Enhanced Accumulation of Arsenate in Carp in the Presence of Titanium Dioxide Nanoparticles

Hongwen Sun · Xuezhi Zhang · Qian Niu · Yongsheng Chen · John C. Crittenden

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Abstract In this study adsorption of arsenic (As) onto TiO₂ nanoparticles and the facilitated transport of As into carp (Cyprinus carpio) by TiO₂ nanoparticles was examined. Adsorption kinetics and adsorption isotherm were conducted by adding As(V) to TiO2 suspensions. Facilitated transport of As by TiO₂ nanoparticles was assessed by accumulation tests exposing carp to As(V) contaminated water in the presence of TiO₂ nanoparticles. The results showed that TiO₂ nanoparticles had a significant adsorption capacity for As(V). Equilibrium was established within 30 min and the isotherm data was described by Freundlich isotherm. The K_F and 1/n were 20.71 mg/g and 0.58, respectively. When exposed to As(V)-contaminated water in the presence of TiO₂ nanoparticles, carp accumulated considerably more As, and As concentration in carp increased by 132% after 25 days exposure. Considerable As and TiO₂ accumulated in intestine, stomach and gills of the fish, and the lowest level of accumulation was found in muscle. Accumulation of As and TiO2 in stomach,

 ${
m TiO_2}$ nanoparticles. ${
m TiO_2}$ nanoparticles that have accumulated in intestine and gills may release adsorbed As and As bound on ${
m TiO_2}$ nanoparticles which cannot be released maybe transported by ${
m TiO_2}$ nanoparticles as they transferred in the body. In this work, an enhancement of 80% and 126% As concentration in liver and muscle after 20 days of exposure was found.

intestine and gills are significant. Arsenic accumula-

tion in these tissues was enhanced by the presence of

Keywords arsenic \cdot TiO₂ \cdot nanoparticles \cdot accumulation \cdot carp \cdot facilitated transport

1 Introduction

Extensive research on the applications of nanomaterials, including catalysis, drug delivery, medical diagnostics, enzyme immobilization, sensors and pollution control has been carried out recently (Kong et al., 2000; Králik & Biffis, 2001; Long & Yang, 2001; Kipp, 2004). Some nanomaterials, such as TiO₂ nanoparticles are now in daily use including popular sunscreens, toothpaste and cosmetics. Currently, more than 140 companies worldwide have already engaged in manufacture of nanoparticles. There are at least 44 elements in the Periodic Table commercially available in nanoscale form, and more elements are being added to this list (ETC Group, 2003). During the next 10–15 years, nanotechnology sectors are expected to

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Y. Chen · J. C. Crittenden Department of Civil and Environmental Engineering, Arizona State University, Tempe, AZ 85287, USA exceed \$1 trillion annually in global industrial output and to employ about 2 million workers (Roco & Bainbridge, 2001). Although these estimates reflect uncertainty in predicting the commercialization of an emerging technology, there is little doubt that an inevitable consequence of this rapid growth is the eventual exposure of humans and other environmental receptors to nanoscale materials. Recent research is now showing that when normally harmless bulk materials are made into nanoparticles they tend to become toxic (Howard & Maynard, 1999). The size effect is considerably more important to nanoparticles toxicity than the actual composition of the material (Donaldson, Stone, Gilmour, Brown, & MacNee, 2000; Öberdörster, 2000; Gumbleton, 2001; Tinkle, Antonini, & Rich, 2003). Tan's study shown TiO₂ nanoparticles used in sunscreen, can get deep enough into the skin to be taken up into the lymphatic system, while larger particles are not (greater than 1 µm in diameter) (Tan, Commens, Burnett, & Snitch, 1996). In vivo studies show that nanoparticles can produce inflammation in lungs of laboratory animals after exposure to nanoparticles 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 altered cell death rates (Afaq, Abidi, Matin, & Rahman, 1998; Rahman et al., 2002).

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. Many studies have shown that colloids, both organic and inorganic, have been implicated in the transport of toxic pollutants such as metals, radionuclides, and certain ionizable organic pesticides in laboratory and field tests (Amrhein, Mosher, & Strong, 1993; Honeyman, 1999). The large surface area, crystalline structure, and reactivity of some nanoparticles may facilitate transport of toxic materials in the environment (Zhang & Masciangioli, 2003). However, there is little to no data indicating how and to what extent emerging nanoparticles may facilitate the transport of toxic pollutants or viruses in the environment.

