoparticles

Natural waters

Aggregation

Aggregate structure

Fractal dimension

## ABSTRACT

Adsorption of natural organic matter, aggregation and disaggregation have been identified as three of the main processes affecting the fate and behaviour of engineered nanoparticles (ENPs) in aquatic environments. However, although several methods have been developed to study the aggregation behaviour of ENPs in natural waters, there are only a few studies focusing on the fate of such aggregates and their potential disaggregation behaviour. In this study, we proposed and demonstrated a simple method for characterising the aggregation behaviour and aggregate structure of ENPs in different natural waters. Both the aggregate size of ENPs and their adsorption capacity for dissolved organic matter (DOM) were strongly related ( $R^2 > 0.97$ ,  $p < .05$ ) to the combined effect of initial concentration of dissolved organic matter (DOM) and the ionic strength of the natural waters. The structure of the formed aggregates was strongly correlated ( $R^2 > 0.95$ ,  $p < .05$ ) to the amount of DOM adsorbed by the ENPs during the aggregation process. Under high ionic strength conditions, aggregation is mainly governed by diffusion and the aggregates formed under these conditions showed the lowest stability and fractal dimension, forming linear, chain-like aggregates. In contrast, under low ionic strength conditions, the aggregate structure was more compact, most likely due to strong chemical binding with DOM and bridging mechanisms involving divalent cations formed during reaction-limited aggregation.

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## 1. Introduction

Over the past few decades, rapid progress in nanomaterial research and development has led to industrial scale production and extensive commercialisation of nanoproducts. As a result,

\* Corresponding author at: School of Civil and Environmental Engineering, University of Technology, Sydney (UTS), Post Box 123, Broadway, NSW 2007, Australia. Tel.: +61 02 9514 2629; fax: +61 02 9514 2633.

E-mail address: [Hokyong.Shon-1@uts.edu.au](mailto:Hokyong.Shon-1@uts.edu.au) (H.K. Shon).

engineered nanoparticles (ENPs) are increasingly released into the environment [1]. With several recent studies reporting potentially negative effects of ENPs [2–7], research into their environmental fate and behaviour is urgently needed to underpin risk assessment and policy development. However, until recently, few studies have investigated the behaviour of ENPs in real environmental samples, and little is known about their transport, fate and probable concentrations in different environmental compartments. A recent modelling study by Keller et al. [8] estimated that in 2010, 63–91% of the global ENP production ended up in landfills; 8–28% was released into soils; 0.4–7% into water bodies; and 0.1–1.5% into the atmosphere. Among the ENPs considered, titanium dioxide (TiO<sub>2</sub>) was released to the environment in the largest quantities, followed by iron and zinc [8]. Gottschalk et al. developed a probabilistic material flow analysis model to predict the environmental concentrations of ENPs and found that silver NPs (Ag NPs) present in sewage treatment effluents and surface waters, and TiO<sub>2</sub> NPs and zinc oxide NPs (ZnO NPs) in sewage treatment effluents, may pose a risk to aquatic organisms [9].

After entering the environment, the fate of ENPs greatly depends on their transport characteristics (i.e. aggregation, sedimentation or adsorption) and transformation (i.e. dissolution or chemical transformation) [10]. Agglomeration/aggregation and sedimentation are major processes affecting the behaviour of ENPs in aquatic systems and results suggest they are mainly controlled by the combined effects of pH, ionic strength, salt composition and the presence and concentration of organic matter [11,12]. Different experimental approaches have been tested to predict the behaviour of ENPs in aquatic systems. One approach is to consider the individual effects of different physical and chemical components (i.e. the effect of pH, a single electrolyte, organic matter, etc.) in order to identify the main factors affecting the stability of ENPs. A more realistic, yet more complex, approach investigates the behaviour of ENPs under environmentally-relevant conditions and ultimately in natural waters. Several recent studies have used these approaches to understand and predict the behaviour of ENPs once they enter the environment [12–24]. Results from these studies confirmed the role of pH, electrolyte composition and the presence of organic matter in the aggregation or stabilization of ENPs. However, very few studies (e.g. [13,25]) have focused on the structure and stability of the resulting aggregates and their potential for disaggregation. Aggregate structure (i.e. whether they are densely packed or loosely bound) is an important criteria to evaluate as it is likely to significantly influence aggregate behaviour and fate [11]. Nevertheless, knowledge in this area is still lacking, partly because this type of investigation provides a significant analytical challenge.

