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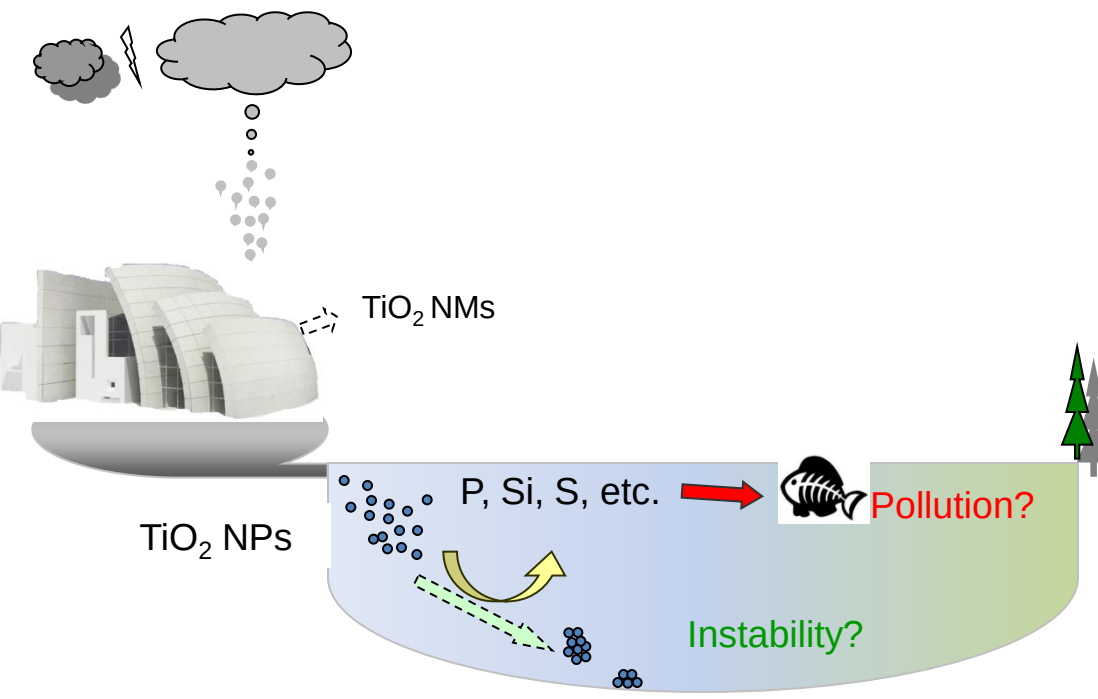
Abstract

Previous studies have found the significant role of impurities (i.e., silicon, phosphorus) in the aggregation and sedimentation of TiO₂ nanoparticles in water environment. However, it is not understood whether dissolution of the impurities potentially impacts the environment or the stability and fate of TiO₂ NPs are affected during the dissolution process. In this study, we investigated the impurity dissolution kinetics and surface transformation of 5 types of TiO₂ nanoparticles (i.e., 5, 10, and 50 nm anatase and 10 × 40, 30 × 40 nm rutile) at various pH and ionic strength. Both acidic and basic conditions accelerated the release of Si, while the basic conditions enhanced the P release greatly. The quantity of dissolved Si increased with increasing reaction time from 2 hr to 19 d in a power mode, while P released to the aqueous solution quickly within the first 2 hr. P dissolved from the 50 nm anatase reached 5000 to 7100 mg/Kg at neutral to alkaline pH, which indicated a potential pollutant source. The variation in impurity dissolution is consistent with the chemical composition of pristine TiO₂, i.e., the most leachable quantity of Si for the 10 × 40 nm rutile and P for the 50 nm anatase, which was verified by Fourier transform infrared spectroscopy. The impurity dissolution did not change greatly within ionic strength of 20–50 mM at pH 8.4. Dynamic light scattering revealed relatively stable surface potential and particle size of the NPs during impurity release process.

Introduction

Titanium dioxide (TiO₂) nanoparticles are important nanomaterials in the market and the production had increased to 5000 t by 2010 (Landsiedel et al. 2010). Although wastewater treatment plants are capable of removing the major part in sewage, TiO₂ nanoparticles were still found in the treated effluent and released to surface waters (Weir et al. 2012).

Previous studies have found significant amounts of impurities (i.e., silicon, phosphorus) in commercial TiO₂ NPs. Release of the impurities, such as P, might be potentially an adverse impact to the aqueous environment system. In addition, the impurities of Si and P result in more negative surface charge and higher stability of TiO₂ at neutral pH in aqueous phase. Therefore it deserves further investigation of the effect of impurity release on the fate and transport of TiO₂ NPs.



