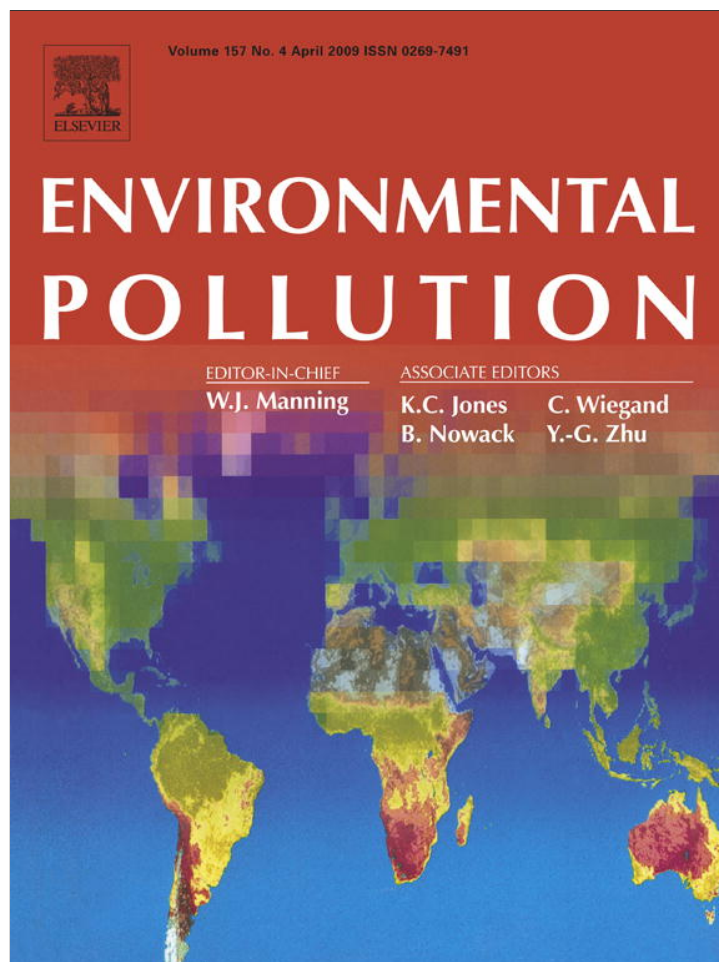


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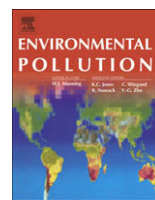
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Influence of titanium dioxide nanoparticles on speciation and bioavailability of arsenite

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The co-existence of TiO₂ nanoparticles could change the speciation of arsenite by adsorption and photo-oxidation, and enhance its bioaccumulation to carp.

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ABSTRACT

In this study, the influence of the co-existence of TiO₂ nanoparticles on the speciation of arsenite [As(III)] was studied by observing its adsorption and valence changing. Moreover, the influence of TiO₂ nanoparticles on the bioavailability of As(III) was examined by bioaccumulation test using carp (*Cyprinus carpio*). The results showed that TiO₂ nanoparticles have a significant adsorption capacity for As(III). Equilibrium was established within 30 min, with about 30% of the initial As(III) being adsorbed onto TiO₂ nanoparticles. Most of aqueous As(III) was oxidized to As(V) in the presence of TiO₂ nanoparticles under sunlight. The carp accumulated considerably more As in the presence of TiO₂ nanoparticles than in the absence of TiO₂ nanoparticles, and after 25-day exposure, As concentration in carp increased by 44%. Accumulation of As in viscera, gills and muscle of the carp was significantly enhanced by the presence of TiO₂ nanoparticles.

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1. Introduction

Research on developing new types of nanomaterials has drawn much recent attention. Now, at least 44 elements in the Periodic Table are commercially available in nanoscale form, and more elements are being added to this list (ETC Group, 2003). Extensive applications of nanomaterials, including catalysis, drug delivery, medical diagnostics, enzyme immobilization, sensors and pollution control, have been developed (NCPI, 2007; Kipp, 2004; Kong et al., 2000; Long and Yang, 2001; Ryu et al., 2007). Currently, more than 140 companies worldwide have already engaged in manufacturing nanoparticles. During the next 10–15 years, nanotechnology sectors are expected to exceed \$1 trillion annually in global industrial output and to employ about 2 million workers (Roco and Bainbridge, 2001).

An inevitable consequence of this rapid growth of nanotechnology is the eventual exposure of humans and other environmental receptors to nanomaterials (Nowack and Bucheli, 2007; Boxall et al., 2008). Meanwhile, research is now showing that when normally harmless bulk materials are made into nanoparticles they tend to become toxic (ETC Group, 2003; Roco and Bainbridge, 2001;

Tinkle et al., 2003). Several literatures have proposed that the size effect seems more important to nanoparticle toxicity than the actual composition of the material (Kreuter et al., 2002; Gumbleton, 2001; Donaldson et al., 2000; Öberdörster, 2000). The study of Tan et al. (1996) shows that the TiO₂ nanoparticles used in sunscreen can get deep enough into the skin, and then be taken up into the lymphatic system, while larger particles (greater than 1 μm in diameter) cannot. In vivo studies show that inflammation occurs in the lungs of laboratory animals after exposure to nanoparticulate aerosols (Donaldson et al., 2000; Öberdörster, 2000). In vitro studies show that nanoparticles could produce free radicals that can cause cellular damage. This damage can be manifested in different ways, including genotoxicity and enhanced cell death rates (Afaq et al., 1998; Rahman et al., 2002). Recently, Lovern and Klaper (2006) reported the first study of TiO₂ nanoparticles on an environmental sentinel organism. In their study, the lethal concentration of TiO₂ nanoparticles was only 10 ppm for *Daphnia magna* following a 48 h of aqueous exposure.