Light scattering detectors are simple, robust and accurate tools that can be used to measure particle size, aggregation behaviour and aggregate structure. They are currently among the most widely used techniques worldwide for aggregation studies. Dynamic light scattering (DLS), in particular, has been applied in most nanoparticle aggregation studies in both synthetic and natural aquatic media [12–14,21,23,26,27]. In this study, we proposed an alternative way to characterise the aggregation behaviour and aggregate structure

of various ENPs in complex environmental samples by performing continuous on-line light scattering analysis (i.e. combining both dynamic and static light scattering techniques) by using a pump to recirculate the sample inside the sample cell as shown in Fig. S1 of the Supporting information (SI). This simple set-up presents several advantages over conventional light scattering measurements. For instance, by recirculating the sample inside the measurement cell, it is possible to change the chemical or physical conditions of the sample or to apply external forces (e.g. by increasing the mixing speed inside the test jar to induce the disaggregation of the aggregates) and to directly observe and measure the effects of such changes on aggregate size. In addition, the fractal dimension (FD) of the aggregates can be studied using a static light scattering (SLS) instrument equipped with a series of photosensitive detectors positioned at different angles. Therefore, the method developed in this study can be useful to other researchers, working on fate of nanomaterials in the environment, to rapidly characterise the aggregation behaviour and aggregate structure of engineered nanoparticles (ENPs) formed in complex environmental system.

The overall objective of this paper was to assess and compare the aggregation behaviour and aggregate structure of different ENPs in a range of natural water sources using on-line laser light scattering detectors. Aggregates were characterised in terms of size, surface charge, DOM and Ca<sup>2+</sup> adsorption capacity, fractal dimension, disaggregation and regrowth potential. To the authors' knowledge, this is the first time that disaggregation and regrowth potential of ENP aggregates formed in natural waters has been investigated.

## 2. Materials and methods

### 2.1. Chemicals and reagents

Commercially available Fe<sub>2</sub>O<sub>3</sub> NPs and citrate coated-Ag NPs were supplied by Sigma–Aldrich, Australia. The Aeroxide P25 TiO<sub>2</sub> nanoparticles were provided by Evonik Degussa Corporation (Parsippany, NJ, USA). Suwannee River natural organic matter (SRNOM), used as a model NOM, was obtained from the International Humic Substances Society (IHSS, St. Paul, USA). Further details are available in Table 1.

### 2.2. Natural water samples

Five natural water samples were collected from a variety of sources across New South Wales, Australia: sewage effluent (Sew-Eff) from Sydney Olympic Park treatment plant, seawater (SeaW) from Chowder Bay (Sydney Harbour), lake water (LW) from Penrith, river water (RW) from Parramatta and groundwater (GW) from Williamstown. All water samples were filtered through a 0.2 μm polyethersulfone (PES) vacuum filtration unit (Vivascience AG, Germany), and stored at 4 °C in the dark prior to use.

More details on the sample preparation and physical and chemical characteristics of the water samples are given in the Supporting information (SI).

**Table 1**  
Characteristics of the tested nanoparticles.

	Fe <sub>2</sub> O <sub>3</sub> NPs	Citrate coated-Ag NPs	TiO <sub>2</sub> NPs	SRNOM-coated Fe <sub>2</sub> O <sub>3</sub> NPs	Source
Average primary particle size (TEM)	<30 nm	40 nm ± 4 nm	21 nm	–	Manufacturer
Density	1.17 g/mL ± 0.1 at 25 °C	0.990 g/mL at 25 °C	3.8 g/mL at 25 °C	–	Manufacturer
pH	3.7 ± 0.3	7.1 ± 0.1	3.5–4.5 (40 g/L)	–	Manufacturer
Initial zeta potential (mV)	+35.4 ± 2.2 (pH 4)	–35.7 ± 2.4 (pH 4)	+20.7 ± 1.5 (pH 4)	–30.1 ± 1.8 (as prepared)	This study
Point of zero charge (PZC)	7.0 (200 mg/L)	<2.0 (1 mg/L)	6.0 (25 mg/L)	<2.0 (as prepared)	This study – Fig. S5
CCC (mM NaCl)	50	73	21	110	This study – Fig. S6
CCC (mM CaCl <sub>2</sub> )	1.5	1.6	0.99	2.1	This study – Fig. S7

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