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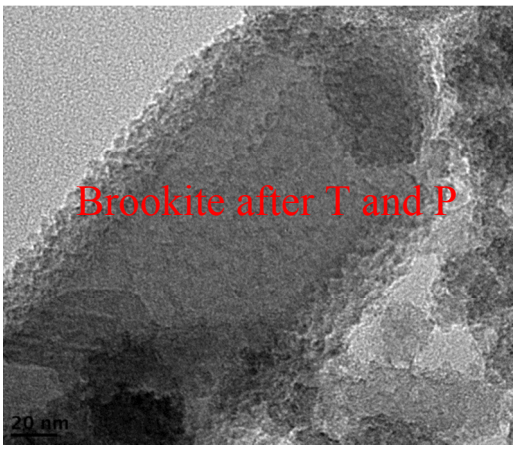

Nano impact

Titanium dioxide nanoparticles are used in a variety of domestic products including paints, plastics, inks, food colorings, toothpastes, cosmetics and sun-screens. Furthermore, TiO_2 is one of the most widely used photocatalysts for water and air purification, and is used as a coating for self-cleaning surfaces and other environmental cleaning purposes. Recently, TiO_2 has been reclassified as a group 2B carcinogen, "possibly carcinogenic to humans", by the International Agency for Research on Cancer. The specific characteristics of various types of TiO_2 nanoparticles and their potential impacts on human health and ecosystems have resulted in a need for further research on the quantification of different polymorphs of TiO_2 nanoparticles in the environment. The present study investigates the digestibility of different polymorphs of TiO_2-nanoparticles using MW-based HF/HNO_3 mixed acid digestion and MF-based KOH alkaline fusion methods. The main goal of the present study is to compare the dissolution efficacy of different TiO_2 nanoparticles polymorphs in different environmental matrix using established MW-based HF mixed acid digestion and modified MF-based KOH fusion. The environmental matrices encompassed stream bed sediments, kaolinite and bentonite.

Polymorph-dependent titanium dioxide nanoparticle dissolution in acidic and alkali digestions

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Abstract

Multiple polymorphs (anatase, brookite and rutile) of titanium dioxide nanoparticles (TiO_2-NPs) with variable structures were quantified in environmental matrices via microwave-based hydrofluoric (HF) and nitric (HNO_3) mixed acid digestion and muffle furnace (MF)-based potassium hydroxide (KOH) fusion. The environmental matrices included stream bed sediments, kaolinite and bentonite. The percentage of Titanium (Ti) recovered from the mixed acid digestion was not statistically different from KOH fusion when anatase and brookite TiO_2-NPs were blended in all three environmental matrices. However, the percentage of Ti recovery of rutile TiO_2-polymorph from the samples digested using mixed acid digestion method was significantly lower [23 (±5), 12 (±6), 11 (±0.6)] than those digested using KOH fusion method [74 (±4), 53 (±7), 75 (±2)]. The recovery percent values reported are for Ti in sediments, kaolinite and bentonite, matrices respectively. Exposing the TiO_2-NP spiked samples to elevated heat and pressure reduced the recovery of Ti from all three polymorphs via mixed acid digestion. In contrast, Ti recoveries from KOH fusion improved after heat and pressure treatment. A narrowing of the X-ray diffraction (XRD) peaks for anatase and brookite after heat and pressure treatment indicated an increase in the aggregation or particle interaction of the TiO_2-NPs. The XRD peaks for rutile TiO_2-NP polymorph was similar before and after heat and pressure treatment. In summary, regardless of the selected environmental matrix type, the mixed acid digestibility of TiO_2-NPs is polymorph-dependent; whereas, the KOH-fusion digestibility is polymorph independent. Therefore, when analyzing environmental samples containing TiO_2-NPs with unknown polymorphs, a KOH-fusion digestion method is recommended for yielding consistent results.

Keywords

Titanium dioxide; nanoparticles; temperature effects, particle structure

Introduction

Titanium dioxide nanoparticles (TiO_2-NPs) are used in various domestic products including paints, plastics, inks, food colorings, toothpastes, cosmetics and sun-screens.[1-3] Additionally, TiO_2 is one of the most widely used photocatalysts for water and air purification, and is used as a coating for self-cleaning surfaces and other environmental cleaning purposes.[1-5] For example, anatase TiO_2 is used in ultraviolet light (UV, $\lambda < 397$ nm) photocatalysis for generating hydroxyl radicals which can inactivate microbes and degrade a variety of organic compounds.[6] It has also been reported that TiO_2 photocatalysts exhibit reactivity under visible light (Vis, $\lambda > 400$ nm) even under the low illumination of interior lighting.[6] Thus, in the presence of both UV and Vis light, photo-reactive species of TiO_2 can be a concern if released into the environment. Recently, TiO_2 has been reclassified as a group 2B carcinogen, "possibly carcinogenic to humans", by the International Agency for Research on Cancer.[7] The specific characteristics of various types of TiO_2-NPs and their potential impacts on human health and ecosystems have resulted in a need for further research on the quantification of different polymorphs of TiO_2-NPs in the environment. Polymorphism is a condition in which a solid chemical compound exists in more than one crystalline form. These forms differ in physical and chemical properties resulting different stability and bioavailability.[8] These polymorphic differences are commonly captured using X-ray diffraction (XRD) patterns but not every environmental research study performs XRD analysis.