Methods and Materials

Characterization of TiO₂ Nanomaterials

Five types of TiO₂ nanoparticles were obtained from Nanostructured & Amorphous Materials, Inc. (Houston, TX). They are three types of anatase nanoparticles with nominal diameters of 5, 10, and 50 nm, and two types of rutile nanoparticles with rod like morphology of 10 × 40 and 30 × 40 nm. The 30 × 40 nm “rutile” was found to be a mixture of rutile and anatase as characterized by the X-Ray Diffractogram (Liu et al. 2011). Transmission electron microscopy (Philips FEI CM20 FEG S/TEM and JEOL 2000-FX S/TEM), Zetasizer (Nano-ZS, ZEN 3600, Malvern) and Fourier transform infrared spectroscopy (FT-IR, VERTEX 70, Bruker) were applied to monitor the morphology, ζ -potential and surface change of TiO₂ NPs. Alkaline fusion was conducted to melt pristine NPs and the chemical composition was determined by the following Inductively Coupled Plasma – Optical Emission Spectrometry (ICP–OES) and – mass spectrometry (ICP–MS). Briefly, 0.01 g of TiO₂ NPs were mixed with 0.4 g of KOH in nickel crucibles and heated to 500 °C for 4 hrs in an oven. DI was used to rinse the crucible after cooling down and all the solution was transferred to a 100-mL plastic volumetric flask. Glassware was avoided during and after fusion process.

Solution Chemistries

The impurity dissolution kinetics was investigated under acid, neutral, and basic pH conditions. Three types of background solutions were used, i.e., 0.01 M HCl, 0.01 M NaOH, and 0.01 M NaCl with 0.01M NaHCO₃. Stock solution of 0.04 M NaCl with 0.01 M NaHCO₃ was prepared to study the influence of ionic strength.

Experiment Procedure

One hundred mg of TiO₂ NPs was weighted and transferred to 50-mL centrifuge tubes (Nalgene, Thermo Scientific), followed by the addition of 30 mL stock solutions. All the kinetics study was conducted in duplicate. The samples were shaken at 200 rpm on a plate shaker at different time intervals, i.e., 2 hr, 12 hr, 1 d, 2 d, 6 d, and 19 d.

Before the end of the specified shaking time (30 min in advance), the tubes were centrifuged at 3600 rpm for 30 minutes to settle out most of the NPs. Then 20 mL of supernatant was separated with caution, and filtered through 0.10 μ m pore size membrane. Similar protocols were reported in the literature (Mudunkotuwa et al. 2011). The filtrate was analyzed for 31 elements using ICP–OES. The pH was measured using the remaining of 10 mL suspensions. The influence of pH was also studied comprehensively in 0.01 M NaCl background solutions with addition of 1.0, 0.6, 0.2, 0.1 and 0.01 mL 1.0 M HCl or 0.01, 0.05, 0.1, 0.25, 0.5 and 1.0 mL of 1.0 M NaOH for the 1 day test.

Results and Discussion

Properties of TiO₂ NPs

The primary size of 5, 10, 50 nm anatase and 10 × 40 nm rutile NPs was similar to their nominal size (Figure 1). Figure 1-D shows that the 30 × 40 nm “rutile” NPs were comprised with different sizes, i.e. ~ 5–10 nm and 30–40 nm. Elemental analysis revealed that the 50 nm anatase contains the highest phosphorous, i.e. 0.81%, followed by the 10 × 40 nm rutile (0.20 %) and the 30 × 40 nm rutile (0.14 %), according to ICP analysis after alkaline fusion (Table 1). In contrast, the 10 × 40 nm rutile contains highest Si (4.63 %), followed by the 50 nm anatase (2.67%). The elemental contents for Ti and impurities treated by alkaline fusion are generally higher than by hot-plate or microwave assisted acid digestions. In addition, it is also noticed that the highest Ti content was 36.7 % for 5 nm anatase, which is lower than the theoretical value of 59.9 % for TiO₂. This inconsistency could be attributed to the incomplete decomposition in the digestion process.

