

Impact of alginate concentration on the stability of agglomerates made of TiO₂ engineered nanoparticles: Water hardness and pH effects

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Abstract The stability of engineered nanoparticles in natural aquatic systems is of high interest for environmental risk assessment since an already important quantity of these reactive species is entering aquatic systems. In the present study, an important issue is addressed by investigating (i) the influence of divalent cations and water hardness (Mg²⁺ and Ca²⁺) in agglomerate formation and (ii) alginate concentration effect on the stability TiO₂ agglomerates formed in environmental freshwater conditions (pH and total hardness) representative of Lake Geneva, France/

Switzerland. Our results indicate that the presence of alginate at typical natural organic matter concentration strongly modifies the stability of TiO₂ nanoparticle agglomerates by inducing their partial disagglomeration. Significant TiO₂ nanoparticles redispersion and formation of small fragments are expected to be induced by alginate adsorbed layer formed at the nanoparticle surfaces within the agglomerates.

Graphical Abstract

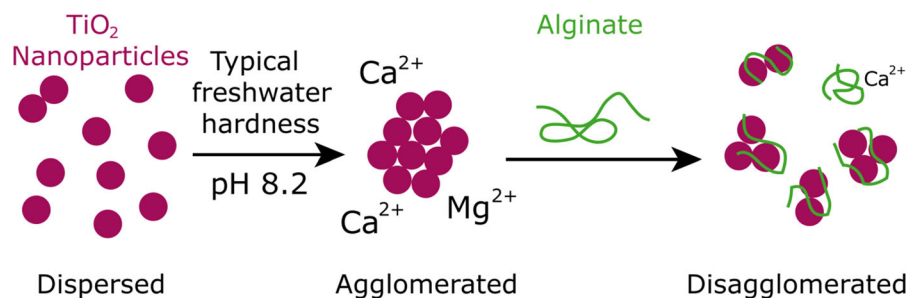
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Introduction

Engineered nanoparticles (ENPs) transport, fate, and transformation processes in aquatic systems are today of high interest because of the already important quantities of ENPs entering natural aquatic systems (Klaine et al. 2008; Ju-Nam and Lead 2008; Gottschalk et al. 2009). Stability of these highly reactive materials is essential to be well understood to evaluate their bioavailability and thus their potential toxic effects toward living organisms (Christian et al. 2008; Handy et al. 2008; von Moos and Slaveykova 2013). Stability is dependent on the nanoparticle intrinsic properties (particle size and shape, crystalline structure, surface chemistry) but also on the modification of the nanoparticle surface chemistry by the surrounding medium and the presence of aquagenic compounds. In particular, the physicochemical conditions such as the pH, presence of ionic species, and natural colloids play a key role on the surface charge properties of the ENPs (Guzman et al. 2006; Chowdhury et al. 2011; Liu et al. 2012). Owing to the ENPs unique properties (Jain et al. 2008; Chen and Mao 2007; Auffan et al. 2009; Dai 2002) investigation of their stability in realistic synthetic or natural waters has to be developed to increase our understanding on the ENPs fate when released into natural aquatic systems (Christian et al. 2008; Horst et al. 2012).

TiO_2 are used in numerous applications and can enter aquatic systems through industrial discharges, from disposal of wastewater treatment effluents or through surface runoff from soils (Gottschalk et al.

2009; Weir et al. 2012; Seitz et al. 2012; Batley et al. 2013). TiO_2 is used in painting industry, cosmetic, energy storage and is known to be produced in high tonnage (Chen and Mao 2007; Saif et al. 2012; Gottschalk et al. 2009). Stability of TiO_2 under different solution physicochemical conditions, i.e., especially pH and ionic strength, has been addressed in many studies (French et al. 2009; Domingos et al. 2010; Shih et al. 2012b; Gallego-Urrea et al. 2014). It was shown that high ionic strength and/or ENPs dispersion with pH near TiO_2 point of zero charge (PZC) results in agglomeration. Effects of various electrolytes were also investigated and specific adsorption of divalent counter ions was found to increase TiO_2 destabilization (Shih et al. 2012a).