Arsenic is widely distributed in the environment and is known to be highly toxic to humans. The accumulation of As in fish has received significant attention as a consequence of human and wildlife concerns resulting from the consumption of fish with elevated As (Davis, Sellstone, Clough, Barrick, & Yare, 1996; Lewis et al., 2002). Nanocrystalline TiO₂ has a great adsorption capacity for arsenic ions due to its high surface area and the presence of high affinity surface hydroxyl groups (Pena, Meng, Korfiatis, & Jing, 2006). Accordingly, the following hypothesis needs to be examined, "Will the accumulation of As in fish be enhanced by the facilitated transport of nanoparticles or diminished because of the reduction of free soluble As in aqueous phase due to its adsorption onto titanium dioxide nanoparticles?" In this research, the adsorption of As(V) onto TiO₂ and the potential of TiO₂ nanoparticles to facilitate the transport of As to carp (Cyprinus carpio) were examined.

2 Materials and Methods

2.1 Reagents and solutions

All reagents used were of analytical reagent grade except for acids, which were of trace metal analysis grade. Mini-Q quality water was used for preparation of stock solution. Laboratory equipment and containers were washed in 25% (v/v) HNO₃ solution for at least 12 h prior to each use.

Na₃AsO₄•12H₂O was used for preparation of As (V) stock solutions (100 mg/l). The standard stock solutions were stored in glass bottles kept at 4°C in the dark. Fresh solutions were made from the stock solution for each experiment. The reductant solution used for hydride generation was 2% (w/v) NaBH₄ dissolved in 0.5% (w/v) NaOH solution, which was prepared immediately prior to use. Degussa P25 titanium dioxide nanoparticles, with an average BET surface area of 50 m²/g and an average particle size of 21 nm, was used for all experiments. Stock suspensions of TiO₂ nanoparticles were prepared (1.0 g/l) and then sonicated for 10 min (50 w/l at 40 kHz) before use.

Standard titanium (IV) stock solution (1.0 g/l) was prepared by heating 0.4169 g TiO_2 nanoparticles in a solution containing sulphuric acid and ammonium sulphate and finally diluted to 250 ml with distilled water. Low-concentration standards were prepared daily by diluting of the stock solution with sulphuric acid (10% v/v).



2.2 Instrumentation

A microwave digestion system (WX-3000 plus, EU Chemical Instruments Co., Ltd, Shanghai, China) was used for sample digestion. An inductively coupled plasma optical emission spectrometry (ICP-OES) (IRIS Intrepid II, Thermo Electron, USA) was used to determine TiO₂ concentration in digested samples. Arsenic was measured using an atomic fluorescence spectrometry equipped with hydride generation (HG-AFS 2201, Haiguang Co., Beijing, China). A transmission electron microscopy (TEM) (Tecnai G² 20 S-Twin, Philip) was used to get the shape and aggregation information of TiO₂ nanoparticles in water. An ion chromatograph (DX120, Dionex, USA) was used for the analysis of ions in water.

2.3 Adsorption of As(V) onto TiO₂ nanoparticles

Adsorption kinetics and isotherm were determined using batch experiments. Dechlorinated tap water was used in the experiment in order to keep similar water circumstances with those in the accumulation tests. The major cations and their concentrations in the dechlorinated water were Ca²⁺(47.8 ± 1.88 mg/l), $Na^{+}(28.0 \pm 0.94 \text{ mg/l}), Mg^{2+}(26.4 \pm 5.94 \text{ mg/l}) \text{ and}$ $K^{+}(5.5 \pm 0.34 \text{ mg/l})$. The major anions and their concentrations were $SO_4^{2-}(81.9 \pm 2.49 \text{ mg/l})$, $Cl^{-}(48.79 \pm 5.24 \text{ mg/l}), NO_{3}^{-}(2.22 \pm 0.49 \text{ mg/l}) \text{ and}$ F^{-} (0.63 ± 0.16 mg/l. The pH of the water was 7.8. In each experiment, 100 ml TiO₂ suspensions containing appropriate amount of TiO2 were prepared and added to a series of 250 ml Pyrex glass Erlenmeyer flasks. Then the required amount of As stock solution was added into the flasks. The flasks were put in a reciprocating shaker and kept in dark at 25 ± 1 °C and 150 rpm. Residual aqueous As concentration was analyzed after the suspensions were centrifuged twice for 10 min at 12,000 rpm using a high-speed centrifuge (Hermle Z323, Germany) at 0, 30, 60, 120, 180, and 360 min. The adsorption isotherm was studied by varying the initial As(V) concentration under a fixed concentration of TiO₂ suspensions of 10 mg/l. Isotherm tests were conducted for 3 h and then residual aqueous As concentration was analyzed. The adsorbed amount of As onto TiO₂ was calculated from the initial and final concentrations of As. Blank experiments were also conducted demonstrated that As adsorption onto the walls of the flasks was negligible (97–100% of initial concentration were observed for time scale of this study).