Microwave (MW)-based hydrofluoric (HF)/nitric (HNO_3) mixed acid and alkaline fusion are the most effective methods for quantifying refractory metals such as Ti.[9-15] Although methods involving HF as a single acid digestion are atypical, MW-based HF mixed acid digestion results in greater metal recovery. In addition, the application of HF is required for the complete digestion and quantification of refractory metals in geological and environmental sample matrices such as soil, sediments and dusts.[16-17] This is because HF dissolves the aluminosilicate structure of environmental materials and facilitates the liberation of metals.[8,18] However, a recent study,[13] reported that Ti recovery by alkaline fusion using lithium metaborate ($LiBO_2$) was greater than open-vessel HF mixed acid digestion for rutile-rich environmental samples. Taylor et al,[17] also reported that the alkaline fusion method was superior to the closed-vessel MW-based acid digestion procedure in determining refractory metals such as Ti. There are other studies to support the superiority of the alkaline fusion method over HF digestion for dissolution of refractory mineral containing samples.[18] Thus, there is still some ambiguity about the effectiveness of digestion procedures in spite of a huge amount of research that has been completed on dissolution and determination of refractory metals in environmental samples. The variety of mineral polymorphs make the digestion methodology and quantification in the sample of interest a challenge.[8] For example, refractory metal Ti has several naturally occurring polymorphs such as anatase, brookite and rutile with different structures, surface enthalpy and stability.[19-20] Generally, the thermodynamic stability is in this order: rutile > brookite > anatase.[21] However, the thermodynamic stability is particle size dependent. At the nano-scale, anatase is more stable than rutile, but rutile becomes the more stable as particle-size increases.[22] Despite known differences in size-dependent thermodynamic stability, literature concerning the

digestion techniques for Ti dissolution and quantification of TiO_2-NP polymorphs is minimal. Most of the existing studies are usually based on the general Ti containing environmental samples.[13,17] The growing demand for TiO_2-NPs for various products and processes has, resulted in the generation of other polymorphs of TiO_2-NPs, which are required to be quantified in the environmental samples.

In addition to the aforementioned polymorph-and size-dependent thermodynamic stabilities impacting the Ti recovery, the Ti recovery can be altered due to the chemical reaction between Ti and other sample matrix elements during sample processing in the heat range of 160-260°C.[19-24] For example, Ti reacts with different calcium and aluminum-bearing compounds during the sample digestion process in the aforementioned heat range.[24] The degree of the reaction is substantial on the surface of particles during the digestion process.[23] During digestion, a film may form on the surface of TiO_2-NPs in the presence of caustic potash altering the metal extraction rate.[20,25] Thus, the release of Ti from TiO_2-NPs may vary based on the surface properties of different TiO_2-NP polymorphs regardless of the digestion procedure.

In a previous paper, we have reported the accuracy and precision of Muffle-furnace (MF)-based fusion compared to traditional Bunsen burner-based fusion in determining Ti from different polymorphs of TiO_2 NPs.[26] In this paper, we further investigate the digestibility of different polymorphs of TiO_2-NPs using MW-based HF/HNO_3 mixed acid digestion and MF-based KOH alkaline fusion methods. The main goal of the present study is to compare the dissolution efficacy of different TiO_2-NP polymorphs using established MW-based HF mixed acid digestion and modified MF-based KOH fusion. Bulk degradation methods are very important for initial

risk assessment in environmental samples. Dependable initial screening procedures for total Ti can aid risk assessors in determining whether or not to pursue more detailed chemical speciation data for a particular sample or site. The impact of heat and pressure on TiO_2-NP stability/reactivity and subsequent Ti recovery from TiO_2-NPs (pure and blended in environmental materials) was the secondary objective of this study.

Experimental Methods and Procedures

TiO_2-NPs types and characterization

The detailed experimental protocols are discussed in a prior study.[26] The three TiO_2-NP polymorphs studied in this study were anatase, brookite and rutile. The anatase TiO_2-NPs were obtained from the National Institute of Standards and Technology (NIST) while rutile TiO_2-NPs were purchased from Sigma (St. Louis, MO, USA). The brookite TiO_2-NPs were synthesized at the U.S. Environmental Protection Agency's (EPA's) Andrew W Breidenbach Environmental Research Center (AWBERC) located in Cincinnati, Ohio. The brookite synthesis method has been described in previous studies.[26-27] In brief, an aliquot of 28.5 g of TiCl4 was dissolved in 50 mL concentrated HCl at room temperature to yield a light yellow solution. The acidified TiCl4 solution was slowly diluted with 450 mL distilled water and then 1 L of isopropanol was added to the diluted solution. The mixture was then refluxed for 20 hours at 80 °C to obtain a homogeneous milky white solution, which was centrifuged, decanted, and air dried. Solids were analyzed as-prepared without further washing or purification. The three selected TiO_2-NPs were characterized before and after heat and pressure treatment. The X-ray diffraction (XRD) was

performed using a PANAnalytical X'pert Pro 2θ diffractometer operating in the reflection mode with Cu-Kα radiation (45 kV, 40 mA) and a step scan mode over the range of 10 to 90°. Diffraction patterns for each TiO_2-NP polymorph were compared with reference patterns from the Joint Committee on Powder Diffraction Standards (JCPDS) database. Brunauer-Emmett-Teller (BET) surface area measurements of heat and pressure treated and untreated TiO_2-NPs were determined using a Tristar 3000 (Micromeritics, GA, USA) porosimeter analyzer after purging with N_2 gas for 2 hrs at 150 °C. Transmission Electron Microscopy (TEM) was used to determine the sizes and the shapes of all three TiO_2-NPs polymorphs before and after heat/pressure treatment. A JEOL-2100 STEM (JEOL Inc., USA) with a side mounted Gatan digital camera was used for imaging TiO_2-NPs. Titanium dioxide samples were prepared by depositing 15 µL of TiO_2-NPs dispersed water suspension on a formvar-carbon coated copper grid. Samples were air-dried at room temperature overnight in a dust-free box. Images were captured at an accelerating voltage of 200 kV, and collected using Gatan software.

