Agglomeration behaviour of titanium dioxide nanoparticles in river waters: A multi-method approach combining light scattering and field-flow fractionation techniques

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ABSTRACT

Titanium dioxide nanoparticles (TiO_2 NPs) are currently one of the most prolifically used nanomaterials, resulting in an increasing likelihood of release to the environment. This is of concern as the potential toxicity of TiO_2 NPs has been investigated in several recent studies. Research into their fate and behaviour once entering the environment is urgently needed to support risk assessment and policy development. In this study, we used a multi-method approach combining light scattering and field-flow fractionation techniques to assess both the aggregation behaviour and aggregate structure of TiO_2 NPs in different river waters. Results showed that both the aggregate size and surface-adsorbed dissolved organic matter (DOM) were strongly related to the initial DOM concentration of the tested waters (i.e. $R^2 > 0.90$) suggesting that aggregation of TiO_2 NPs is controlled by the presence and concentration of DOM. The conformation of the formed aggregates was also found to be strongly related to the surface-adsorbed DOM (i.e. $R^2 > 0.95$) with increasing surface-adsorbed DOM leading to more compact structures. Finally, the concentration of TiO_2 NPs remaining in the supernatant after sedimentation of the larger aggregates was found to decrease proportionally with both increasing IS and decreasing DOM concentration, resulting in more than 95% sedimentation in the highest IS sample.

Keywords: Titanium dioxide, river waters, aggregation, aggregate structure, field-flow fractionation.

1 Introduction

Progress in the nanotechnology research and development market has led to large-scale production and widespread commercialisation of nanoproducts (Ju-Nam and Lead 2008). Since their applications are expected to further broaden and increase in the future, this will inevitably result in the increasing release of engineered nanomaterials into the environment (Colvin 2003; Chen and Mao 2007; Kunhikrishnan et al. 2014). With several recent studies raising concerns about their potential negative effects on the environment (Lead and Wilkinson 2006; Handy et al. 2008; Chae et al. 2009; Gao et al. 2009; Hofmann and Von der Kammer 2009; Poynton et al. 2010; Scown et al. 2010), risk assessment of these new materials is urgently needed to support policy development and also to help in designing effective yet benign nanomaterials.

Among the various engineered nanoparticles (ENPs), titanium dioxide nanoparticles (TiO_2 NPs) are among the most heavily commercialized, finding applications in paints, cosmetics, catalysts and food colorants (Joo et al. 2009; Robichaud et al. 2009). A recent modelling study (Keller et al. 2013) demonstrated that in comparison to other commercially available ENPs, TiO_2 NPs were released to the environment in the largest quantities. The principal pathway for TiO_2 NPs into the environment is through wastewater treatment plants (WWTPs) (Gottschalk et al. 2009; Kiser et al. 2009; Gottschalk et al. 2010; Kunhikrishnan et al. 2014). In some studies (Gottschalk et al. 2009; Kiser et al. 2009), it has been demonstrated that TiO_2 NPs are only partly removed in WWTPs and thus a large quantity can enter the natural water system. TiO_2 NPs have also been detected in freshwater in concentrations in the range of a few μg/L following runoff from painted-house facades (Kaegi et al. 2008). The release of TiO_2 NPs into the environment raises concerns about contamination, both by the nanoparticles themselves and by their potential to co-transport sorbed contaminants into surface and groundwaters. As river waters are an important source of drinking water and a major component of surface waters, understanding the fate and behaviour of TiO_2 NPs in these natural systems is necessary to underpin robust risk assessment of these emerging contaminants.

The main processes controlling the behaviour of ENPs in the aquatic environment were found to be natural surface coatings, aggregation/disaggregation and sedimentation (Lowry et al. 2012). Previous studies suggested that these processes are mainly influenced by the combined effects of ionic strength (IS), salt composition, pH and the presence and concentration of organic matter (Dunphy Guzman et al. 2006; Phenrat et al. 2007; Christian et al. 2008; Keller et al. 2010; von der Kammer et al. 2010). These studies have used different methods to predict the behaviour of ENPs in natural waters among which the study of the individual or combined effects of different physical and chemical components (e.g. pH, single electrolyte or natural organic matter concentration). Although results from this approach can help in gaining quantitative data and are easily reproducible, they are only valid for the test conditions used and cannot necessarily be extrapolated to predict ENP behaviour in natural systems.