Although there is an increasing amount of research on the toxicology of nanomaterials, little is currently known about the fate, transport, and transformation of nanosized materials once they enter the environment (Vikesland et al., 2008; Benn and Westerhoff, 2008). Many laboratory and field test studies have shown that colloids, both organic and inorganic, could facilitate the transport of toxic pollutants, such as metals, radionuclides, and

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certain ionizable organic pesticides (Amrhein et al., 1993; Honeyman, 1999). Similarly, the large surface area, crystalline structure, and reactivity of nanoparticles may facilitate the transport of toxic chemicals in the environment (Zhang and Masciangioli, 2003; Zhang et al., 2007). Hence, how and to what extent the emerging nanoparticles may influence the transfer, fate and ecorisk of toxic pollutants should be addressed as an important research hotspot.

Arsenic (As) is widely distributed in the environment, and it is known to be highly toxic to humans. It is now well recognized that consumption of arsenic, even at low levels, may lead to carcinogenesis (NRC, 1999; Zhu et al., 2008). Moreover, arsenic is found to be accumulative in freshwater fish. Thus, understanding the accumulation of arsenic in fish is important because of the concerns regarding human and wildlife exposure via consumption (Davis et al., 1996; Lewis et al., 2002). It has been recently reported that TiO₂ nanoparticles have a great adsorption capacity for arsenic ions due to the high surface area of TiO₂ nanoparticles and the presence of high affinity hydroxyl groups on their surface (Pena et al., 2006). We have reported that when cadmium and arsenate (As(V)) co-exist with TiO₂ nanoparticles, their bioaccumulation into carp increases significantly due to the carrying effect of TiO₂ nanoparticles (Sun et al., 2007; Zhang et al., 2007). Toxicity of arsenic changes with its speciation, and arsenite [As(III)] is reported to be 60 times more toxic than As(V). Hence, in the present study, the influence of TiO₂ nanoparticles on the speciation and bioavailability of As(III) was examined.

2. Material and methods

2.1. Material

All chemical reagents used were of analytical-reagent grade except for acids, which were of trace metal analysis grade. Solutions were prepared in deionized water. Laboratory equipment and containers were dipped in 25% (v/v) HNO₃ solution for at least 12 h prior to each use.

Chemicals used for preparation of As stock solutions were As₂O₃ for As(III) and Na₃AsO₄·12H₂O for As(V). Fresh solutions were prepared from the stock solutions for each experimental run.

Degussa P25 titanium dioxide nanoparticles (<http://www.degussa.com/degussa/en/products/>) were used as a representative nanoparticle in adsorption and accumulation experiments. P25 is widely applied as industrial catalyst and heat stabilizer. It is a common catalyst for photocatalytic researches, hence it is easily available in laboratory. The average Brunauer–Emmett–Teller (BET) surface area of P25 used was 50 m²/g, and average particle size was 21 nm. Standard titanium (IV) stock solution (1.0 g/L), which served as the calibration standard in the instrumental analysis, was prepared using the method described by Ophus et al. (1979). Briefly, 0.4170 g TiO₂ nanoparticles were boiled in 30 ml sulfuric acid–ammonium sulphate solution (400 g ammonium sulphate in 700 ml boiling concentrated sulfuric acid) and finally diluted to 250 ml with distilled water. Low-concentration standards were prepared daily by diluting the titanium (IV) stock solution with sulphuric acid (10% v/v).

2.2. Adsorption of As(III) and As(V) onto TiO₂ nanoparticles

Adsorption kinetics of As(III) and As(V) as comparison were determined using two 16 L tanks. Dechlorinated tap water was used in the experiment in order to keep similar water circumstances with those in the bioaccumulation tests, except that the tanks were put in a dark room. An ion chromatograph (DX120, Dionex, U.S.) was used for the analysis of common ions in the dechlorinated water, and the major cations were Ca²⁺ (47.8 ± 1.88 mg/L), Na⁺ (28.0 ± 0.94 mg/L), Mg²⁺ (26.4 ± 5.94 mg/L) and K⁺ (5.5 ± 0.34 mg/L). The major anions were SO₄²⁻ (81.9 ± 2.49 mg/L), Cl⁻ (48.79 ± 5.24 mg/L), NO₃⁻ (2.22 ± 0.49 mg/L) and F⁻ (0.63 ± 0.16 mg/L). The pH of the water was 7.8, and TOC was 2.6 mg/L. At the beginning of the experiment, specific amount of As stock solutions was added into the tanks containing 16 L dechlorinated tap water, and then 0.160 g (10 mg/L) of TiO₂ nanoparticles was added to start the adsorption. At 0, 10, 20, 30, 60, 120, 180, and 360 min, 10 ml of the suspensions were taken out and centrifuged for 5 min at 12,000 rpm using a high speed centrifuge (Hermle Z323, Germany), and residual aqueous As(III) and As(V) concentrations were analyzed. The sorbed amount was calculated by the difference of the initial and residue aqueous As concentrations.

2.3. Speciation of arsenic in the presence of TiO₂ nanoparticles

Speciation of As when only As(III) was initially added in the presence of TiO₂ nanoparticles both with and without sunlight was examined under the similar

water circumstances with those in the bioaccumulation tests except that no fish was added. At 0, 10, 20, 30, 60, 120, 180, and 360 min, 10 ml of the suspensions were taken out and centrifuged, and then the suspension was divided into two parts, one for As(III) determination and the other for total As determination.