Environmental matrices used for TiO_2-NP spikes

River sediment, bentonite and kaolinite were used as environmental matrices. These materials were digested with and without additions of the three polymorph TiO_2-NPs to determine the background Ti concentrations and Ti spike recoveries. River sediment was collected from experimental stream beds at EPA's Experimental Stream Facility (ESF) located in Milford, Ohio. Plastic trays with porous side walls and a solid base were used to collect the river sediment and processed as follows: A 250 µm sieve was placed on top of a 20 L plastic container and the sample was wet sieved. The sieved material, which was collected in 20 L containers, was

allowed to settle for 5 days. After 5 days, the bottom sediment layer was collected by siphoning out the supernatant prior to drying in an oven at 105 °C for 5-7 days. The dried sediment sample was then gently crushed using mortar and pestle and again passed through a 250 μm sieve.[26]

The kaolinite (1:1) and bentonite (2:1) clay minerals were purchased from Sigma Chemical Company (St. Louis, MO, USA). Three sets of TiO_2-NP-spiked samples were prepared from each environmental matrix separately. In a glove box, ten grams of each environmental matrix were spread evenly on aluminum foil and 0.2 g of each TiO_2-NP type was sprinkled uniformly to achieve a 2% TiO_2-NP spiking rate on the basis of TiO_2 or 1.2% Ti. While 2% TiO_2-NP spiking samples were used for digestion, a separate set of 5% TiO_2-NP-spiked samples were also prepared for XRD analysis. It is highly unlikely to find high Ti concentrations in conventional environmental samples, but these spike rates were required to achieve uniform distribution of TiO_2-NP in samples for digestion and polymorph determination. For example, the XRD analysis requires a minimum of 5% analyte for consistent and repeatable results. Each mixture was then transferred to separate sampling bottles and mixed for 30 minutes using an end-over-end rotator (Rotamix, ATR Inc. Laurel, MD, USA). A portion of environmental material with and without spiked TiO_2-NPs was heat/pressure treated (described in section 2.5). The dissolution efficacy of TiO_2-NPs with and without environmental materials was tested using MW-based HF mixed acid and MF-based KOH digestion techniques. The background Ti concentrations of the environmental materials were used in the calculation of Ti-spike recoveries.

HNO_3/ HF mixed acids microwave digestion

In the mixed acid digestion method, 0.25 ± 0.001 g of pure TiO_2-NPs, 0.25 ± 0.001 g of environmental material and 0.25 ± 0.001 g of TiO_2-NPs-blended environmental material were digested separately in triplicate using a mixture of HF (3 mL) and HNO_3 (9 mL) following EPA Method 3052.[28] Each sample solution was diluted to 100 mL using nano-pure water and was transferred to acid-washed (HNO_3), triple-rinsed (de-ionized H_2O) plastic bottles and stored at 4°C prior to analysis.

KOH alkaline MF fusion

To be consistent with the mixed acid digestion method, the same amount of TiO_2-NPs, and environmental materials with and without spiked TiO_2-NPs were digested with 1.6 g KOH in nickel crucibles in triplicate. Fusion was performed using a pre-heated Lindberg MF (Riverside, MI, USA) at 700 °C for 20 minutes.[26] After 20 minutes, fused samples were allowed to cool to room temperature, and nano-pure water was added to dissolve the solidified fusion mixture. Similar to the standard fusion technique, the fusion mixture was brought up to 250 mL using nano-pure water after adding 50 mL of 50% HCl solution and 0.5 g of oxalic acid. Samples were immediately analyzed for total Ti content or stored at 4°C until analysis.[29]

Heat and pressure effects on Ti recovery from environmental matrices

Portions of TiO_2-NPs, environmental materials with and without spiked TiO_2-NPs, were treated in triplicate at constant heat (300 °C) and pressure (10.3 bar) for 4 hours to evaluate the effects of heat and pressure on the stability and reactivity of TiO_2-NPs. A series of stainless-steel reaction

vessels (50 ml, Pressure Products Industries, Warminster, PI) maintained at aforementioned conditions were used to treat the samples. The vessel temperatures were kept at set condition using Duo-Thermo-O-Watch (Glass-Col,) equipped with digital thermocouple, while the vessel pressures were monitored using digital pressure controllers (Omega Engineering, Inc.). Natural air was used to pressurize the reactor system when heat was nearing preset values. Heat and pressure treated samples were removed and characterized prior to digestion as described previously.