In our previous study (Chekli et al. 2014), we developed a novel set-up combining both dynamic and static laser light scattering techniques to study the aggregation behaviour and aggregate structure of ENPs in various natural water samples. Light scattering techniques are widely available but suffer from the strong particle size dependence of the scattering intensity (Hiemenz and Rajagopalan 1997). This leads to Z-average or intensity values being skewed toward larger particles/aggregates (Domingos et al. 2009). To circumvent this limitation, we further developed this light scattering set-up by combining it with different off-line analytical techniques to better assess the polydispersity of the sample. The larger aggregates formed under a fast-aggregation regime were characterised in terms of size and structure by use of the on-line light scattering set-up. After sedimentation, the smaller particles/aggregates were collected and characterised by both dynamic light scattering (DLS) and flow field-flow fractionation (FlFFF).

The overall objectives of this study were:

a) to investigate the agglomeration behaviour of TiO_2 NPs in different river water samples using various analytical techniques. The benefit of using a multi-method approach to characterise ENPs in complex environmental samples has already been demonstrated (Domingos et al. 2009; Chekli et al. 2013) but has not been systematically applied in aggregation studies using natural waters;

b) to assess the strength and recovery factors and the structure of the aggregates formed in the river waters.

2 Materials and methods

2.1 TiO_2 nanoparticles

Commercial Aeroxide P25 TiO_2 NPs (average primary particle size reported by the manufacturer 21 nm) were purchased from the Evonik Degussa Corporation (Parsippany, NJ, USA). Further details on this material including the zeta potential profile, scanning electron microscopy (SEM) images and critical coagulation concentration (CCC) for both NaCl and $CaCl_2$ suspensions, are available in the Supporting information (Tables S1, S4 and Figure S1, S2). The methodology for the sample preparation of TiO_2 NPs is also described in the Supporting information (SI).

2.2 Natural river water samples

Four river water samples were collected along the Parramatta River (NSW, Australia) at different distances from the sea to obtain a gradient in both DOM concentrations and solution

IS. More details on the sample preparation methods and the physical and chemical characteristics of the water samples are given in the Supporting Information (Table S2).

2.3 Aggregation study in river waters

The work of Phenrat et al. (2007) formed the basis for the study of the aggregation/sedimentation process. According to their study, there is a critical size (d_c) above which aggregates will sediment rapidly while aggregates having lower sizes ($d < d_c$) will remain suspended. Aggregation of the residual smaller aggregates will then occur slowly with time followed by sedimentation when their size reaches d_c. In this study, we firstly characterised the large aggregates ($d > d_c$) formed under a fast-aggregation regime or reaction-limited aggregation (RLA) (Weitz et al. 1985; Klein and Meakin 1989) using an on-line light scattering method. After this initial fast sedimentation process, the smaller aggregates remaining in suspension were collected and analysed by both DLS and FlFFF.

2.3.1 On-line light scattering measurements

TiO_2 NPs were added to the different river water samples (final concentration in river waters of 12.5 mg/L) using a variable-speed jar tester (ZR4-2, Zhongrun Water Industry Technology Development Co., Ltd., China) which was connected to a peristaltic pump (Model 77521-47, Masterflex, Cole Palmer, Australia). Details on the experimental protocol of the on-line light scattering set-up can be found in our previous study (Chekli et al. 2014). The water samples were pumped directly to the light scattering instrument for continuous particle/aggregate size analysis: a dynamic light scattering (DLS) instrument (model ZEN3600; Malvern Instruments, Worcestershire, UK) was used for particle size ranging from 10 nm to 6 µm and a static light scattering (SLS) system (Malvern Mastersizer 2000, Malvern Instruments, Worcestershire, UK) was utilised for measuring the larger particles.