2.4. Accumulation of arsenics in the carp with and without TiO₂ nanoparticles

A group of carp (*Cyprinus carpio*) was purchased from a local pet shop. The initial body weight and length of the fish were selected as 2.5–3.2 g and 3.3–4.1 cm, respectively. All fish were acclimatized in dechlorinated tap water with a natural light/dark cycle for 10 d before each experiment. At the beginning of the test, specific amount of As(III) stock solutions was added into two glass tanks containing 16 L dechlorinated tap water, respectively, and the initial concentration of As was 200.0 ± 10.2 µg/L. In one tank, 0.160 g TiO₂ nanoparticles were added and allowed to equilibrate for 2 h. 30 carp were then added into each tank. The fish were fed with a commercial fish-worm once a day during the experiment. The worms were measured for As level, and no As was found (<0.1 µg/g).

To maintain a relative stable aqueous phase concentrations of As and TiO₂, the solution was refreshed every other day. During the tests, the tanks were aerated slightly and the temperature (20 ± 2 °C) of water was maintained for each exposure. A control test without the contaminants was conducted under the same conditions. Three fish were removed and sacrificed at 2, 5, 10, 15, 20 and 25th day, and on the 20th day, 5 extra carp from each of the three treatments were dissected into skin and scales, muscle, gills, and viscera. After pretreatment, arsenic and TiO₂ concentrations in carp or different parts of carp were analyzed, respectively. As described by Rosen (2002), organisms take up As(V) via phosphate transporters and As(III) by aquaglyceroporins. In the body of organisms, As(V) can be reduced to As(III), and inorganic As can be methylated. Because the transformation of As could occur simultaneously in water and in fish body, no efforts were addressed to follow the speciation of As in fish and total As in carp was determined in this study.

2.5. Analysis of As and TiO₂

The pretreatment and analysis methods for As and TiO₂ were the same with our former study (Sun et al., 2007). Briefly, dried fish samples were digested in concentrated HNO₃ by a microwave digestion system (WX-3000 plus, EU Chemical Instruments Co., Shanghai, China). For As analysis, the excess acid was removed from the digested solution by heating the digested solution to near dryness. The efficiency of the digestion method has been evaluated by a reference material (Sun et al., 2007). Both total As and As(III) were measured using an atomic fluorescence spectrometer equipped with hydride generation (HG-AFS 2201, Haiguang Co., Beijing, China). For total As determination, thiourea (5%)–ascorbic acid (5%) mixing reagent was used for pre-reduction of arsenate, and hydrochloric acid (5%) media was used for hydride generation (Lu et al., 2002). Selective determination of As(III) was achieved using 40% m/v citric acid media because the transformation of As(V) to As(III) and the ensuing generation of arsine by hydride generation are considerably slow under this condition (González et al., 2003). As(V) concentration was obtained by subtracting the As(III) content from the total As concentration. The speciation method was checked by determining a series of different concentration of As(III) and As(V) mixtures. As(III), As(V) and total As recoveries in these samples ranged from 93 to 104%, 92–102%, and 95–102%, respectively.

For TiO₂ analysis, the TiO₂ released by digestion were decomposed into titanium (IV) ion by heating in 5 ml of the sulphuric acid–ammonium sulphate solution. Ti (IV) analysis was performed using an inductively coupled plasma–optical emission spectrometry (ICP-OES, IRIS Intrepid II, Thermo Electron, U.S.) at the wavelength of 336.121 nm (Sun et al., 2007). The pretreatment method could recover 95 ± 5% TiO₂ in fish tissues. The detection limits when using 0.2 g fish tissues were 0.1 µg/g for As and 0.01 mg/g for TiO₂.

2.6. Statistical analyses

For As(III) and As(V) concentration in water, and As and TiO₂ concentrations in fish, the mean values were calculated from the three replicates and expressed with standard deviation ($n = 3$). The homogeneity of variance was evaluated and a one-way analysis of variance (ANOVA) was then performed using a statistical soft, Origin 7.5 to assess the significance of differences observed between As concentrations in fish exposed to As-contaminated water with and without TiO₂. All statistical analyses were conducted at a significance level of 0.05.

3. Results and discussion

3.1. Adsorption of As(III) and As(V) on TiO₂ nanoparticles

Adsorption kinetics was observed for 6 h in the dark, and the results are shown in Fig. 1. Both As(III) and As(V) were adsorbed onto TiO₂ nanoparticles quickly, and equilibrium was reached within 30 min. No change in As speciation was found in the dark tank. The equilibrium time is in agreement with that reported by

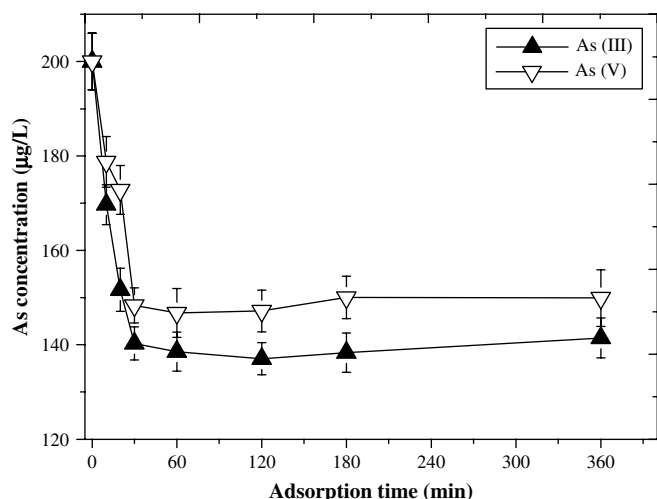


Fig. 1. Adsorption kinetics of As(III) and As(V) onto TiO₂ nanoparticles. Initial concentration of As = 200 µg/L; TiO₂ nanoparticles = 10 mg/L. pH = 7.8; ▲, As(III); ▼ As(V).