When TiO_2 ENPs enter aquatic systems they are expected to also interact with aquagenic compounds such as natural organic matter (humic substances and non-humic substances such as polysaccharides) and inorganic particles (clays, silicates, metal hydroxides). The adsorption of natural organic matter (NOM) modifies the surface physicochemical properties (surface charge, surface chemistry, coating) and thus the stability of ENPs (Baalousha et al. 2013; Baalousha et al. 2008; Lee et al. 2011). ENPs when being coated with NOM are usually electrostatically and sterically stabilized, and thus, normally not undergo agglomeration (Hyung et al. 2007; Liu et al. 2010; Palomino and Stoll 2013; Domingos et al. 2009). Recently, the presence of NOM was not only found to prevent agglomeration but also to promote the partial redispersion of ENP agglomerates. This is a key result for risk assessment in particular when agglomerated ENPs are entering natural systems and have the possibility to disagglomerate in small fragments (Baalousha 2009; Loosli et al. 2013). The presence of NOM can also induce ENPs destabilization depending on the physicochemical conditions prevailing in the medium. Indeed,

calcium ions were found to promote NOM conformational changes and the destabilization of NOM-coated nanoparticles through charge neutralization or ENPs bridging mechanisms (Chen et al. 2006; Liu et al. 2011; Kunhi Mouvenchery et al. 2012).

An important fraction of NOM is represented by the extracellular polymeric substances. Alginate has been shown as a relevant model of these polymeric substances and is used in many studies (Gregor et al. 1996; Bernhardt et al. 1985). Alginate is a natural constituent of the cell of brown algae and is thus widely used in biomedicine as a drug carrier and in food industry as thickener agent (Lee and Mooney 2012; Liu et al. 2008; Helgerud et al. 2009). The presence of divalent cation and especially Ca^{2+} promote important conformational changes, as the well known “egg box” model, due to the complexation of the carboxylic moieties from guluronate monomer which lead to alginate gelation (Grant et al. 1973; Morris et al. 1978; Li et al. 2007).

In the present study, an important issue is addressed by investigating the alginate concentration effect on the stability of TiO_2 agglomerates formed in environmental fresh water condition (pH and total hardness representative of Lake Geneva, France/Switzerland). To the best of our knowledge, it is the first time that the disagglomeration of TiO_2 ENPs agglomerates, formed in typical environmental freshwater conditions, and induced by the presence of alginate is studied.

Materials and methods

Materials

A 15 wt % TiO_2 anatase dispersion in water purchased from Nanostructured & Amorphous Material Inc (Houston, TX, USA) was used without further treatment steps. The TiO_2 ENPs, as given by the manufacturer, display a primary diameter equal to 15 nm and a specific surface area equal to $240 \text{ m}^2/\text{g}$. A solution of 1 g/L sodium alginate (A2158, Sigma Aldrich, Buchs, SG, Switzerland) was prepared by dissolving the low viscosity (50 kDa) polysaccharide in deionized water (Milli Q water, Millipore, Zoug, ZG, Switzerland, with $R > 18 \text{ M}\Omega\cdot\text{cm}$, T.O.C. $< 2 \text{ ppb}$) and used after 24 h of agitation. To adjust the dispersions pH before and during experiments, when necessary, sodium hydroxide and hydrochloride acid (1 M NaOH or HCl,

Titrisol[®], Merck, Zoug, ZG, Switzerland) were used after dilution. Sodium chloride (NaCl, 99.5 %, Acros Organics, Wohlen, AG, Switzerland), calcium chloride (CaCl_2 , purum, Fluka, Buchs, SG, Switzerland), and magnesium chloride (MgCl_2 , puriss, Sigma Aldrich, Buchs, SG, Switzerland) were used to adjust the salt concentration to the desired values. Experiments were performed in $25 \times 90 \text{ mm}$ polypropylene tubes (Milian, Vernier, GE, Switzerland) with a $8 \times 10 \text{ mm}$ crosshead magnetic stirrer (VWR, Nyon, VD, Switzerland) and the agitation speed was set to gently homogenize the dispersions.