In addition to particle size analysis, the amount of DOM adsorbed during the aggregation process was also measured at the end of the aggregation experiments. Surface-adsorbed DOM was measured by a TOC analyser (TOC-VCPH, TNM-1, Shimadzu, Japan) using 50 mL samples which were first centrifuged for 10 min at 2500 *g* (Model 2040, Centurion Scientific Ltd, UK) to separate the solution phase from the solid particles. The amount of DOM adsorbed on the surface of TiO_2 NPs during the aggregation process was calculated using the following equation:

$$q = (C_0 - C_f)\frac{V}{m} \qquad (1)$$

where q (mg/g) is the amount of DOM (mg) adsorbed per mass (g) of TiO_2 NPs, C_0 and C_f (mg/L) are the initial and final concentration of DOM in solution, V (L) is the solution volume and m (g) is the mass of the TiO_2 NPs injected into the river water samples. Measurements were performed in triplicate and the results presented are average values with standard deviations.

After the aggregation experiments, the larger aggregates were allowed to settle before the supernatant was collected following the protocol described in v.d. Kammer et al. (2010) (i.e. the supernatant should be collected after the fast aggregation reaction and before the most stable dispersion starts to settle). Concentration of the stable fraction of TiO_2 in the supernatant was determined by measuring the nephelometric turbidity as described earlier.

2.3.2 Dynamic light scattering – batch mode

After sedimentation of the larger aggregates, the supernatant (5 mL) was collected and analysed with a Zetasizer (model ZEN3600; Malvern Instruments, Worcestershire, UK) operating with a He-Ne laser at a wavelength of 633 nm to determine both the zeta potential and hydrodynamic diameter of the different samples. Physical principles, mathematical treatment, and limitations of the DLS data can be found elsewhere (Filella et al. 1997).

2.3.3 Flow Field-Flow Fractionation

The FlFFF system used in this study has been described in our previous studies (Chekli et al. 2013; Chekli et al. 2013). The theory and principles of FlFFF can be found elsewhere (Giddings 2000).

The operating conditions are summarised in the Supporting Information (Table S3). At least three independent replicates were run per sample and the data were averaged. In general, good agreement was observed between replicates (i.e. peak heights differed by less than 5 %). Samples used in FlFFF experiments were the same as for DLS experiments to ensure data comparability.

2.3.4 Data analysis

In order to assess the independent and combined effect of both the ionic strength and initial TOC concentration of the natural waters on the aggregate size and surface-adsorbed DOM; single and multiple linear regression analysis were carried out. In fact, preliminary screening showed that both the ionic strength and initial TOC concentration of the natural waters tested were the two main variables controlling the aggregate size and surface-adsorbed DOM.

The statistical significance of the effect of each variables (independently and combined) on each property tested was assessed by analysis of variance (one-way ANOVA, $p < .05$).

2.4 Aggregate structure

2.4.1 Strength and recovery factors

The aggregates formed under the fast-aggregation regime were subjected to a high mixing speed of 200 rpm (i.e. 315 g) for 5 minutes to induce their disaggregation. After breakage, slow mixing (i.e. 40 rpm; 25 g) was reintroduced for 15 minutes to allow the aggregates to regrow. The size of the aggregates was measured by drawing the sample through the optical unit of the SLS detector and back into the jar using the peristaltic pump. Size measurements were taken every 30 seconds for the duration of the experiment and recorded on a computer.

To evaluate both the strength and recoverability of the formed aggregates, the strength factor (SF) and recovery factor (RF), were calculated as follows (Yukselen and Gregory 2002; Jarvis et al. 2005; Zhao et al. 2012):

$$\mathrm{SF} = \frac{d_2}{d_1} \times 100 \tag{2}$$

$$\mathrm{RF} = \frac{d_3 - d_2}{d_1 - d_2} \times 100 \tag{3}$$

where d_1 is the average aggregate size of the plateau before applying the shear force, d_2 is the average aggregate size after breakage, and d_3 is the average aggregate size after regrowth to a new plateau.

Greater SF values are indicative of aggregates that are better able to resist shear. These aggregates are thus considered to be stronger than those in a suspension with a lower SF. Similarly, an increase in the RF value indicates the presence of aggregates that have better regrowth after exposure to high shear.