Sample and data analysis

The total Ti concentration was measured using a PerkinElmer 2300 DV inductively coupled plasma-optical emission spectrometer (ICP-OES). Prior to analyses for Ti, the total dissolved solids (TDS) content of alkaline fused samples was determined using standard American Public Health Association (APHA) methods,[30] and samples were diluted to reduce TDS content. All acids (HNO_3, HF and HCl) were of trace metal grade and nano-pure water (≥18 μΩ cm^{-1} resistivity) was obtained from a Nanopure™ (Barnstead Thermo Scientific, Dubuque, IA, USA) water purification system. An ICP single-element Ti standard solution (Spex Cetriprep, Metuchen, NJ, USA) of 1000 mg L^{-1} was diluted as needed for calibration and internal quality checks. A diluted ICP multi-element standard solution of 1000 mg L^{-1} (AccuStandard, New Haven, CT, USA) was used as an external standard for calibration verification. In order to overcome the matrix effects, matrix-matched standards were used for calibration. Titanium concentrations were determined in all three environmental materials, TiO_2-NP-spiked environmental materials and pure TiO_2-NPs.

To distinguish the effect of heat-pressure on TiO_2-NP polymorphs stability or dissolution, data for each digestion were analyzed separately using analysis of variance (ANOVA). Significant differences among means were determined using protected Fisher's least significant different test, only when ANOVA indicated significant differences. The SYSTAT (Systat for Windows, version 11) program was used to perform statistical analyses.

Results and discussion

Characterization of pure Ti-NPs

The XRD patterns for the three Ti-NP polymorphs exhibited strong diffraction patterns consistent with standard JCPDS diffraction for anatase (01-086-1157), brookite (01-075-1582) and rutile (01-075-1750) (Fig. 1a-c). Diffraction patterns of both anatase and brookite TiO_2-NPs exhibited a decrease in the peak width at half max and an increase in intensity after exposing to heat and pressure (Fig. 1a and b). However, diffraction peak positions of both polymorphs were similar before and after exposing to heat and pressure. The diffraction peak shapes of untreated rutile TiO_2-NPs were comparatively narrower than the anatase and brookite TiO_2-NPs. In addition, rutile diffraction peak shape did not change after exposing to heat and pressure, suggesting a well-defined stable crystalline structure in the rutile TiO_2-NPs (Fig. 1c). The BET surface area of rutile polymorph TiO_2-NPs before heat and pressure exposure is approximately 1 $m^2\ g^{-1}$ and about 159 and 203 times smaller than anatase and brookite polymorphs, respectively (Table 1). This large difference in surface area could be attributed to larger particle size or

aggregation of the rutile TiO_2-NPs. The surface area of rutile polymorph TiO_2-NPs increased marginally after exposing to heat and pressure. The surface area of anatase 159 m^2 g^{-1} and brookite 204 m^2 g^{-1} before heat and pressure treatment reduced to 66 and 37 m^2 g^{-1}, respectively, after exposing to heat and pressure (Table 1). Particle size measurements by TEM images (Fig. 2) for the three pure polymorphs are in agreement with that of surface area. For example, the TEM-measured anatase and brookite TiO_2-NPs ranged from 2-5 nm prior to heat and pressure treatment (Fig. 2 a and c). The image for rutile TiO_2-NPs before heat and pressure treatment showed comparatively bigger particle aggregate ranging between 25-50 nm (Fig. 2e). Both anatase and brookite TiO_2-NPs exhibited a clear aggregation after heat and pressure treatment (Fig. 2 b and d). The changes in rutile TiO_2-NPs particle size after heat and pressure were not apparent in TEM images but did not show detectable crystal growth. To verify the impact of heat and pressure treatment, the crystallite sizes were estimated for anatase and brookite polymorphs from XRD patterns using Scherrer equation (Table 2). The lack of variability between treated and untreated rutile XRD patterns prevented estimating rutile polymorph size. It was observed that brookite polymorph sample contained both anatase and rutile polymorphs (Table 2), and rutile particle size in brookite sample increased due to heat and pressure treatment. The peaks corresponding to anatase (101) plane, rutile (110) plane, and brookite (121) plane were used to calculate the sizes. The particle size estimated using XRD patterns are in line with the TEM particle size.

Effect of digestion type on different polymorphs of TiO_2-NPs with and without environmental matrices

The concentration of Ti in the blank was below the instrument method detection limit of 0.45 µg L^{-1} and none of the reagents used contained any detectable concentration of Ti indicating that measured concentration of Ti was associated to the samples (Tables 3 and 4). Amount of Ti in the environmental matrices was subtracted to determine the percent Ti recovery from TiO_2-NPs when TiO_2-NP polymorphs were blended in environmental matrices. Of the three environmental matrices, the kaolinite contained the highest Ti content (~8 mg g^{-1}) which is about two-fold greater than the sediment Ti content. The bentonite clay contained around 1 mg g^{-1} of Ti. Both digestion techniques resulted in similar Ti concentrations for the two clay materials before heat and pressure treatment. In contrast, mixed acid digestion resulted in comparatively lower Ti concentration than the KOH fusion from sediments (Table 3).