2.4 Accumulation experiment

A group of carp (*Cyprinus carpio*) was purchased from a local pet shop. The initial body weight and length of the fish were 6.1 ± 1.2 g and 4.0 ± 0.7 cm respectively. All fish were acclimatized in dechlorinated tap water with a natural light/dark cycle for 10 d before each experiment. For the accumulation tests, specific amount of As(V) stock solutions were added into two glass tanks containing 16 l dechlorinated tap water respectively, and the initial concentration of As was $200.0 \pm 10.2~\mu g/l$. In one tank, $0.160~g~TiO_2$ nanoparticles were added and allowed to equilibrate for 2~h. 36~carp were then added to each tank. The fish were fed with a commercial food once a day during the experiment.

When TiO₂ nanoparticles were added to the water, a translucent and unstable suspension of TiO2 nanoparticles formed. Some of the unstable particles settled out of solution. To maintain a relative stable aqueous phase concentrations of 200.0 µg/l As and 10.0 mg/l TiO₂, the solution was replaced every day. During the tests, the tanks were aerated slightly and the temperature $(23 \pm 2^{\circ}C)$ 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 2nd, 5th, 10th and 20th day, four carp from each of the three treatments were dissected into skin and scales, muscle, gills, liver, stomach and intestine. After pretreatment, arsenic and TiO2 concentrations in carp or different tissues of carp were analyzed, respectively.

2.5 Analytical procedures

Arsenic was measured using HG-AFS. The following instrumental parameters were used: current of lamp 40 mA; high voltage of PMT 300; carrier gas (Ar) flow rate 0.3 l/min; shielded sheath (Ar) flow rate 0.5 min/l; peristaltic pump rate 130 rmp; observation height 8 mm and resonance wavelength 193.7. Thiourea (5%)—ascorbic acid (5%) mixing reagent was used for pre-reduction of arsenate, and hydrochloric acid (5%) media was used for hydride generation.



Fish or fish tissues were dried at 105°C for at least 24 h until a constant weight was achieved. Then the dried fish were ground into powder. Approximately 0.20 g dried sample and 4.0 ml concentrated HNO₃ was added into each of six PTFE digestion tubes. After 10 min, the vessels were sealed and put in the microwave. Then the samples were digested using a three-stage digestion protocol presented in Table I. Afterwards the vessel was allowed to cool. Filtration of the samples was not required since the dissolution was complete.

For As analysis, the excess acid was removed from the digested solution by heating the digested solution to near dryness at 90°C using an electric furnace. Then total As in carp was determined after prereduction of As(V). Triplicate analyses were performed for each sample. The accuracy of the measurement was tested by the analysis of a certified reference material, GBW 08571 (mussel sample, National Research Center for CRM's, Beijing), which has a certified value of $6.1 \pm 1.1 \, \mu g/g$ As. The value we obtained was $5.8 \pm 0.7 \, \mu g/g$.

For TiO₂ analysis, the digest solutions were transferred to triangular flasks and evaporated to dryness. TiO₂ nanoparticles released by digestion were decomposed into titanium (IV) ion by heating with 5 ml of the sulphuric acid–ammonium sulphate solution. After cooling, the above solution was transferred quantitatively to a 25-ml volumetric flask. TiO₂ concentration in digested samples was determined by ICP-OES. The instrumental parameters were: RF power 1150 W; nebulizer pressure 22 psi; carrier gas (Ar) flow rate 0.5 l/min; peristaltic pump rate 130 rmp; integration time high WL range 5 s, low WL range 30 s; and wavelength 336.121 nm.

Several quality control (QC) measures were taken during the analysis of samples. First, a calibration blank and a calibration standard (10.0 mg/l) were run before and after every five samples. The standard concentration was required to be within 5% of its

Table I Microwave sequence for sample digestion

Stage	Power (1–9)	Temperature (°C)	Pressure (MPa)	Time (min)
1	8	150	1	5
2	6	180	2	5
3	6	190	2	5

nominal concentration for the analysis of bracketed samples to be considered valid. Second, a calibration standard was also prepared at a concentration within the calibration range using a titanium stock solution purchased from another vendor (GSB G 65014-90 (2201), Central Iron & Steel Research Institute, Beijing). This calibration standard was then analyzed to verify analyte concentration and instrument calibration. Third, triplicate digestions and analyses were performed for each sample.