Zeta potential and size distribution measurements

Determination of z-average hydrodynamic diameters and zeta (ζ) potential values was achieved by dynamic light scattering and laser doppler velocimetry methods, respectively, using a Zetasizer Nano ZS instrument (Malvern Instruments, Worcestershire, UK). For ζ potential values determination, the Smoluchowski approximation model, i.e., when particle are large in comparison of double layer thickness, was applied (Ohshima 1995a, b; Baalousha 2009). Characterization of TiO_2 ENPs suspensions in the presence of sodium alginate was realized for a 50 mg/L TiO_2 mass concentration.

Experimental conditions in presence of alginate

The influence of alginate on TiO_2 stability was investigated by considering a suspension with a pH and total hardness similar to the values found in Geneva Lake. Ca^{2+} and Mg^{2+} concentrations were set equal to 45 and 5 mg/L, respectively, and the pH was adjusted to 8.2–8.0 (Graham et al. 2014). Then the alginate was added to the suspension at variable concentrations. An illustration of the experimental procedure is presented in Fig. 1.

Results and discussion

TiO_2 behavior as a function of pH and in presence of divalent electrolyte

In Fig. 2 is shown the ζ potential values of TiO_2 ENPs as a function of pH in presence of a 0.001 M NaCl background electrolyte. When $\text{pH} < 5$, TiO_2 surface

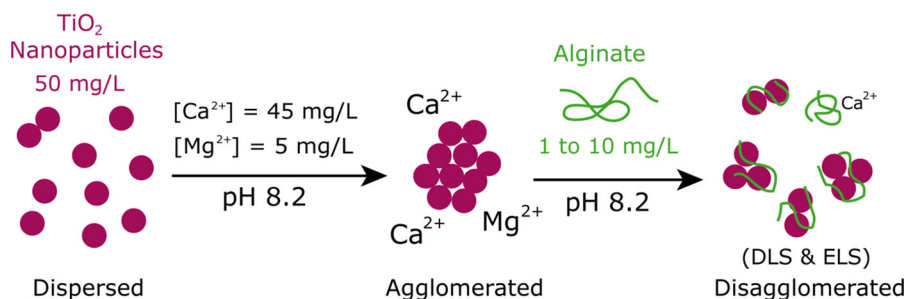


Fig. 1 Experimental procedure. The pH and the total hardness of a 50 mg/L TiO₂ ENPs dispersion (initially stable at pH 3) is adjusted to finally reach pH 8.2 and a Ca²⁺ and Mg²⁺ concentration equal to 45 and 5 mg/L, respectively. These conditions promote the agglomeration of the ENPs dispersion. Then alginate is added to the ENPs dispersion to investigate the effect of alginate concentration (from 1 to 10 mg/L) on

agglomerates made of TiO₂ for typical freshwater pH and total hardness. Determination of z-average diameters and ζ potential values as a function of time after alginate addition is done by measuring the diffusion coefficients by dynamic light scattering (DLS) and electrophoretic mobility by electrophoretic light scattering (ELS). (Color figure online)