Dutta et al. (2004), who found that the adsorption equilibria of both As(III) and As(V) onto P25 TiO₂ nanoparticles were established in approximately 1 h. Unlike other porous media, in which adsorption possibly occurs through pore diffusion steps and takes a longer time to reach equilibrium, Degussa P25 is nonporous TiO₂ particles where only intermolecular diffusion adsorption processes occur. This kind of adsorption process would thus require less time to reach equilibrium.

Due to the high surface area (50 m²/g) and the presence of high affinity surface hydroxyl groups, TiO₂ nanoparticles have a great adsorption capacity for arsenic ions. The EXAFS (Extended

X-ray Absorption Fine Structure) analyses indicate that both As(V) and As(III) form bidentate binuclear surface complexes as evidenced by an average Ti–As(V) bond distance of 3.30 Å and Ti–As(III) bond distance of 3.35 Å. Due to their high adsorption capacity, TiO₂ nanoparticles have been evaluated for their capacity to remove As from water (Pena et al., 2006). As shown in Fig. 1, at the adsorption equilibrium, about 30% of the initial As(III) and 25% of the initial As(V) were adsorbed onto TiO₂ nanoparticles, respectively.

3.2. Arsenic speciation in water in tanks

As(III) and As(V) behave differently; at the pH level (7.8) used in the experiment, As(III) is uncharged and can cross biological membranes easily, whereas As(V) is charged. On the other hand, TiO₂ nanoparticles show excellent performance in pollutant destruction due to their strong oxidation potential of the photo-generated valence band (VB) holes in TiO₂ ($E_{VB} = +2.7$ V vs. NHE at pH 7) (Hoffmann et al., 1995). In order to disclose whether or not the speciation of As(III) will be changed by TiO₂ nanoparticles, As(III) and As(V) aqueous concentrations in the tanks were measured when As(III) was initially added into the tank containing TiO₂ nanoparticles both with and without sunlight. The results are presented in Fig. 2. In the absence of TiO₂ nanoparticles, the change of As(III) to As(V) was negligibly small both with and without sunlight, and As(III) was the predominant specie (more than 98%) in water phase (Fig. 2a and b).

When TiO₂ nanoparticles were introduced, dissolved As concentration decreased due to the adsorption. Without sunlight, only a small amount of As(III) changed to As(V) (less than 3%, Fig. 2c). However, with sunlight, dissolved As(III) concentration dropped quickly while dissolved As(V) concentration increased sharply simultaneously (Fig. 2d). About 73% of the initial As(III) changed to As(V) in 1 h, and almost all of the initial As(III) changed

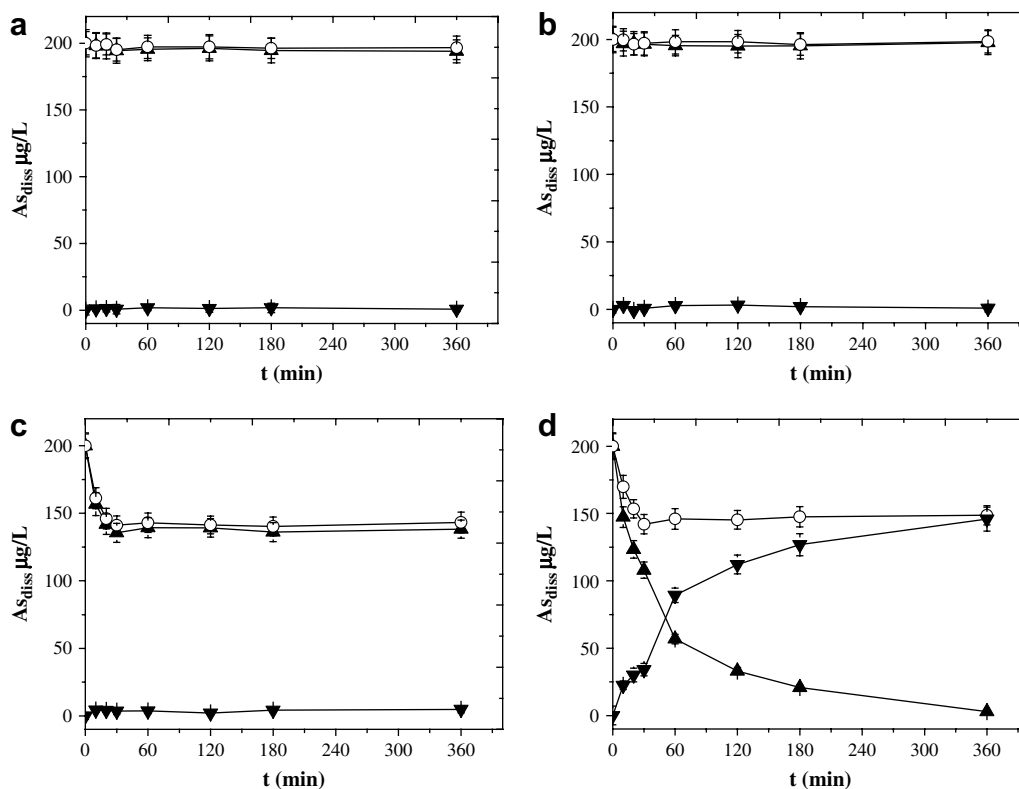


Fig. 2. Speciation of As in water. (a) As(III) without sunlight, (b) As(III) with sunlight, (c) As(III) + P25 nanoparticles without sunlight, (d) As(III) + P25 TiO₂ nanoparticles with sunlight. The average light intensity in the tank was about 0.32 W/m². ▲, As(III); ▼, As(V); ○, total As.

to As(V) after 6 h of sunshine. Ferguson et al. (2005) also reported the oxidation of As(III) to As(V) by TiO₂ photocatalysis.