Titanium percent recoveries for TiO_2-NPs in anatase form was 80 (±14.0) and for brookite form was 81 (±3), by the MW-based HF/HNO_3 mixed acid digestion procedure. The corresponding percent recoveries were 96 (±2) and 85 (±2) by MF-based KOH fusion. In contrast, the Ti percent recovery of 14 (±1) for pure rutile TiO_2-NPs by the MW-based HF/HNO_3 mixed acid digestion was significantly lower than 87 (±5) by MF-based KOH fusion (Ti concentration for pure TiO_2-NPs are not presented). Similarly, the percent Ti recoveries for rutile polymorph when blended in the environmental matrices were significantly lower by MW-based HF/HNO_3 mixed acid digestion compared to MF-based KOH fusion (Fig. 3). Both anatase and brookite resulted in similar Ti recoveries when blended in the environmental matrices regardless of the method of digestion. Relatively higher variability was observed for anatase in sediments under mixed acid digestion before treatment (Fig. 3), which could be a result of uneven dispersion of

applied TiO_2-NPs in three replicates.[26] The experimental results show that MW-based HF/HNO_3 acids digestibility may not be an effective technique to dissolve rutile TiO_2-NPs either in pure form or blended in environmental materials. These results reveal that the type of TiO_2-NP polymorph present in the environmental samples can influence recovery of Ti under different digestion techniques. It is recommended that the KOH fusion technique be used to determine the amount of Ti present in unknown environmental samples.

The chemical reactions and thermodynamic properties of reactants are complex during the mineral digestion process and have not yet been clearly identified. [24] However, alkali compounds have been reported as metal (including refractory metal Ti) recovery enhancing compounds.[24] The spontaneous formation and dissolution of oxide films in the presence of strong alkaline electrolytes (KOH) are the possible reasons for higher Ti recoveries by MF-based KOH fusion.[25] The rate of dissolution of oxide films formed on the surface of TiO_2-NPs in the presence of the strong acid solution is slower, and low recovery of thermodynamically stable rutile TiO_2-NPs by HF/HNO_3 mixed acids in the current study is consistent with the literature.[12] However, the deviation of anatase and brookite TiO_2-NPs from the same trend, indicated that HF/HNO_3 mixed acid digestion may not be a poor dissolution technique across all polymorphs of TiO_2-NPs as previously noted,[16,18] but dissolution appears to be polymorph crystal structure-dependent (Table 4).

Effect of heat and pressure on different polymorphs of TiO_2 mineral digestion

The heat and pressure treatment resulted in a decrease in the percent Ti recoveries across all TiO_2-NP-blended environment matrices by HF/HNO_3 acid digestion (Fig. 3). In contrast, percent Ti recoveries increased when the heat and pressure treated TiO_2-NP-blended environment matrices were KOH digested (Fig. 3). The decreased Ti recoveries in the HF/HNO_3 digestion were more prominent for the anatase and brookite polymorphs than rutile. Previous research revealed that nano-scale anatase and brookite polymorphs may alter phase stability and transfer to rutile when heated.[16,22] For example, Smith et al.[31] revealed that the transformation of anatase to rutile is thermodynamically favorable at all temperatures between 0 and 1,300 K on the basis of Gibbs free energy calculations. However, others reported that conversion of anatase and brookite to rutile only occurred at temperature ranges between 800-1,023 K, much greater than the 573 K in the current experiment.[32] Therefore, the lower recoveries for Ti in the heat and pressure treated TiO_2-NP-environment materials from HF/HNO_3 digestion may not be an effect of phase transformation, rather an increase in particle-particle interaction and/or particle aggregation of anatase and brookite compared to rutile (Fig. 2). Even low heating under pressure has a profound effect on particle interaction and aggregation of anatase and brookile TiO_2-NP as illustrated by a reduction in the peak width and half max and an increase in the kurtosis of the diffraction peaks.[20] This was apparent by the XRD peak positions of anatase and brookite before and after heat (300 °C)/pressure (10.3 bar) treatment in the current experiment (Fig. 1). The impact of heat and temperature on digestion technique was not only confined to TiO_2-NPs but also to the environmental matrices (Table 3). Similar to TiO_2-NPs, Ti concentrations of environmental matrices declined for the MW-based mixed acid digestion while the opposite occurred for the MF-based KOH fusion after exposing to heat and pressure treatment.

The particle reaction-limited aggregation may have resulted in a surface area reduction of 58% and 82% for anatase and brookite, respectively, after heat and pressure treatment (Table 1). In contrast to the two aforementioned types of TiO_2-NP polymorphs, diffraction peaks of rutile did not change after heat and pressure treatment, indicating a stable crystal structure of rutile (Fig. 2). This is in agreement with the subtle change in surface area of rutile after the heat and pressure treatment.

The change of surface properties of TiO_2 polymorphs due to heat and pressure treatment may have altered the surface enthalpy and the stability in the order of anatase > brookite > rutile.[20] Additionally, the thermodynamic stability is particle size dependent, and anatase is thermodynamically stable at smaller size, brookite at intermediate sizes and rutile at the largest sizes.[20,22] The XRD results (Table 2 and Fig. 2) clearly indicate that heat and pressure treatment results in phase transformations where the anatase and brookite polymorphs are converted to a more stable rutile form. These phase transformations combined with the particle disaggregation in the presence of KOH may have resulted in greater recovery of Ti by MF-based KOH fusion. The growth in particle size due to reaction-limited aggregation of anatase and brookite (Table 2 and Fig. 2), may have decreased the Ti released by the MW-based HF digestion similar to rutile.