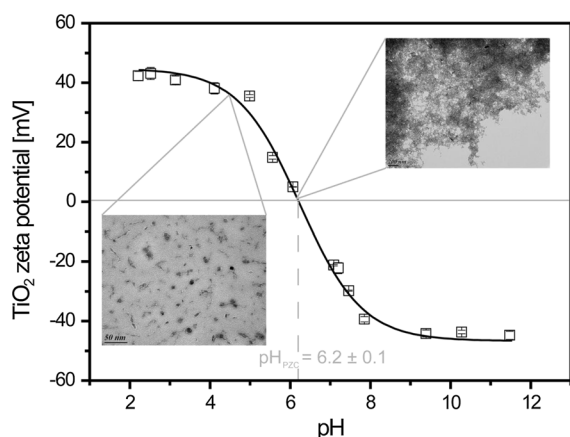


Fig. 2 TiO₂ zeta potential values as a function of pH. The point of zero charge (PZC) is found equal to 6.2 ± 0.1 . [TiO₂] = 50 - mg/L and [NaCl] = 0.001 M. For pH values lower than 5 and higher than 8, the ENPs are stable due to important electrostatic repulsions as shown by TEM (500,000× magnification, pH 4.5, scale bar represent 50 nm, [TiO₂] = 100 mg/L). Individual and small TiO₂ agglomerates are observed. At pH value corresponding to the PZC large agglomerates are observed as shown by TEM (60,000× magnification, pH 6.2, scale bar represent 200 nm, [TiO₂] = 100 mg/L)

charge is found strongly positive and exhibit a constant ζ potential value equal to $+40.0 \pm 3.1$ mV. By increasing the pH, the PZC is reached with a value found here equal to 6.2 ± 0.1 which is in good agreement with literature (Parks 1965). By further increasing the pH, TiO₂ ENPs exhibit a negative surface charge which stabilizes at a ζ potential value of -43.0 ± 2.6 mV for a pH ranging from 8 to 12. When pH <5 and pH >8, the TiO₂ ENPs are found stabilized

against agglomeration and the “baseline” z-average hydrodynamic diameter is found to be stable and equal to 50 nm (ESI, Fig. S1). Consequently at pH 8.2, no agglomeration is expected to occur between the negatively charged nanoparticles due to electrostatic repulsions. ENPs stability and agglomeration are also illustrated by TEM pictures in Fig. 2 to corroborate DLS measurements.

The addition of one divalent electrolyte (CaCl₂) is then found to strongly modify the stability of TiO₂ ENPs by specific adsorption of Ca²⁺ ions on the negatively charged TiO₂ and induce agglomeration at low electrolyte concentrations (Figs. S2–S4). The critical coagulation concentration is found here equal to 6.5×10^{-5} M as shown in Fig. S3. According to these results, TiO₂ ENPs are then expected to form large positively charged agglomerates at typical pH and water hardness which have been considered to mimic Lake Geneva freshwater conditions.

Alginate behavior as a function of pH and in presence of divalent cations

The pH titration curves of a 50 mg/L sodium alginate suspension in presence of Ca²⁺ and Mg²⁺ at 45 mg/L and 5 mg/L are given in Fig. 3. Alginate z-average diameters and ζ potential values (108 ± 11 nm and -11 ± 1 mV) are found constant in the pH range 3.5–10. It is shown here that the presence of Ca²⁺ and Mg²⁺ is found to decrease the alginate negative structural charge as well as z-average size (more compact structure). Indeed in previous study, for the

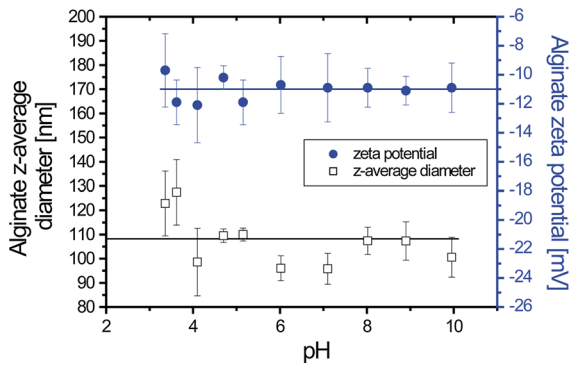


Fig. 3 Alginate z-average diameter (open black squares) and zeta potential values (blue dots) as a function of pH. The z-average diameter and zeta potential are constant in the pH range 3.5–10 with values equal to 108 ± 11 nm and -11 ± 1 mV, respectively. [Alginate] = 50 mg/L, $[Ca^{2+}] = 45$ mg/L and $[Mg^{2+}] = 5$ mg/L. (Color figure online)