3.3. Enhanced accumulation of As in carp in the presence of TiO₂

The accumulation of As in carp exposed to 200 µg/L As both with and without TiO₂ is shown in Fig. 3. When TiO₂ nanoparticles were added to water, arsenic aqueous concentration decreased due to the adsorption of TiO₂. As a result, arsenic aqueous concentrations were 140.0 ± 6.8 µg/L for the tank in the presence of TiO₂ and 200.0 ± 10.2 µg/L for the tank in the absence of TiO₂. Initial TiO₂ concentrations were 10.0 ± 1.3 mg/L.

Arsenic concentrations in carp increased rapidly in the first 15 days, after which the rate slowed down. Arsenic concentrations in carp in the controls remained almost unchanged, with As concentrations less than 0.8 µg/g. There was a significant difference ($P < 0.05$) in As concentration in carp exposed to As-contaminated water with and without TiO₂ nanoparticles. Arsenic concentration in the carp increased by 42.0% (20th day)–185.7% (2nd day) due to the existence of TiO₂ nanoparticles.

Accumulation of toxic pollutants can be described using the following standard exponential equation (Pendleton et al., 1995):

$$C_t = A(1 - e^{-Bt}) \quad (1)$$

where C_t is pollutant concentration in the whole fish (µg/g dry weight), A is As concentration at the equilibrium (µg/g dry weight), and B is the first-order rate constant (d^{-1}), which gives an insight at how rapidly the chemical is accumulated, and t is the exposure time (d).

Bioconcentration Factor (BCF) is the ratio of a substance's concentration in tissue vs. its concentration in water in situations where the organism is exposed through water only, which is the most commonly used indicator of a substance's tendency to be accumulated. BCF in dry weight were calculated from the following equation:

$$BCF = \frac{\text{chemical concentration in fish}(\mu\text{g/g dry weight})}{\text{chemical concentration in water}(\mu\text{g/L})} \times 1000 \quad (2)$$

The regression analysis results of the experimental data using Eq. (1) and BCFs calculated according to Eq. (2) using the equilibrium concentrations are presented in Table 1.

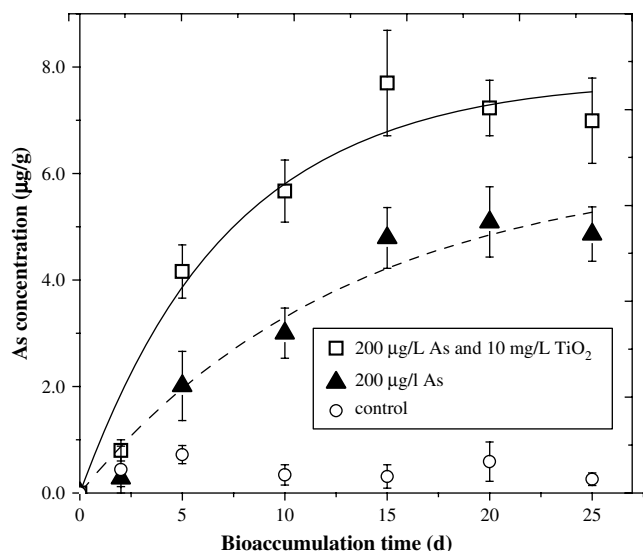


Fig. 3. The accumulation of As in the carp exposed to As-contaminated water both with and without TiO₂ nanoparticles. The curves represent the exponential regression of the mean values.

Table 1

The exponential accumulation parameters and BCFs for arsenic.

Exposed media	A (µg/g)	B (d^{-1})	R ²	BCF
As	6.19	0.076	0.964	31.0
As and TiO ₂	7.79	0.137	0.960	55.7 ^a

^a The dissolved concentration in water is 140 ± 6.8 µg/L due to the adsorption of TiO₂.

Initial uptake rate of arsenic by carp (B value) was 0.076 and 0.137 d^{-1} for the carp exposed to As and As + TiO₂ nanoparticles. Hence, the presence of TiO₂ nanoparticles enhanced bioaccumulation rate of arsenic significantly. BCF at the equilibrium in the presence of TiO₂ nanoparticles was 55.7, which is significantly higher than that in the absence of TiO₂ nanoparticles (31.0). Although the free dissolved As concentration in water in the presence of TiO₂ nanoparticles decreased from 200 to 140 µg/L, the carp accumulated considerably more As. In our former similar study, we have reported that BCF in the carp was 22.7 and 55.6, respectively, when the carp was exposed to arsenate [As(V)] without and with TiO₂ nanoparticles (Sun et al., 2007). The two BCF values were different for arsenite (BCF = 31.0) and arsenate (BCF = 22.7) without TiO₂ nanoparticles. This is because, at the pH (7.8) used in the experiment, As(III) was uncharged and could cross biological membranes more easily. However, when TiO₂ nanoparticles were present, BCF values became almost the same for As(III) (BCF = 55.7) and As(V) (BCF = 55.6). During the bioaccumulation tests, most days (>80%) were sunny, hence, it is reasonable to deduce that most of the As(III) in aqueous phase was changed to As(V) during bioaccumulation test in the tank with TiO₂ nanoparticles (see Section 3.2), which led to a similar BCF when As (III) and As(V) were added, respectively, in the presence of TiO₂.