2.4.2 Aggregate structural analysis

There are two distinct regimes of irreversible colloid aggregation: reaction-limited aggregation (RLA) and diffusion-limited aggregation (DLA). The DLA regime will occur when there are no or negligible repulsive forces between particles, and aggregation is mainly controlled by diffusion (Klein and Meakin 1989), whereas the RLA regime will occur when there are significant but not insurmountable repulsive forces between particles (Weitz et al. 1985; Klein and Meakin 1989; Lin et al. 1990).

The highly disordered structure of colloidal aggregates can be characterised by its scaling behaviour, defined as the mass fractal dimension (FD) (Weitz et al. 1985; Rice and Lin 1993). Typical FD values are FD ~ 1.8 for DLA, and FD ~ 2.1 for RLA, indicating a more compact structure for aggregates formed under the RLA regime (Klein and Meakin 1989).

The use of Mastersizer 2000 for the determination of FD has been previously reported (Rieker et al. 2000; Jarvis et al. 2005; Zhao et al. 2012). The total scattered light intensity I, the scattering vector Q and the FD followed a power law as follow (Gregory and Duan 2001):

$$I \propto Q^{-FD} \tag{4}$$

The scattering vector Q is determined as follow (Rieker et al. 2000):

$$Q = \frac{4n\pi \sin(\theta/2)}{\lambda} \tag{5}$$

where, n, θ and λ are the refractive index of the medium, the scattering angle and the laser light wavelength in vacuum, respectively.

3 Results and discussion

3.1 Characteristics of the river waters and stability of TiO_2 NPs in DI water

The characteristics of the tested river waters are presented in the Supporting Information (Table S2). The pH of the different river samples was restricted to a narrow range (i.e. 7.36 – 8.04). However, as expected, a gradient in both the DOC concentration (3.21 – 10.01 mgC/L) and solution IS (2.8 – 342.0 mmol/L) was obtained. The ionic composition and more specifically the ratio between mono- and divalent cations also varied significantly between the tested samples with monovalent cations (especially Na^+) becoming dominant in the highest IS river sample due to the vicinity of the ocean. This will have an important impact on the aggregation behaviour as the critical coagulation concentration (CCC) of mono- and divalent cations is approximately 1:0.033 (molar ratio) (Elimelech et al. 1998; Stumm and Morgan 2012). This suggests that, if only considering electrostatic interactions and neglecting the effects of specific adsorption (e.g. with NOM), the concentration of divalent cations should dominate the behaviour of ENPs in most surface waters (von der Kammer et al. 2010).

The hydrodynamic diameter of the TiO_2 NPs in DI water (pH 4) was measured to ensure their stability before being subjected to the natural river waters. The results are presented in Table 3 and the supporting information (Figure S6 and Table S2, SI) and showed a small variation in size (< 5%) over the 30-minute test period (Figure S6, SI). Size measurements by both online DLS and scanning electron microscope (SEM) were not in agreement with the data reported by the manufacturers (Table S1, SI). TiO_2 NPs were present in small aggregates of around 250 nm in diameter rather than well-dispersed as 21-nm primary particles. This is consistent with previous studies which found that TiO_2 NPs form strongly bound aggregates when dispersed in aqueous solutions (Jiang et al. 2009; von der Kammer et al. 2010; Romanello and de Cortalezzi 2013).

3.2 Characterisation of aggregate size and DOM adsorption capacity

Tables 1 and 2 gather the results of the aggregation experiments. In all tested samples, TiO_2 NPs formed larger aggregates in river water than in DI water with aggregate sizes ranging from submicron (i.e. 987 nm ± 8 nm in $R_{2.8}$) to tens of micrometers in the higher IS river samples. These results are in agreement with previous studies by French et al. (2009) and Ridley et al. (2006) who measured TiO_2 NPs aggregate size through optical images and laser diffraction analyses respectively, and found aggregate sizes up to 30 μm in aqueous media at different IS and ionic composition.