Because biological standard reference materials containing TiO₂ were not available, laboratory controls were prepared. Fish samples were pooled together and mechanically homogenized to form a uniform control tissue matrix. About 0.20 g fish simple aliquots were transferred directly into each of six acid-cleaned PTFE digestion tubes. Four of the matrix aliquots were fortified with 0.020 g TiO₂ nanoparticles (0.80 g Ti/ml of final analysis solution), while the remaining two were not fortified and served as matrix blanks. These samples were digested, evaporated, decomposed and analyzed as described above. The titanium dioxide recovery in these samples ranged from 90 to 105%.

2.6 Statistical analysis

For As(V) concentrations 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 checked out and a one-way analysis of variance (ANOVA) was then performed to assess the significance of differences observed between As concentrations in fish or tissues exposed to Ascontaminated water with and without TiO₂. All statistical analyses were conducted at a significance level of 0.05.

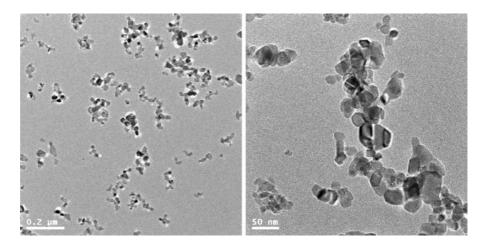
3 Results and Discussion

3.1 Characterization of TiO₂ nanoparticles in water

Nanomaterials have a much smaller size, larger surface area and surface energy compared to normal materials, so they are prone to aggregate. TEM images of TiO₂ nanoparticles in water are presented in Figure 1. The images show that although most



Figure 1 TEM images of TiO₂ nanoparticles in water.



particles aggregate together, due to the small original particle size (of about 21 nm), the aggregations are still relatively small, and most of the particles are within 50–400 nm.

3.2 Adsorption of As onto TiO₂ nanoparticles

The adsorption of As onto nanoparticles was observed for 6 h, and the results are shown in Figure 2. As(V) was adsorbed onto TiO_2 nanoparticles quickly, and equilibrium was reached within 30 min. At the adsorption equilibrium, about 25% of the initial As(V) was adsorbed onto TiO_2 nanoparticles. The equilibrium time is in agreement with that reported by Dutta et al. (Dutta, Ray, Sharma, & Millero, 2004), who found that the adsorption equilibria of both As(III) and As (V) onto P25 TiO_2 nanoparticles were established in

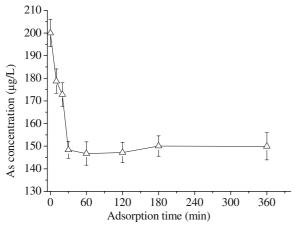


Figure 2 Adsorption kinetics of As(V) onto TiO₂ nanoparticles.

approximately 1 h. Unlike other porous media in which adsorption is possibly occurring through pore diffusion steps and takes a longer time to reach equilibrium, Degussa P25 is made of nonporous TiO_2 particles where only liquid phased diffusion occurs, This type of mass transfer requires less time to reach equilibrium (Dutta et al., 2004).

3.3 Adsorption isotherm

The adsorption isotherm was determined using 2 h of equilibrium time. Experimental data of As(V) adsorption onto TiO_2 nanoparticles was described by the Freundlich isotherm [Equation (1)] and the correlation coefficients (R^2) was 0.946. The date and the Freundlich fit are shown in Figure 3.

$$\log q = \log K_F + \frac{1}{n} \log C_e \tag{1}$$

where q (mg/g) is the amount of adsorbed As, Ce is the equilibrium As concentration in solution (mg/l), $K_{\rm F}$ and 1/n are the Freundlich constants. The Freundlich parameters were obtained by nonlinear least-squares regression analysis. The constants $K_{\rm F}$ and 1/n were found to be 20.71 mg/g and 0.58. It has been reported that the $K_{\rm F}$ values of activated alumina and Portland cement for the adsorption of As were less than 0.224 and 3.89 mg/g (Kundu et al., 2004; Singh and Pant, 2004), respectively. In comparison, it is clear that the $K_{\rm F}$ obtained in this study is very high. The small particle size (21 nm) and large BET surface area of P25 TiO₂ nanoparticles (50 m²/g) may account for their strong adsorption ability.



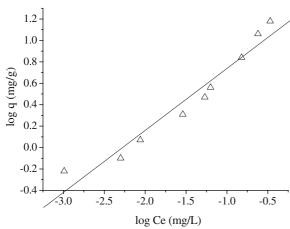


Figure 3 Freundlich plot for adsorption of As(V) onto TiO_2 nanoparticles.