Conclusions

Experimental results reveal that the digestibility of TiO_2-NPs is more closely associated with the particle aggregation and TiO_2-NP polymorphs. At the spiked levels studied, the HF/HNO_3 acids digestibility of TiO_2-NPs is polymorph dependent while MF-based KOH digestibility is

polymorph independent. The HF/HNO_3 acids digestibility was impaired by greater aggregation whereas MF-based KOH digestibility was not affected by the degree of particle aggregation and/or crystallization. The use of heat and pressure treatment considerably influenced the particle characteristics and surface properties of TiO_2-NPs. The aggregation mechanism has an effect on surface enthalpy. The dissolution efficacy of HF further diminished with increasing aggregation of the TiO_2-NP polymorphs. In contrast, the dissolution capacity of aggregated TiO_2-NP polymorphs further increased by KOH fusion. Thus, KOH can be used to dissolve all three TiO_2-NP polymorphs evaluated in this study while HF is only effective for anatase and brookite dissolution. Further studies are necessary to verify the trends observed in this experiment at a lower environmentally relevant concentrations. These results provide useful information for the selection of digestion techniques to determine Ti content in TiO_2-NP contaminated environmental samples.

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Notice

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Table and Figure Captions

Table 1 Characteristics of TiO_2-NPs before and after heat and pressure treatments

Table 2 Particle size estimation from XRD using Scherrer equation

Table 3 Concentration (mg g^{-1}) of Ti in sediments, kaolinite and bentonite before and after heat and pressure treatment determined by ICP-OES using MW-based HF/HNO_3 acids and MF-based KOH fusion digestions

Table 4 Concentration (mg g^{-1}) and percent recovery of Ti in TiO_2-NP-spiked sediment, kaolinite, and bentonite by ICP-OES using MF-based KOH fusion and MW-based HF/HNO_3 acids before and after heat and pressure treatments.

Figure 1 XRD patterns of anatase (a), brookite (b) and rutile (c) TiO_2-NPs before and after heat and pressure treatment.

Figure 2 TEM images for anatase (a and b), brookite (c and d) and rutile (e and f) TiO_2-NPs before and after heat and pressure treatment, respectively.

Figure 3 Percent recovery of Ti as a function of polymorph and digestion technique before and after heat and pressure treatment. The letters along the top of the figure indicate the specific sample. The first letter indicates the TiO2 polymorph: A = Anatase, B= Brookite, R=Rutile. The second letter indicates the environmental matrix: S = Sediment, K=Kaolin, B = Bentonite.

Table 1

Material	Source	Surface area before (m^2 g^{-1})	Surface area after (m^2 g^{-1})
TiO_2-Anatase	NIST	158.8	66.4
TiO_2-Brookite	Prepared	203.5	36.9
TiO_2-Rutile	Sigma Aldrich	0.9	1.3

Table 2.

XRD pattern	Heat/Pressure	Anatase	Brookite	Rutile
Fig 1A	Untreated	5.4 nm (diff. 2θ=1.5)		
	Treated	9.0 nm (diff. 2θ=0.9)		
Fig 1B	Untreated	3.8 nm (diff. 2θ=2.1)	11.6 nm (diff. 2θ=0.7)	11.6 nm(diff. 2θ=0.7)
	Treated	26.9 nm (diff. 2θ=0.3)	40.8 nm (diff. 2θ=0.2)	20.2 nm(diff. 2θ=0.4)

Table 3

Material	Ti concentration mg g^{-1} (±SD) MW-based HF/HNO_3 digestion		Ti concentration mg g^{-1} (±SD) MF-based KOH fusion	
	before	After	before	after
Sediment	3.0 (±0.1)	2.5 (±0.0)	4.2 (±0.0)	6.7 (±0.0)
Kaolin	8.1 (±0.1)	6.9 (±0.1)	8.0 (±0.4)	9.2 (±0.3)
Bentonite	1.0 (±0.0)	0.5 (±0.0)	1.0 (±0.1)	2.9 (±0.0)

Data in parentheses are ± standard deviation (SD) of mean

Table 4

TiO_2-NP polymorphs	Environmental Material	Heat/Pressure Ttreatment	Acid extracted Ti concentration mg g^{-1}	Alkali fusion Ti concentration mg g^{-1}
Anatase	Sediment	Untreated	19.2a	13.6a
		Treated	8.4b	19.1b
Anatase	Sediment	Untreated	15.0a	16.0a
		Treated	13.4a	17.5a
Anatase	Bentonite	Untreated	10.9a	10.6a
		Treated	7.3b	13.7b
Brookite	Sediment	Untreated	15.0a	13.0a
		Treated	6.1b	16.0b
Brookite	Kaolin	Untreated	14.2a	13.2a
		Treated	7.5b	21.1b
Brookite	Bentonite	Untreated	8.8a	8.8a
		Treated	6.7a	11.9b
Rutile	Sediment	Untreated	5.9a	13.2a
		Treated	2.6b	18.6b
Rutile	Kaolin	Untreated	9.5a	14.4a
		Treated	5.2b	20.8b
Rutile	Bentonite	Untreated	2.3a	10.1a
		Treated	1.2a	13.8b

Data followed by the same letter for a polymorph/environmental material mixture within a digestion method are not significantly different at p 0.05.