TiO₂ concentration in carp was analyzed simultaneously, which followed the similar pattern with what reported in our former study (Sun et al., 2007). Experimental data of TiO₂ nanoparticles accumulation in carp fit the exponential equation ($R^2 = 0.917$) well, where A and B are 6.80 mg/g and 0.200 d^{-1} , respectively. Moreover, a positive correlation between As concentration and TiO₂ concentration during the exposure period existed with a correlation coefficient (R^2) of 0.927.

Maia et al. (2000) reported the great potential of solid lipid nanoparticles (SLN) to improve drug absorption by the skin. In their study, penetration of prednicarbate incorporated into SLN into human skin increased by 30% as compared to prednicarbate cream. Kreuter (2001) reported that essential drugs, such as the hexapeptide dalargin and doxorubicin, have been successfully transported across the blood–brain barrier (BBB) into the brain of rats using polymeric nanoparticles. Unfortunately, toxic pollutants might also be transported and delivered into organisms in the manner similar to that used for drug delivery. Our former studies provide the evidence of facilitated bioaccumulation of the heavy metals by TiO₂ nanoparticles in aquatic organisms (Sun et al., 2007; Zhang et al., 2007). In this study, it is found that TiO₂ nanoparticles first changed the speciation of As(III), then accelerated its bioaccumulation. Recently, Hartmann and Baun (2008) reported a reduced cadmium intracellular concentration in algal cells (*Pseudokirchneriella subcapitata*) in the presence of TiO₂ nanoparticles. This effect may be due to the inability of TiO₂ nanoparticles to penetrate the membrane of the algal cell. Similarly, Kanuer et al. (2008) reported a reduced toxicity of diuron to the same algae. Navarro et al. (2008) proposed that only ionic silver released from Ag nanoparticles could be incorporated into alga cells in a medium of Ag nanoparticles and algae (*Chlamydomonas reinhardtii*). Hence, whether the adsorption of contaminants onto nanomaterials increases or decreases their bioavailability should be evaluated using a variety of nanoparticles, chemicals, and organisms.

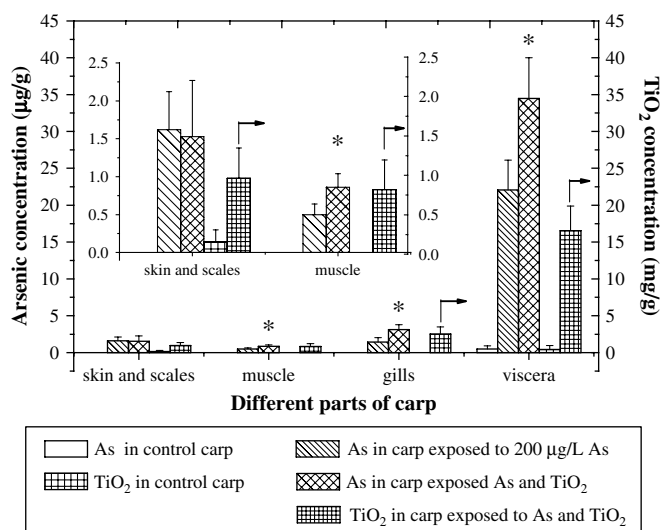


Fig. 4. Arsenic and TiO₂ concentrations in different parts of carp (µg/g for As concentration and mg/g for TiO₂ concentration). Asterisks denote mean As concentrations which are significantly different from those exposed to without TiO₂ nanoparticles at that duration ($P < 0.05$).

3.4. Arsenic and TiO₂ distribution in different parts of carp

In order to understand the pathway of the facilitated bioaccumulation of As, carp taken on the 20th day were dissected. Skin and scales, muscle, gills and viscera were analyzed for As and TiO₂ content. The As and TiO₂ concentrations in different parts of the carp are shown in Fig. 4, and BCFs for As and TiO₂ in the different parts and whole bodies of the carp are presented in Table 2. Considerably As and TiO₂ accumulation occurred in the viscera and gills of the fish, and the lowest level of accumulation was found in muscle. The order of As and TiO₂ accumulation in different parts of carp was viscera > gills > skin and scales > muscle. Comparing As concentration in the tissues of carp exposed to As-contaminated water in the presence of TiO₂ nanoparticles with those in the absence of TiO₂ nanoparticles, arsenic concentration in viscera, gills and muscle is significantly higher. As has been analyzed in our former study (Sun et al., 2007), TiO₂ nanoparticles may facilitate As bioaccumulation both through gills and intestine uptake. Inside the body of the carp, the sorbed As may be released from TiO₂ nanoparticles and distributed to other parts of the carp. Hence, though the BCF of TiO₂ nanoparticles in muscle was not high, arsenic concentration in muscle of the carp exposed in the presence of TiO₂ nanoparticles increased by 72%, as compared to that in the absence of TiO₂ nanoparticles.

4. Conclusions

Due to their small particle size, large specific surface area and the presence of high affinity surface hydroxyl groups, P25 TiO₂ nanoparticles have strong adsorption capacity for As. In the aqueous mixtures tested, adsorption equilibrium was established within

Table 2

BCFs for As and TiO₂ in different parts and whole body of carp on the 20th day.

	Exposed media	Skin and scale	Muscle	Gills	Viscera	Whole body
As	As	8.09	3.57	7.08	110	25.5
	As and TiO ₂	11.0	6.14	22.3	246	51.6
TiO ₂ ^a	As and TiO ₂	98.0	83.0	251	1655	617

^a The initial TiO₂ concentration of 10 mg/L was used to calculate BCF for TiO₂.