Release Kinetics of Si in the Aqueous Phase

Figure 2 shows the dissolution kinetics of Si at pH 8.4 (in 0.01 M NaCl and 0.01 M NaHCO₃), pH 2.4 (in 0.01 M HCl), and pH 11.3 (in 0.01 M NaOH) for TiO₂ nanoparticles. Figure 2-A shows that the Si concentration in liquid phase increased within the dissolution period of 2 hr to 19 d. The power mode fitted the experimental data best for dissolution of TiO₂ NPs at pH 8.4. The releasing quantity of Si from the 10 × 40 nm rutile was the highest, followed by the 50 nm anatase and the 30 × 40 nm rutile NPs. The release of Si from the 5, and 10 nm anatase could not be detected at pH 8.4. This order for Si dissolution is consistent with the elemental composition of pristine TiO₂ NPs (Table 1). At pH 2.4 (in 0.01 M HCl), the amount of Si dissolution was around twice of that at pH 8.4 for all of the three NPs.

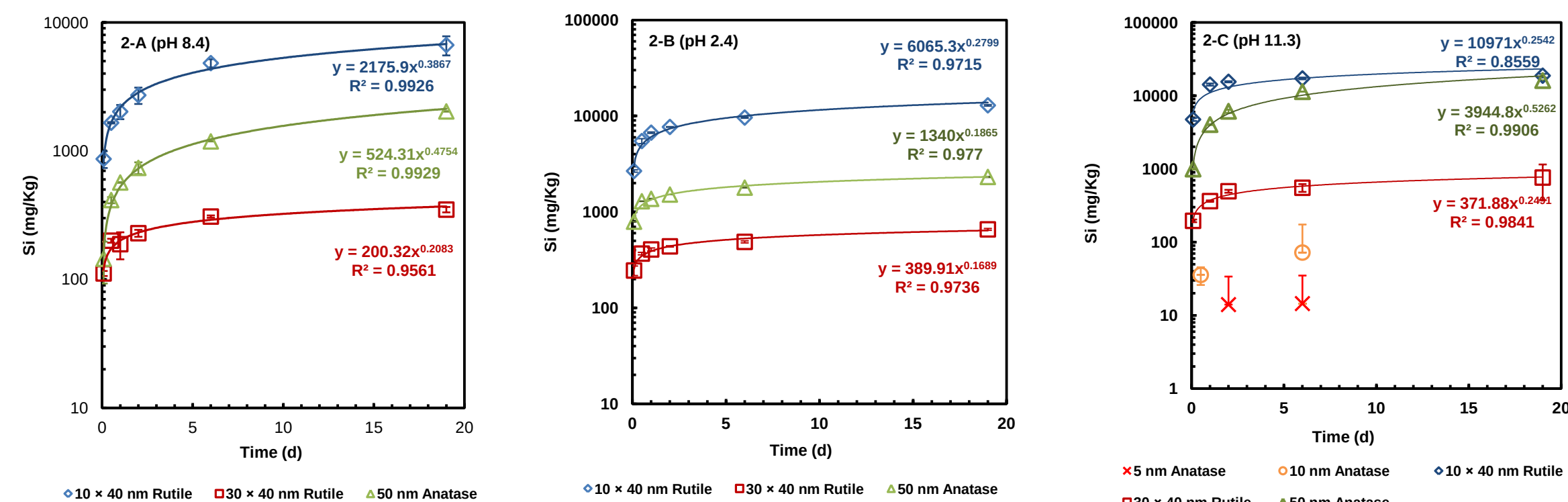


Figure 2. Dissolution kinetics of Si at pH 8.4, 2.4, and 11.3 within test period of 2 hours to 19 days.

Table 1. Elemental analysis of Ti, Si, and P in TiO₂ NPs in alkaline fusion and acid digestion experiments.

Alkaline fusion or Acid digestion	Analyzed Elements	TiO ₂ NPs				
		5 nm Anatase	10 nm Anatase	10 × 40 nm Rutile	30 × 40 nm Rutile	50 nm Anatase
Alkaline Fusion	Ti	31.654%	30.507%	20.985%	27.729%	23.798%
	Si	0.000%	0.000%	4.631%	0.000%	2.673%
	P	0.126%	0.072%	0.205%	0.136%	0.805%
Hot Plate Acid Digestion	Ti	0.690%	1.387%	5.135%	0.342%	0.297%
	Si	0.034%	0.017%	1.181%	0.091%	0.260%
	P	0.000%	0.000%	0.000%	0.039%	0.601%
Microwave Acid Digestion	Ti	0.468%	0.251%	0.749%	0.055%	0.225%
	Si	0.019%	0.015%	2.022%	0.077%	0.858%
	P	0.000%	0.000%	0.001%	0.018%	0.525%

At pH 11.3, the Si release was higher than those at pH 8.4 and pH 2.4 in solutions (Figure 2-C). The same order of Si dissolution was found for various TiO₂, i.e. 10 × 40 rutile > 50 nm anatase > 30 × 40 nm “rutile” NPs. The Si release from 5 and 10 nm anatase NPs was found to be minimal among all TiO₂ at pH 11.3.