same alginate grade and same instrumental methods, but in absence of Ca^{2+} and Mg^{2+} , the alginate z-average diameter was found constant on the pH range 3–11 with a value equal to 178 ± 21 nm and ζ potential values were comprised between -13 mV at pH 3 and -30 mV when $pH > 5.5$ (Loosli et al. 2014). This is an important result explaining the electrostatic affinity between the negatively charged alginate and alginate-divalent cations complexes with the positively charged agglomerates.

TiO₂ agglomerates stability in presence of alginate

To investigate the influence of alginate on the stability of TiO₂ agglomerates formed in presence of divalent cations (Mg^{2+} , Ca^{2+}) at pH 8.2, the z-average diameters and ζ potential values are considered as a function of time. Alginate concentration is also adjusted between 1 and 10 mg/L. As shown in Fig. 4, disagglomeration is observed and two regimes are distinguishable according to the z-average diameter variation. In the first regime, corresponding to the first 30 min after alginate addition, the z-average diameters decrease significantly as a function of time. Then after 30 min, a steady state is reached and a second regime, where both the fragment z-average diameters and ζ potential values are constant, is achieved. The importance of TiO₂ disagglomeration is found dependent on the added alginate concentration. TiO₂ agglomerate fragment sizes as a function of alginate concentration at $t = 60$ min after alginate

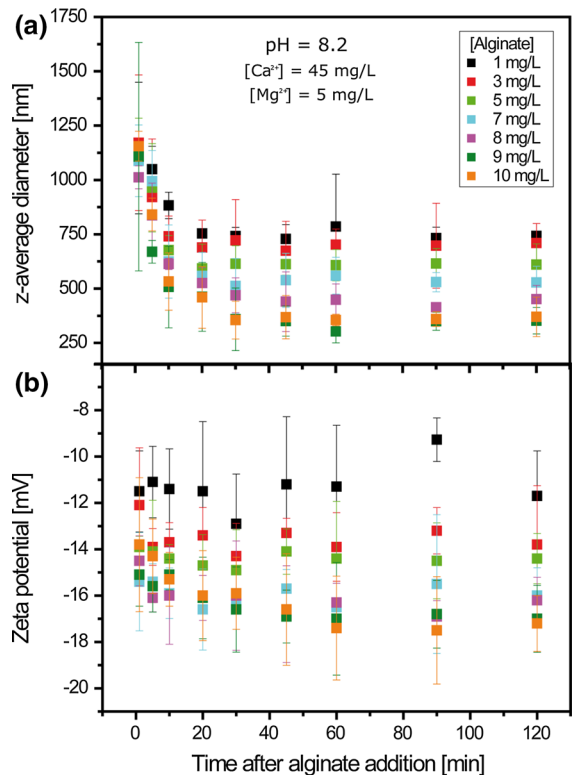


Fig. 4 Influence of alginate concentration (from 1 to 10 mg/L) on TiO₂ agglomerate **a** z-average diameters and **b** zeta potential values as a function of time. Alginate is found to induce disagglomeration of TiO₂ aggregates at pH 8.2. $[TiO_2] = 50$ mg/L, $[Ca^{2+}] = 45$ mg/L and $[Mg^{2+}] = 5$ mg/L. Prior alginate addition the z-average diameter and ζ potential values were found equal to $3,033 \pm 620$ nm and 17.5 ± 0.9 mV, respectively. (Color figure online)

addition are illustrated in Fig. 5. Maximum of disagglomeration and a plateau are obtained here for an alginate concentration ≥ 8 mg/L with fragment sizes of 386 ± 101 nm. The corresponding ζ potential values also exhibit a plateau, as shown in Fig. 5b, with a value equal to -16.8 ± 1.9 mV. It should be noted that the adsorption of alginate, and Ca^{2+}/Mg^{2+} - alginate water complexes, leads to TiO₂ agglomerate charge inversion if comparison is made when agglomerate is formed in presence of Mg^{2+} and Ca^{2+} cations. In presence of alginate, the agglomerate and fragment ζ potentials are equal to -11 to -16 mV. This is an interesting result which is in agreement with the ζ potential measurements made by Graham et al. on a series of natural colloidal suspensions and aggregates from the Geneva Lake (Graham et al. 2014). It should be noted that based on the results presented in Fig. 2