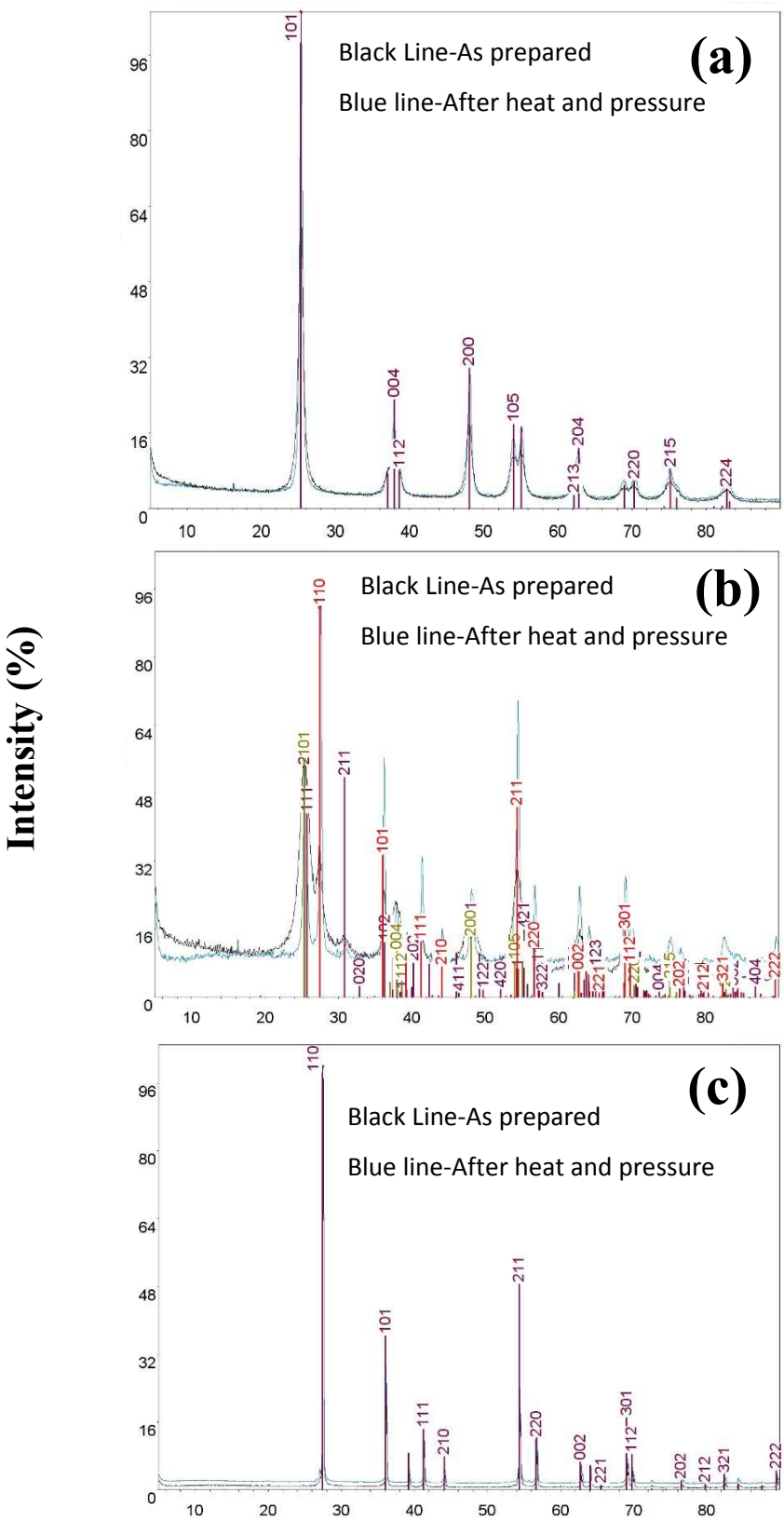
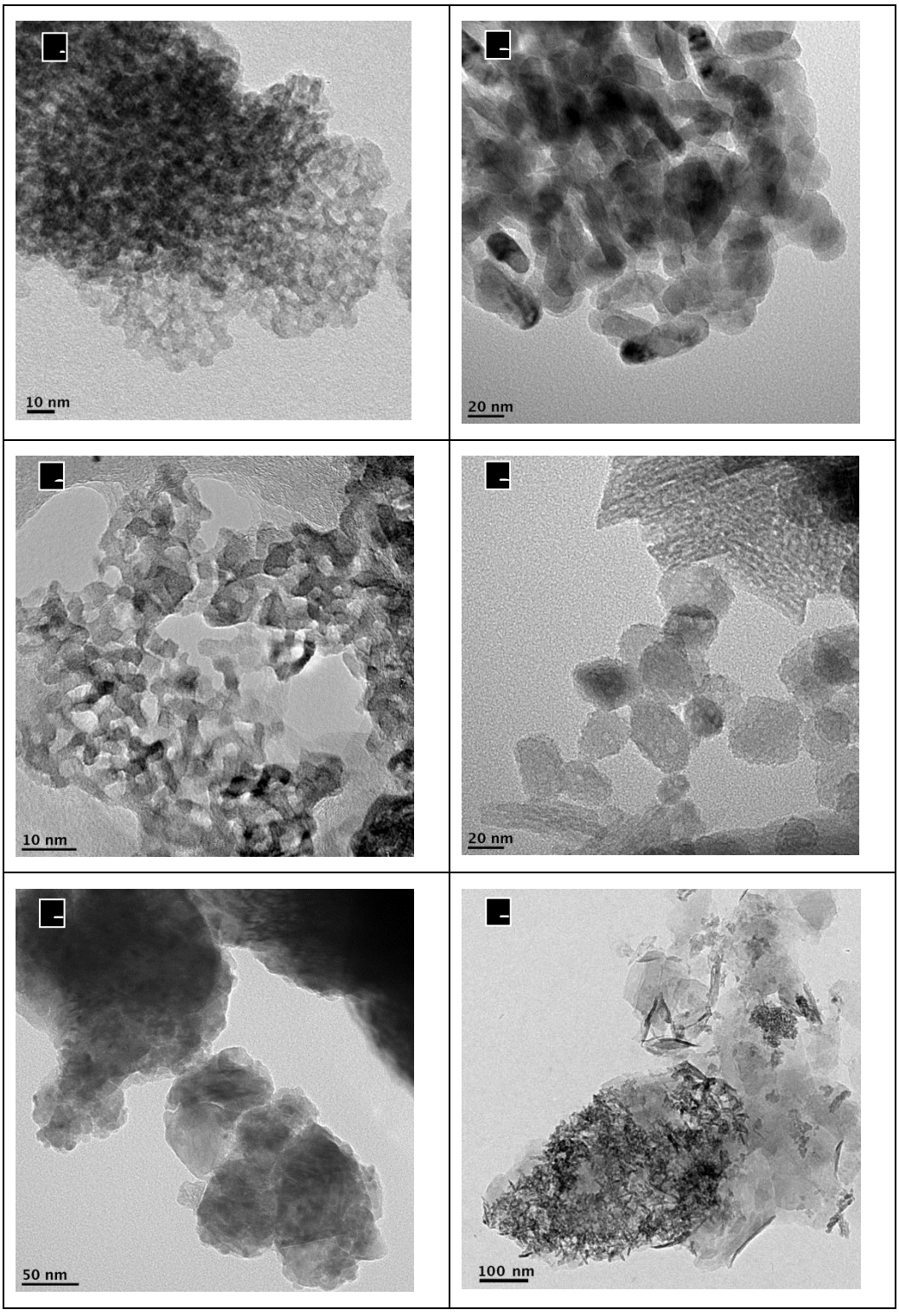