Release Kinetics of P in the Aqueous Phase

The amount of released P kept relatively stable for the TiO₂ NPs within the monitoring period of 2 hr to 19 d (Figure 3). P dissolved very quickly within the first 2 hrs, which is different from Si release. The 50 nm anatase contains the highest amount of released P among all of the TiO₂ NPs at pH 8.4, followed by 30 × 40 nm rutile, 10 and 5 nm anatase NPs. At pH 2.4, the P concentration in solutions was lowest among all tested pH values. In contrast, the P concentration at pH 11.3 was highest for all types of TiO₂ NPs (Figure 3-C). More significantly, the values for P dissolution were on the same order of magnitude in the pristine NPs. For instance, the average value for the released P was back calculated as 3647, 5062 and 7115 mg/Kg at pH 2.4, 8.4 and 11.3, respectively for the 50 nm anatase. The content of P was 8050 mg/Kg for the 50 nm anatase NPs as revealed in the alkaline fusion test (Table 1). That is, a significant amount of P was released to the liquid phase from the 50 nm anatase NPs.

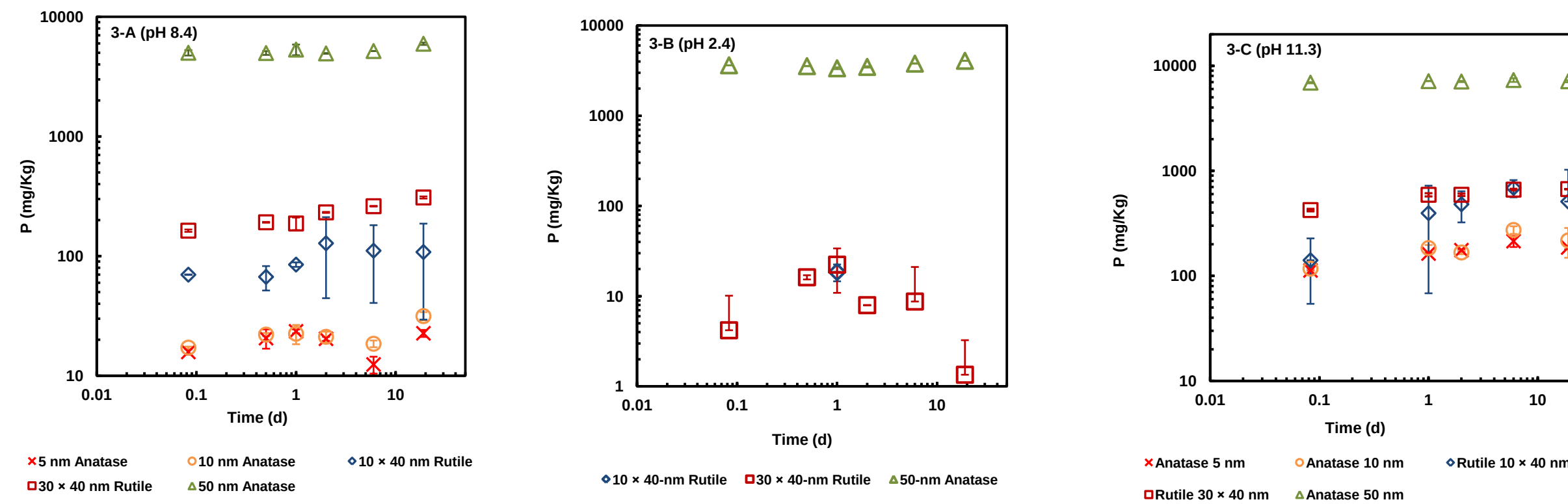


Figure 3. Dissolution kinetics of P at pH 8.4, 2.4, and 11.3 within test period of 2 hours to 19 days.

For the 30 × 40 nm rutile, the amount of dissolved P increased moderately from 2 hr (423 mg/Kg) to 6 d (662 mg/Kg), and then did not change greatly till 19 d (670 mg/Kg) at pH 11.3. This is around half of the P content in pristine 30 × 40 nm rutile NPs (i.e., 1360 mg/Kg) (Table 1). The dissolution of P for the 10 × 40 nm rutile is a little lower than the 30 × 40 nm rutile, which is around 1/4 of the total P (alkaline fusion) in the pristine 10 × 40 nm rutile NPs. The lowest amount of P dissolution was observed for 5 and 10 nm anatase, i.e. ~200 mg/Kg at pH 11.3. The P dissolution is not significant compared with the P content, i.e., 1260 and 720 mg/Kg, in pristine 5 and 10 nm anatase, respectively.