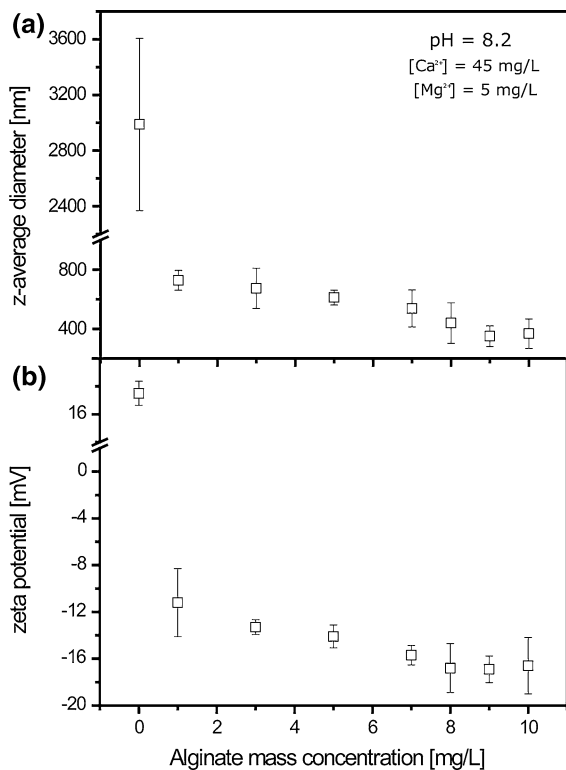


Fig. 5 **a** z-average diameters and **b** zeta potential of TiO_2 agglomerates as a function of alginate concentration at $t = 60$ min after alginate addition at pH 8.2. Maximum of disagglomeration is obtained for an $[\text{Alginate}] \geq 8$ mg/L with z-average diameters and zeta potential values found equal to 386 ± 101 nm and -16.8 ± 1.9 mV, respectively. $[\text{TiO}_2] = 50$ mg/L, $[\text{Ca}^{2+}] = 45$ mg/L and $[\text{Mg}^{2+}] = 5$ mg/L

and Fig. S1 such a charge inversion and ζ potential values are not high enough to induce a significant electrostatic disagglomeration process.

Molecular information to deeply understand what happens at the nanoparticle surface is relatively difficult to obtain and interpret so as to explain alginate conformational changes at the surface of the ENPs and to identify the “true” disagglomeration process. These difficulties of interpretation arise from the fact that once adsorbed on a nanoparticle surface, a polyelectrolyte molecule such as alginate is able to adopt diverse conformations which depend on the nature of the polymer and the nanoparticle surface, the surface charge density of the nanoparticle, the linear charge density of the polyion, and the degree of surface coverage. Furthermore, a polyelectrolyte may progressively change its conformation in the adsorbed state.