30 min, and about 30% of the initial As(III) and 25% of the initial As(V) was adsorbed onto TiO₂ nanoparticles, respectively. The presence of TiO₂ nanoparticles together with sunshine changed the valence of As(III), and almost all As existed as As(V) after 6 h of exposure. Facilitated transport of As occurred when carp were exposed to As-contaminated water in the presence of TiO₂ nanoparticles. Although the free dissolved As concentration in water decreased from 200 to 140 µg/L, and most of aqueous As(III) had changed to charged As(V) in the presence of TiO₂ nanoparticles, the carp accumulated considerably more As than in the exposure without TiO₂ nanoparticles. After 25-day exposure, As concentration in carp increased by 44%. Considerable As and TiO₂ accumulation occurred in viscera and gills of the carp. As TiO₂ nanoparticles accumulated though gills and intestine, the adsorbed As on the surface of TiO₂ nanoparticles may be released and taken up by the body.

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References

- Afaq, F., Abidi, P., Matin, R., Rahman, Q., 1998. Cytotoxicity, pro-oxidant effects and antioxidant depletion in rat lung alveolar macrophages exposed to ultrafine titanium dioxide. *Journal of Applied Toxicology* 18, 307–312.
- Amrhein, C., Mosher, P.A., Strong, J.E., 1993. Colloid-assisted transport of trace metals in roadside soils receiving deicing salts. *Soil Science Society of America Journal* 57, 1212–1217.
- Benn, T., Westerhoff, P., 2008. Fate and transport of ionic and nanoparticle silver released from commercially available socks. In: *Proceedings of NanoECO, Nanoparticles in the Environment Implications and Applications*. March 2–7. Centro Stefano Franscini, Monte Verità, Ascona, Switzerland, p. 29.
- Boxall, A., Chaudhry, B., Tiede, C., Jone, D., Jefferson, E., Watts, F., 2008. Exposure analysis of engineered nanoparticles in the environment. In: *Proceedings of NanoECO, Nanoparticles in the Environment Implications and Applications*. March 2–7. Centro Stefano Franscini, Monte Verità, Ascona, Switzerland, p. 27.
- Davis, A., Sellstone, C., Clough, S., Barrick, R., Yare, B., 1996. Bioaccumulation of arsenic chromium and lead in fish: constraints imposed by sediment geochemistry. *Applied Geochemistry* 11, 409–423.
- Donaldson, K., Stone, V., Gilmour, P.S., Brown, D.M., MacNee, W., 2000. Ultrafine particles: mechanisms of lung injury. *Philosophical Transactions of the Royal Society of London* 358, 2741–2749.
- Dutta, K.P., Ray, K.A., Sharma, K.V., Millero, J.F., 2004. Adsorption of arsenate and arsenite on titanium dioxide suspensions. *Journal of Colloid and Interface Science* 278, 270–275.
- ETC Group, 2003. No small matter II: the case for a global moratorium. In: *Occasional Paper Series*, vol. 7 Available from: http://www.etcgroup.org/documents/Occ.Paper_Nanosafety.pdf.
- Ferguson, M.A., Hoffmann, M.R., Hering, J.G., 2005. TiO₂-photocatalyzed As(III) oxidation in aqueous suspensions: reaction kinetics and effects of adsorption. *Environmental Science & Technology* 39, 1880–1886.
- Gumbleton, M., 2001. Caveolae as potential macromolecule trafficking compartments within alveolar epithelium. *Advanced Drug Delivery Reviews* 49, 281–300.
- González, C.J., Lavilla, I., Bendicho, C., 2003. Evaluation of non-chromatographic approaches for speciation of extractable As(III) and As(V) in environmental solid samples by FI-HGAAS. *Talanta* 59, 525–534.
- Hartmann, N.B., Baun, A., 2008. Effect of micron- nanosized titanium dioxide on algal growth: inherent inhibitory effects and as modifying factor on cadmium toxicity. In: *Proceedings of NanoECO, Nanoparticles in the Environment Implications and Applications*. March 2–7. Centro Stefano Franscini, Monte Verità, Ascona, Switzerland, p. 68.
- Hoffmann, M.R., Martin, S.T., Choi, W., Bahnemann, D.W., 1995. Environmental applications of semiconductor photocatalysis. *Chemical Reviews* 95, 69–96.
- Honeyman, B.D., 1999. Colloid culprits in contamination. *Nature* 397, 23–24.
- Kanuer, K., Sobek, A., Bucheli, T.D., 2008. Reduced toxicity of diuron to the freshwater green alga *Pseudokirchneriella subcapitata* in the presence of black carbon. In: *Proceedings of NanoECO, Nanoparticles in the Environment Implications and Applications*. March 2–7. Centro Stefano Franscini, Monte Verità, Ascona, Switzerland p.112.
- Kipp, J.E., 2004. The role of solid nanoparticle technology in the parenteral delivery of poorly water-soluble drugs. *International Journal of Pharmaceutics* 284, 109–122.
- Kong, J., Franklin, R.N., Zhou, C.W., Chapline, G.M., Peng, S., Cho, K., Dai, H.J., 2000. Nanotube molecular wires as chemical sensors. *Science* 287, 622–625.