Effect of pH and Ionic Strength on the Impurity Release of TiO₂ NPs

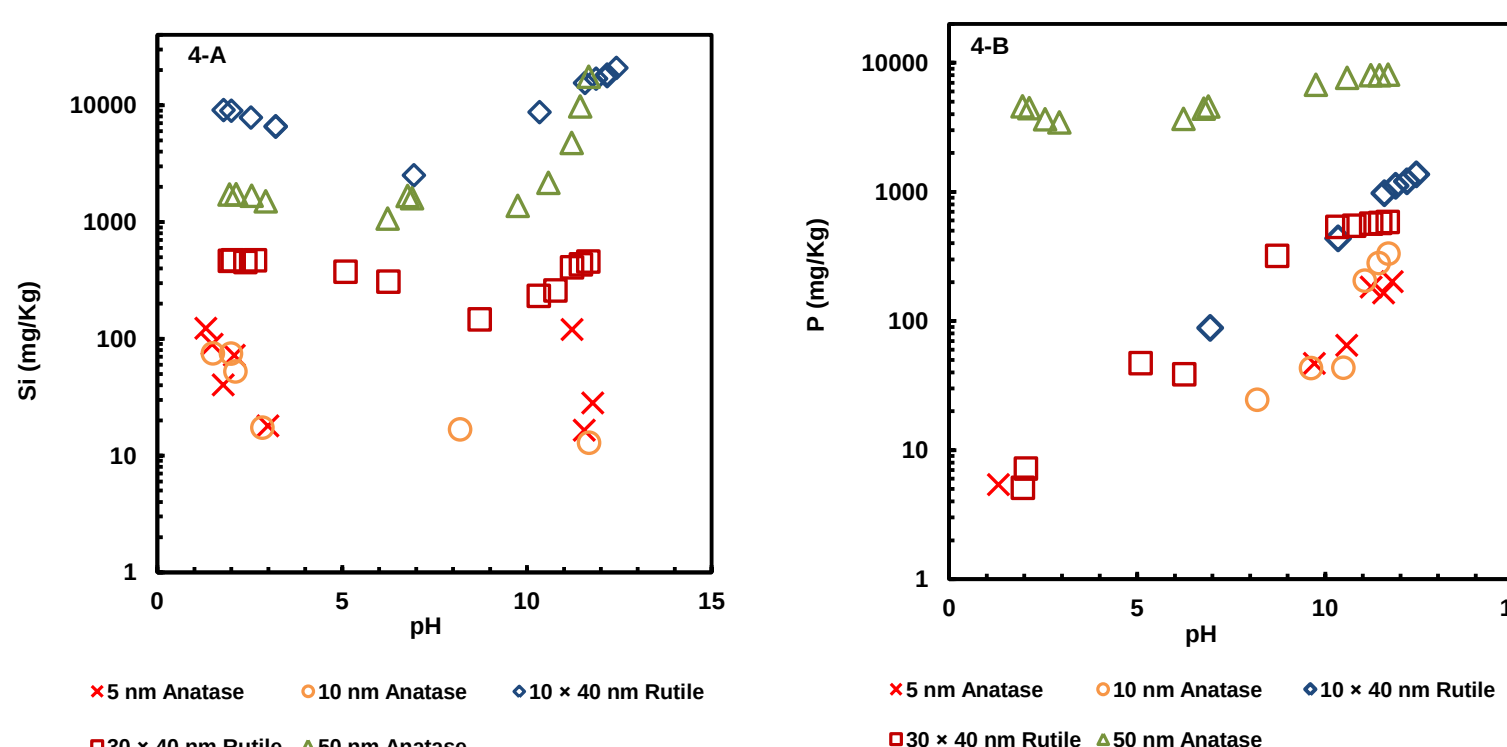


Figure 4. Effect of pH on the dissolution of Si and P in 1-day test.