Figure 1



Anatase TiO_2-NPs untreated (A) and temperature and pressure treated (B)

Brookite TiO_2-NPs untreated (C) and temperature and pressure treated (D)

Rutile TiO_2-NPs untreated (E) and temperature and pressure treated (F)

Figure 2

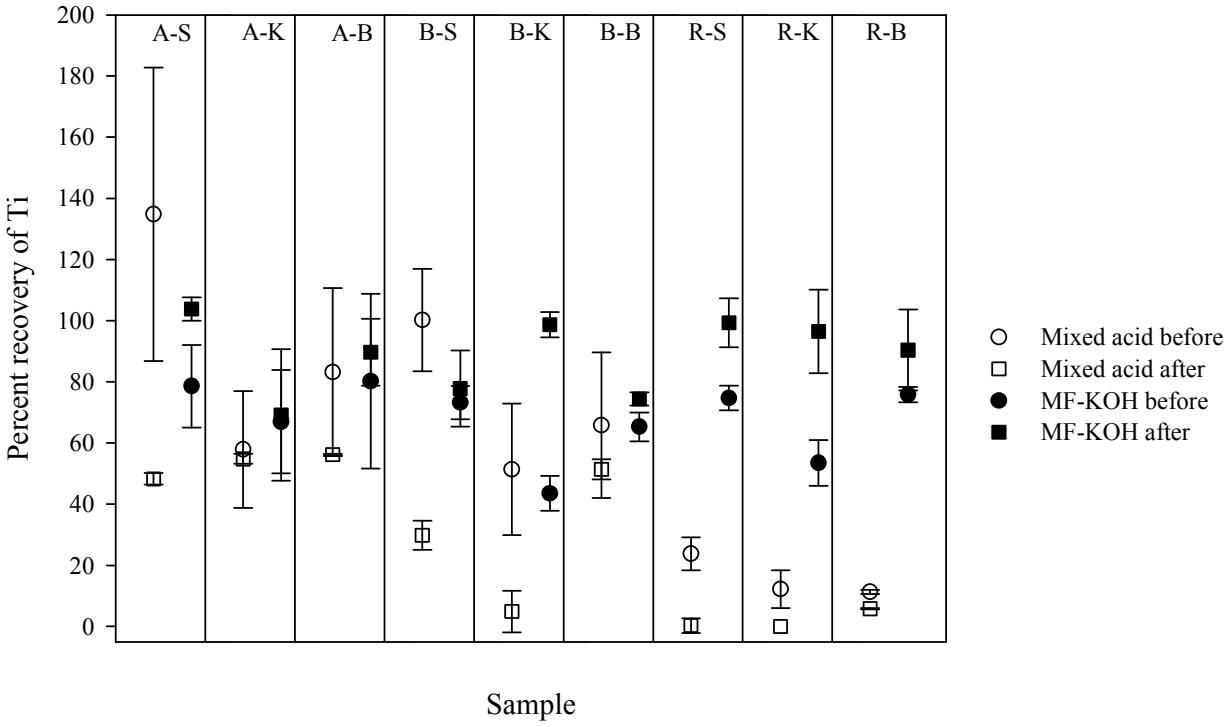


Figure 3