- Kreuter, J., 2001. Nanoparticulate systems for brain delivery of drugs. *Advanced Drug Delivery Reviews* 47, 65–81.
- Kreuter, J., Shamenkov, D., Petrov, V., Ramge, P., Cychutek, K., Koch-Brandt, C., Alyautdin, R., 2002. Apolipoprotein-mediated transport of nanoparticle-bound drugs across the blood–brain barrier. *Journal of Drug Targeting* 10, 317–325.
- Lewis, A.M., Scott, I.G., Bearden, W.D., Quarles, L.R., Moore, J., Strozier, D.E., Sivertsen, K.S., Dias, R.A., Sanders, M., 2002. Fish tissue quality in near-coastal areas of the Gulf of Mexico receiving point source discharges. *Science of the Total Environment* 284, 249–261.
- Lovern, S.B., Klaper, R., 2006. *Daphnia magna* mortality when exposed to titanium dioxide and fullerene (C₆₀) nanoparticles. *Environmental Toxicology and Chemistry* 25, 1132–1137.
- Long, Q.R., Yang, R.T., 2001. Carbon nanotubes as superior sorbent for dioxin removal. *Journal of the American Chemical Society* 123, 2058–2059.
- Lu, Y., Sun, H., Yuan, C., Yan, X., 2002. Simultaneous determination of trace cadmium and arsenic in biological samples by hydride generation–double channel atomic fluorescence spectrometry. *Analytical Chemistry* 74, 1525–1529.
- Maia, S.C., Mehnert, W., Schafer-Korting, M., 2000. Solid lipid nanoparticles as drug carriers for topical glucocorticoids. *International Journal of Pharmaceutics* 196, 165–167.
- National Research Council, 1999. Health effects of arsenic. In: *Arsenic in Drinking Water*. National Academy Press, Washington, DC., pp. 83–149.
- Navarro, E., Piccapietra, F., Wagner, B., Kägi, R., Odzak, N., Sigg, L., Behra, R., 2008. Toxicity and sorption of silver nanoparticles to *Chlamydomonas reinhardtii*. In: *Proceedings of NanoECO, Nanoparticles in the Environment Implications and Applications*. March 2–7. Centro Stefano Franscini, Monte Verità, Ascona, Switzerland, p. 67.
- NCPI nanotechnology Consumer Product Inventory, 2007. Project on Emerging Nanotechnologies. Woodrow Wilson International Center for Scholars. Available from: <http://www.nanotechproject.org/44>.
- Nowack, B., Bucheli, T.D., 2007. Occurrence, behavior and effects of nanoparticles in the environment. *Environmental Pollution* 150, 5–22.
- Öberdörster, G., 2000. Toxicology of ultrafine particles: in vivo studies. *Philosophical Transactions of the Royal Society of London* 358, 2719–2740.
- Ophus, E.M., Rode, L., Gylseth, B., Nicholson, D.G., Saeed, K., 1979. Analysis of titanium pigments in human lung tissue. *Scandinavian Journal of Work, Environment & Health* 5, 290–296.
- Pendleton, W.G., Whitworth, R.M., Olsen, H.G., 1995. Accumulation and loss of arsenic and boron, alone and in combination, in Mallard ducks. *Environmental Toxicology and Chemistry* 14, 1357–1364.
- Pena, M., Meng, X., Korfiatis, G.P., Jing, C., 2006. Adsorption mechanism of arsenic on nanocrystalline titanium dioxide. *Environmental Science & Technology* 40, 1257–1262.
- Rahman, Q., Lohani, M., Dopp, E., Pemsel, H., Jonas, L., Weiss, D.G., Schiffmann, D., 2002. Evidence that ultrafine titanium dioxide induces micronuclei and apoptosis in Syrian hamster embryo fibroblasts. *Environmental Health Perspectives* 110, 797–800.
- Roco, M.C., Bainbridge, W., 2001. *Societal Implications of Nanoscience and Nanotechnology*. Kluwer Academic Publishers, Boston.
- Rosen, P.B., 2002. Biochemistry of arsenic detoxification. *FEBS Letters* 529, 86–92.
- Ryu, S.Y., Choi, J., Balcerski, W., Lee, T.K., Hoffmann, M.R., 2007. Photocatalytic production of H₂ on nanocomposite catalysts. *Industrial & Engineering Chemistry Research* 46, 7476–7488.
- Sun, H., Zhang, X., Niu, Q., Chen, Y., Crittenden, J.C., 2007. Enhanced accumulation of arsenic in carp in the presence of titanium dioxide nanoparticles. *Water, Air and Soil Pollution* 178, 245–254.
- Tan, M.H., Commens, C.A., Burnett, L., Snitch, P.J., 1996. A pilot study on the percutaneous absorption of microfine titanium dioxide from sunscreens. *Australasian Journal of Dermatology* 37, 185–187.
- Tinkle, S.S., Antonini, J.M., Rich, B.A., 2003. Skin as a route of exposure and sensitization in chronic beryllium disease. *Environmental Health Perspectives* 111, 1202–1208.
- Vikesland, P., Marr, L., Jinschek, J., Chang, X., Duncan, L., 2008. Effects of solution chemistry on C60 aggregate formation and transport. In: *Proceedings of NanoECO, Nanoparticles in the Environment Implications and Applications*. March 2–7. Centro Stefano Franscini, Monte Verità, Ascona, Switzerland p. 36.
- Zhang, W., Masciangioli, T., 2003. Environmental technologies at the nanoscales. *Environmental Science & Technology* 37, 102A–108A.
- Zhang, X., Sun, H., Zhang, Z., Niu, Q., Chen, Y., Crittenden, J.C., 2007. Enhanced bioaccumulation of cadmium in carp in the presence of titanium dioxide nanoparticles. *Chemosphere* 67, 160–166.
- Zhu, Y., Williams, P.N., Meharg, A.A., 2008. Exposure to inorganic arsenic from rice: a global health issue? *Environmental Pollution* 154, 169–171.