Results from Table 1 also show that the aggregation of TiO_2 NPs and more specifically the aggregate size varied positively with the increase in IS and negatively with the amount of DOM present in the natural waters. This is in accordance with the classical DLVO theory (Derjaguin and Landau 1941) which demonstrates that an increase in the IS will lead to a decrease in the repulsive forces between particles and thus enhance aggregation. Similarly, the amount of DOM adsorbed on the surface of TiO_2 aggregates (Table 1) decreased with increasing IS and increased with increasing amount of DOM present in the natural waters. Other recent studies reported the strong influence of both IS and DOM on the stability of TiO_2 NPs (French et al. 2009; Ottofuelling et al. 2011; Brunelli et al. 2013; Romanello and de Cortalezzi 2013; Erhayem and Sohn 2014).

Table 1

Single and multiple linear regression analyses combined with one-way ANOVA tests were then performed to investigate the independent and combined effect of IS and initial TOC concentration on both the aggregate size and surface-adsorbed DOM in order to determine which variables influence the most on these 2 parameters. The results are gathered in Table 2.

Table 2

These analyses show that 91% of the aggregate size variability was explained by the initial TOC concentration whereas the IS of the natural waters did not significantly affect the aggregate size (i.e. $R^2 = 0.58$, $p > .05$). This is in accordance with our previous study (Chekli et al. 2014) where we found that 85% of the ENPs aggregate size variability was related to the initial TOC concentration of the natural waters. The multiple regression analysis (i.e. combining the effect of both IS and initial TOC concentration), even though not statistically significant (i.e. $p > .05$), confirmed that the aggregate size was positively related to the IS of the solution and negatively related to the initial TOC concentration (i.e. slope values on Table 2).

The amount of DOM adsorbed on the surface of TiO_2 NPs was also found to be strongly dependent (i.e. $R^2 > 0.99$, $p < .005$) to the initial TOC concentration of the river waters. The combined effect of IS and initial TOC concentration was also found to significantly affect the surface-adsorbed DOM (i.e. $R^2 > 0.99$, $p < .05$) although the initial TOC concentration had much more influence than the IS of the solution (Table 2, slope values: 0.01 against 21.8 for IS and initial TOC concentration respectively).

3.3 Characterisation of aggregate structure

3.3.1 Aggregate strength and recoverability

The strength and recoverability of the formed aggregates were firstly assessed by using a high mechanical shear force to induce their breakage followed by a 15-minute period of slow stirring to let the aggregates grow again. The strength and recovery factors (SF and RF) of the aggregates were then calculated based on equations 2 and 3. Results are presented in Figure 1 and Table 1.

Figure 1

Figure 1 shows that, when the aggregates were subjected to the high shear force, their size immediately decreased in all river waters. Following the breakage period, a slow stirring was reintroduced and aggregates started to regrow in all samples. The SF values were negatively correlated to the ionic strength of the samples whereas a positive correlation was observed between RF and IS. The recoverability of the aggregates in all river waters was only partial (i.e. RF < 100%). RF values generally provide information about the internal bonding structure. In previous studies focusing on the coagulation/flocculation process (Jarvis et al. 2005; Zhao et al. 2012), the irreversible breakage of the flocs was explained by their formation mechanisms which were due not only to pure charge neutralisation (i.e. which would have caused complete recoverability) but also to the formation of internal chemical bonds such as hydrogen bonding. In the present study, internal chemical bonds could originate from the interaction between the negatively charged carboxylic groups of DOM (i.e. $R\text{-}COO^-$) and the positively charged surface of TiO_2 NPs (i.e. + 28.5 mV at the beginning of the experiments). Table 1 shows the amount of DOM adsorbed during the aggregation process and it can be seen that this amount proportionally decreased with increasing IS. Simultaneously, the increase in RF correlates well with the increase in IS and thus with the decreasing amount of DOM adsorbed by the NPs during the aggregation process. These results suggest that DOM may play an important role in the aggregate recoverability.