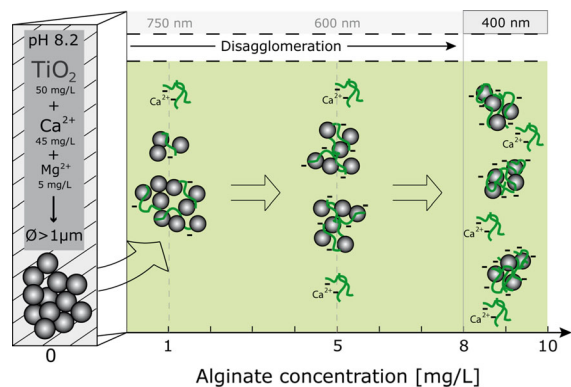


Fig. 6 Schematic illustration on the effect of alginate concentration on the disagglomeration process of TiO_2 ENP aggregates at typical fresh water pH and divalent electrolyte concentration. Alginate promotes the disagglomeration of aggregates with initial sizes in the few microns range and maximum of disagglomeration is obtained here for an $[\text{Alginate}] \geq 8$ mg/L with fragment sizes equal to around 400 nm. $[\text{TiO}_2] = 50$ mg/L, $[\text{Ca}^{2+}] = 45$ mg/L, $[\text{Mg}^{2+}] = 5$ mg/L and pH = 8.2. (Color figure online)

When agglomerates exist the presence of non-adsorbed polymers and slow adsorption at the level of the confined interfacial layers tends to fragment the nanoparticle agglomerates. Results, as presented by Pefferkorn (Pefferkorn 1995), suggest that the polymer reptation in the starved diffuse layer and adsorption induce electrostatic and steric repulsions within the agglomerate structures. Polymer concentration and initial degree of coverage is also shown to govern the rate of fragmentation (in good agreement with the results we are presenting here where disagglomeration importance is increasing with the alginate concentration).

The reason for the particularly slow reformation of polyelectrolytes and resulting time observed here for fragmentation process can also reside in the ionic nature of the process. In fact, the small ions of the medium and the ionic groups of the polyelectrolyte compete for the surface ionic groups and charge equilibrium in the diffuse layer is conserved during the adsorption since the transfer of polyelectrolyte from solution to surface is compensated by the transfer of small ions from the surface to the liquid phase as shown by Carnal et al. (Carnal and Stoll 2011).

The stability diagram which is presented in Fig. 6 is giving an overview of the disagglomeration process of TiO_2 agglomerates formed in the presence of Ca^{2+} and Mg^{2+} at pH 8.2 and when alginate is added to the dispersion. Prior alginate addition, TiO_2 ENPs form large agglomerates with sizes greater than one

micrometer. Then, addition of alginate promotes the disagglomeration of the TiO₂ agglomerates. For a 1 mg/L alginate concentration, the TiO₂ agglomerate fragments size is already reduced to 750 nm. By further increasing the alginate concentration, a more efficient redispersion of the TiO₂ ENPs is observed as indicated by the black arrow. For an alginate concentration ≥ 8 mg/L, maximum of disagglomeration is reached with a plateau value and TiO₂ fragments with z-average diameters equal to 400 nm. It should be noted that partial, but significant, disagglomeration is obtained, with fragment sizes 8 times greater than the TiO₂ 50 nm “baseline” z-average diameter for dispersed ENPs.

Conclusions

The influence of alginate on already formed agglomerates in environmental relevant pH, calcium, and magnesium concentrations, representative of Lake Geneva (France/Switzerland), indicates that environmental NOM concentrations and presence of polysaccharides can induce a partial, but significant, disagglomeration of already formed TiO₂ nanoparticle agglomerates. Our study also suggests that the main driving force which permits disagglomeration is related to steric repulsions between nanoparticles in agglomerates due to the presence of adsorbed alginate molecules. We believe this constitutes an important outcome since from an environmental and risk assessment point of view partial remobilization of the TiO₂ nanoparticles, via the formation of small fragments, will enhance their mobility and transport throughout aquatic systems. It should also be noted that the adsorption of alginate, and Ca²⁺/Mg²⁺-alginate water complexes at environmental freshwater conditions, on already formed agglomerates leads to TiO₂ agglomerates charge inversion with negative zeta potential values similar to the values obtained on a series of natural colloidal suspensions and aggregates from the Geneva Lake. This denotes the key role of NOM, such as natural polysaccharides, on the stability and fate of (nano) particles in aquatic systems.

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