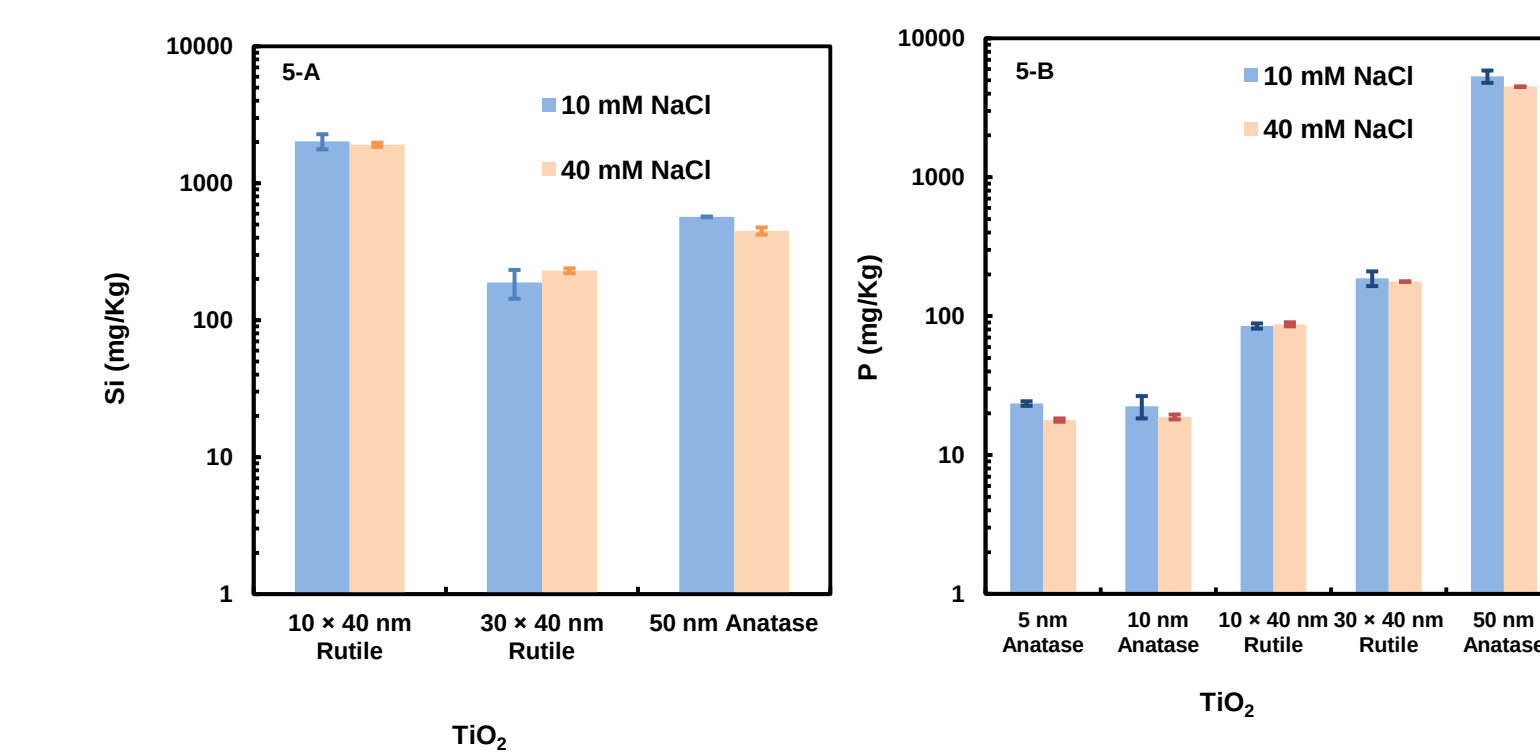


Figure 5. Influence of different ionic strength on the dissolution of Si and P.