The SF values were also strongly correlated (linear relationship, $R^2 = 0.9809$) with the surface-adsorbed DOM as seen in Figure 2a; suggesting the formation of more compact aggregates when increasing quantities of DOM are adsorbed during the aggregation process. Similar findings were observed in a previous study (Baalousha et al. 2008) where it was found that the addition of humic acid (HA) induced a change in aggregate structure.

Figure 2

3.3.2 Aggregate structural analysis

The structure of nanoparticle aggregates can also be described by their mass FD (Weitz et al. 1985; Rice and Lin 1993) which can provide valuable information about the morphology of the aggregates (Christian et al. 2008). Table 1 shows the FD values obtained in the different river waters before the shear force was applied. These values decreased with increasing IS suggesting that aggregates formed under low IS conditions will have a more compact structure than the ones formed under higher IS. In fact, in R_{342}, aggregates were formed under high IS conditions, much higher than the CCC of TiO_2 for Ca^{2+} which resulted in fast aggregation or diffusion limited aggregation (DLA) under which linear and loosely bound aggregates are generally formed (Klein and Meakin 1989). However, in $R_{2.8}$, the low IS condition promoted reaction-limited aggregation (RLA) or slow aggregation giving rise to more compact aggregates.

The difference in aggregate compactness observed in the different river waters can also be explained by the amount of DOM adsorbed during the aggregation process. In fact, Baalousha et al. (2008) demonstrated that in the presence of HA, compact aggregates with high FD were formed, whereas in the absence of HA, the nanoparticles formed open porous aggregates with a lower FD. In another study, Christian et al. (2008) explained that the adsorption of HA on ENP surfaces may occur in two steps. First, HA will cover the ENPs surface in a fast adsorption step. This can be then followed by slow diffusion of HA molecules within the formed aggregates leading to a more compact structure. Results from this study confirmed the role of DOM adsorption in aggregate compactness as the highest FD values were observed in the samples where DOM adsorption was the highest.

Finally, Figure 2b also shows that there is a strong correlation (linear relationship, R^2 = 0.9882) between FD and SF values. This was already demonstrated in a previous study by

Wang et al. (2009) where they observed a good relationship between floc SF and floc structure. This is also in accordance with our previous study (Chekli et al. 2014) where it was also found that the aggregate SF was strongly related to the aggregate FD. This correlation can be explained by the disaggregation kinetic which was found to be largely dominated by the compactness of the aggregates related to their FD (Jarvis et al. 2005; Christian et al. 2008; Chowdhury et al. 2013). Two disaggregation mechanisms were identified by Jarvis et al. (2005) and found to be dependent on the aggregates FD: low FD aggregates will breakup via fragmentation by splitting into smaller aggregates of comparable size leading to low SF value whereas high FD and thus more compact aggregates will preferentially disaggregate via surface erosion leading to higher SF values.

3.4 Characterisation of the stable fraction remaining after sedimentation: Particle concentration, size distribution and surface charge

Following sedimentation of the larger aggregates, the supernatant (5 mL) in each river water sample was collected and analysed for particle concentration, size distribution and surface charge. The results are presented in both Table 3 and Figure 3.

The size analysis showed significant differences among the measurement techniques, except for the lowest IS river samples (i.e. $R_{2.8}$). In fact, the PDI of this sample was quite low (Table 3); suggesting a relatively narrow monomodal particle size distribution (Basnet et al. 2013). The sizes reported by both DLS (Table 3) and FlFFF (Figure 3) were in close agreement to the size measured in DI water (i.e. 248 nm), indicating that most of the particles (i.e. 90.4 %) in this sample (i.e. $R_{2.8}$) did not undergo aggregation.

In the higher IS samples, the hydrodynamic diameters measured by DLS were larger than the particle size measured by FlFFF and varied from about 1100 nm to 1800 nm which is in accordance with previous studies reporting TiO_2 aggregates of similar size (measured by DLS) formed in both synthetic and natural waters (Zhang et al. 2009; Ottofuelling et al. 2011; Brunelli et al. 2013; Romanello and de Cortalezzi 2013). The high PDI of these samples may indicate some degree of polydispersity and because DLS is known to be very sensitive to larger particles, the size reported may be more representative of the large particles formed during the aggregation process (Domingos et al. 2009) whereas the size measured by FlFFF may be representative of the smaller particles/aggregates. These results clearly demonstrated the importance of using a multi-method approach when characterising ENPs in complex environmental samples.