Transformation of TiO₂ NPs in the Aqueous Phase

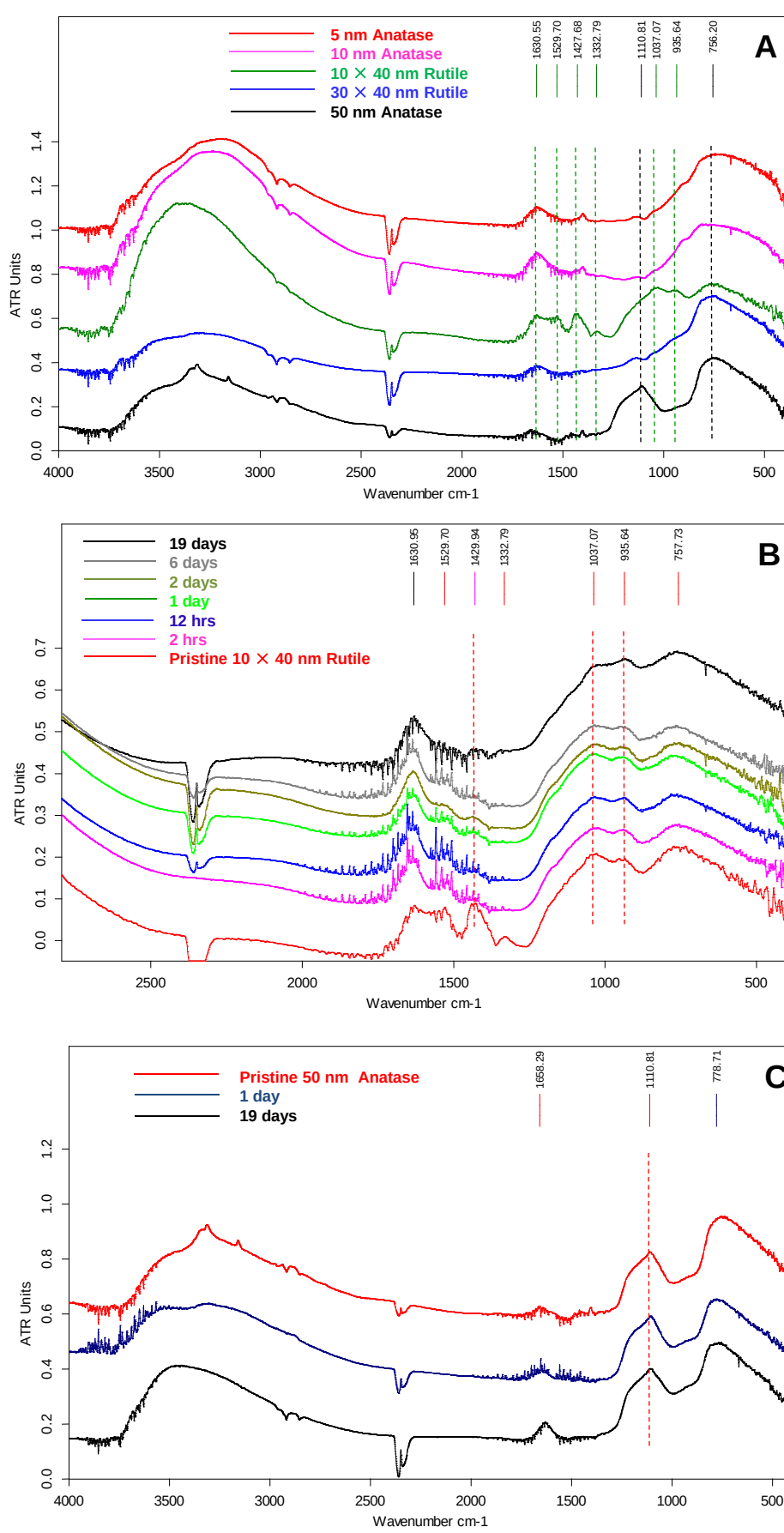


Figure 6. FT-IR spectra for (A) pristine TiO₂ NPs, (B) the 10 × 40 nm rutile after dissolution and (C) the 50 nm anatase after dissolution.