In both samples $R_{6.7}$ and $R_{18.7}$, FlFFF results (Figure 3) showed that some of the particles did not aggregate as the measured size is close to the size measured in DI water (first peak in the fractogram). In sample $R_{6.7}$, the FlFFF fractogram showed that this fraction is higher than in $R_{18.7}$ while another peak (with smaller intensity) showed some particles at around 440 nm. In the fractogram of $R_{18.7}$, this trend is reversed as the second peak (i.e. representative of particle size around 440 nm) was of higher intensity. In the highest IS samples (i.e. R_{342}), only the second peak was present in the fractogram suggesting that the physico-chemical conditions of this sample promoted the aggregation of all the particles. The zeta potential value measured in this sample (i.e. + 3.7 mV) may suggest that the high IS of this sample destabilised the nanoparticles through charge neutralisation.

Figure 3

The concentration of TiO_2 NPs remaining in the supernatant varied widely among the samples (i.e. from 11.3 mg/L to 0.6 mg/L) and decreased proportionally with both increasing IS and decreasing DOM concentration as previously observed in a recent study on TiO_2 stability in natural waters (Ottofuelling et al. 2011). This indicates that more aggregates were formed in the fast-aggregation regime under the highest IS conditions and their sizes were higher than the critical size d_c resulting in their sedimentation. In fact, in R_{342}, the combined effect of high IS and low DOM content promoted fast aggregation resulting in 95% aggregation and sedimentation (Table 3). Moreover the low FD observed in this sample (Table 3), resulting in the formation of more porous aggregates, will ultimately lead to faster sedimentation in comparison to higher fractal aggregates or impermeable spheres (Johnson et al. 1996; Li and Logan 2001). Finally, the presence of divalent cations and especially Ca^{2+} in this sample may further destabilise the nanoparticles via a bridging effect (Chen et al. 2006; Chowdhury et al. 2013). The high PDI observed in R_{342} (Table 3) can also be seen as evidence of the low stability of TiO_2 NPs in this high IS sample, even after sedimentation.

Table 3

4 Conclusions

In the present study, we have demonstrated that the stability of TiO_2 NPs is strongly dependant on the physico-chemical characteristics of the surface waters (i.e. ionic strength (IS), ionic composition and the presence of NOM). Aggregates formed under high IS and low dissolved organic matter (DOM) conditions will present a more porous structure with a low fractal dimension (FD), resulting in fast sedimentation. Adsorption of NOM during the aggregation process will lead to more compact aggregates with high FD. Results from this study also showed a strong correlation between strength factor (SF) and FD. Compact aggregates will most likely undergo surface erosion leading to the formation of smaller aggregates which can be potentially resuspended in the water column.

In addition, we have demonstrated that the use of a multi-method approach is crucial to circumvent the limitations of each individual technique. While light scattering techniques can provide information on the larger aggregates (i.e. size and structure), FlFFF proved to be a very accurate technique for characterising the smaller particles remaining in suspension after sedimentation. When combined, these techniques can offer complementary data on the particle size distribution of the samples.

Finally, aggregation of nanoparticles is also known to be concentration-dependent, and the predicted environmental concentrations for the incidental release of ENPs into the environment (e.g. TiO_2 NPs) are currently estimated to be in the nanogram- to microgram-per litre range which is quite low compared to the current concentrations used in most aggregation studies including the present one. However, due to analytical challenges, very few instruments are capable of detecting, characterising and quantifying ENPs in complex environmental media at environmentally relevant concentrations. The method proposed and demonstrated in this paper provides a simple and convenient way to characterise the aggregation behaviour and aggregate structure of ENPs in a range of different water types. With a rapidly multiplying suite of ENPs now identified as potential environmental contaminants, screening methods such as this are clearly required.

Supporting Information

Additional text, tables, and figures containing information about the materials used, preparation procedures and selected results from data analyses not presented in the main text.

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