Effect of Impurity Release on NP Stability

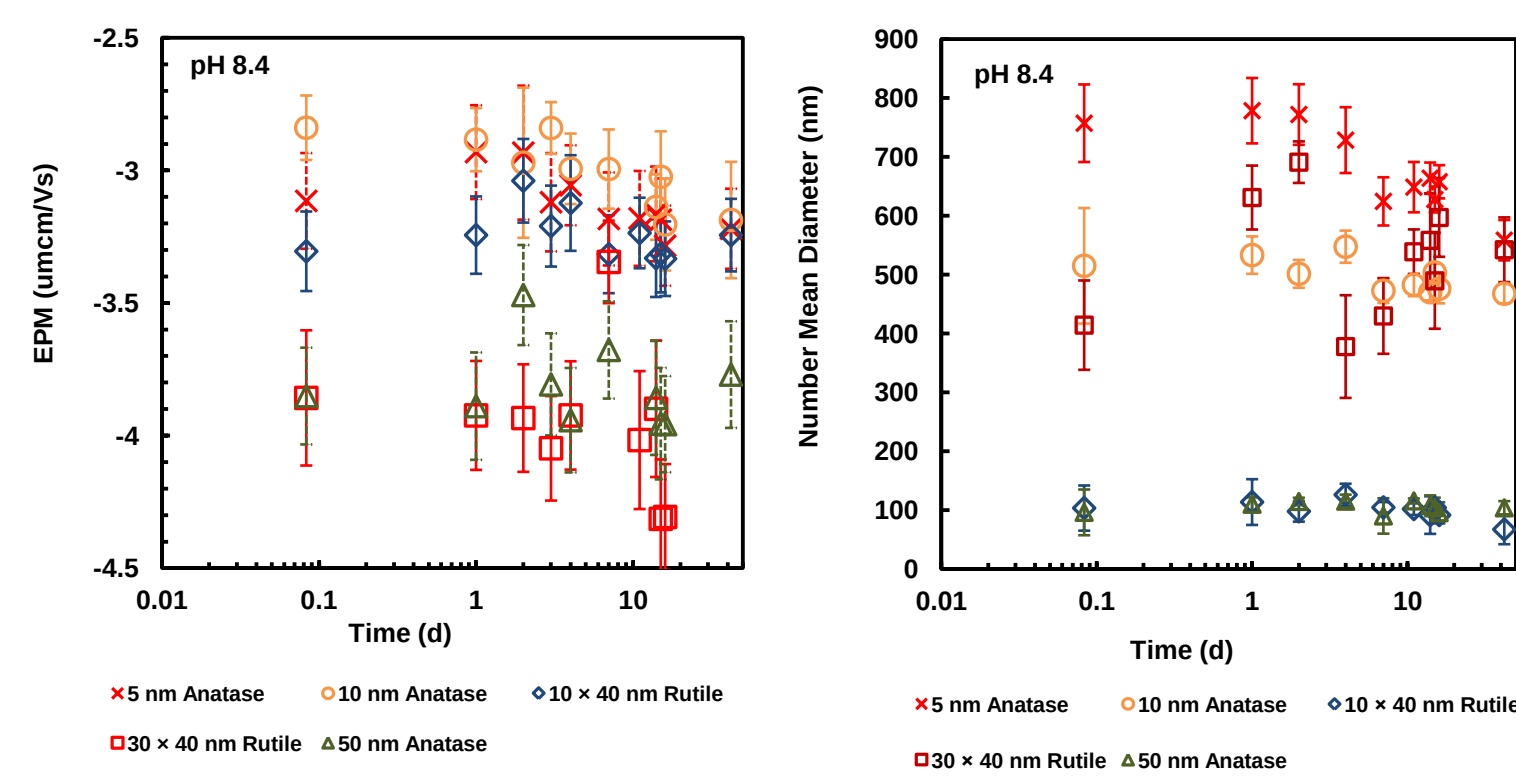


Figure 7. Measurement of EPM and number mean diameter of TiO₂ during dissolution period by DLS.

Environmental implication

This study revealed that P and Si release from TiO₂ NPs may adversely impact the aquatic environment. The impurity dissolution did not greatly change the surface potential and hydrodynamic size, and therefore may not affect their fate and transport in the aqueous environment.

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FT-IR spectra show some similar peak positions for the five types of TiO₂ NPs, e.g. ~ 1631 and 756 cm⁻¹ (Figure 6). The most significant peaks were at 1037 cm⁻¹ and 936 cm⁻¹ for the 10 × 40 nm rutile, which are probably related to the high content of Si. In contrast, the most featured one is at 1111 cm⁻¹ for the 50 nm anatase which is relevant to P.

Figure 6-B reveals that the peak height at 1037 cm⁻¹ decreased gradually within the dissolution period of 2 hr to 19 d. The spectra were consistent with Si dissolution data, i.e. gradual dissolution of P leading to less content remaining in the NPs. It is noticeable that another peak at 936 cm⁻¹ did not change greatly, probably due to different Si species. For the 50 nm anatase, the P related peak at 1111 cm⁻¹ did not change significantly within the test period (Figure 6-C). This is in accordance with the dissolution test that P dissolution was nearly complete within the first 2 hr. Moreover, the FT-IR spectra also indicate the moderate portion of P remaining in the 50 nm anatase NPs. As revealed in the dissolution kinetics study, the average amount of released P is 5319 mg/Kg within 2 hr to 19 d at pH 8.4, which is lower than the content of P in the pristine 50 nm anatase NPs, i.e. 8050 mg/Kg (Table 1).

During the experiment, the EPM of TiO₂ NPs did not change greatly from 2 hr to 42 d at pH 8.4, which lead to the relatively stable hydrodynamic size in the aqueous phase (Figure 7). The slight decrease in hydrodynamic size for the 5 nm anatase might be attributed to mechanical shaking during experiment period. The steady surface potential and size is consistent with FT-IR spectra. As revealed in Figures 6, the peaks for Si at 936 cm⁻¹ and for P at 1111 cm⁻¹ were predominant after 19 d for the 10 × 40 nm rutile and 50 nm anatase respectively. Experimental data on dissolution and alkaline fusion also indicated that a large portion of Si and P remained in TiO₂ NPs after 19 days.

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