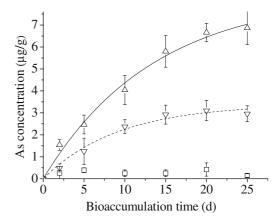
3.4 The enhanced accumulation of As in carp in the presence of TiO₂

When TiO_2 nanoparticles were added into water, As (V) concentration decreased due to the adsorption of TiO_2 . As a result, As(V) aqueous concentrations were $150.0 \pm 7.6 \ \mu g/l$ for the tank in the presence of TiO_2 nanoparticles and $200.0 \pm 10.2 \ \mu g/l$ for the tank in the absence of TiO_2 nanoparticles. TiO_2 concentrations were $10.0 \pm 1.3 \ mg/l$ when TiO_2 nanoparticles were added into the tank.

The accumulation results of As in carp exposed to $200 \mu g/l \text{ As(V)}$ both with and without TiO_2 nanoparticles are shown in Figure 4. In the figure, the accumulation of As was described using standard exponential equation as follows (Pendleton et al., 1995):

$$C_t = A \cdot \left(1 - e^{-Bt}\right) \tag{2}$$

where C_t is the As concentration in whole fish (μ g/g dry weight), A is the As concentration at equilibrium (μ g/g dry weight), B is the first-order rate constant (d^{-1}), which give an insight at how rapidly the



- △ As concentration exposed to As(V) and TiO
- \triangledown As concentration exposed to 200 μ g/L As(V)
- □ Control
- Exponential regression of As exposed to As(V) and TiO₂

----- Exponential regression of As exposed to 200 μg/L As(V)

Figure 4 The accumulation of As in carp exposed to Ascontaminated water both with and without TiO₂ nanoparticles.

element is accumulated, and t is the exposure time (day).

Arsenic concentrations in carp in the controls remained unchanged, with As concentrations less than 0.5 μ g/g. Arsenic concentrations in carp exposed to As-contaminated water increased gradually and after 25 days exposure it reached 2.96 μ g/g. When exposed to As-contaminated water in the presence of TiO₂ nanoparticles, the carp accumulated considerably more As. As can be seen from Figure 4, arsenic concentration in the carp increased sharply, and reached 6.86 μ g/g after 25 days exposure, which increased by 132% than that without TiO₂ nanoparticles, suggesting that the presence of TiO₂ nanoparticles greatly enhanced the accumulation of As in carp.

Bioconcentration factor (BCF) are typically used to reflect the relation between chemical concentrations in water and in the target organism. BCF in dry weight was calculated from the following equation:

$$BCF = \frac{chemical\ concentration\ in\ fish(\mu g/g\ dry\ weight)}{chemical\ concentration\ in\ water(\mu g/l)} \times 1000 \tag{3}$$

The regression analysis results of the experimental data using Equation (2) and BCFs calculated accord-

ing to Equation (3) using the equilibrium concentrations are presented in Table II. Arsenic concentration

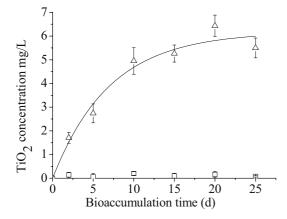


Table II The exponential accumulation parameters and BCF

Exposed media	A (μg/g)	$B(d^{-1})$	R^2	BCF
As As and TiO ₂	3.40	0.109	0.983	22.67
	8.34	0.074	0.991	55.60

in carp at equilibrium (A value) in the presence of TiO_2 nanoparticles is much higher than that exposed to As (V) only. Also the BCFs at equilibrium in the presence of TiO_2 nanoparticles is 55.6, which is almost twofold higher than that in the absence of TiO_2 nanoparticles (22.67). Although the free soluble As concentration in water in the presence of TiO_2 nanoparticles decreased from 200 to 150 μ g/l due to the strong adsorption onto TiO_2 nanoparticles, the carp exposed to the contaminated media accumulated more As, suggesting that the presence of TiO_2 nanoparticles greatly enhanced the accumulation of As in carp.

 ${
m TiO_2}$ concentration in carp was analyzed simultaneously and the results are given in Figure 5. Strong accumulation of ${
m TiO_2}$ nanoparticles in carp was observed. ${
m TiO_2}$ concentration in carp reached 4.95 mg/g on the 10th day. Experimental data of ${
m TiO_2}$ nanoparticles accumulation in carp gave a better fit using the exponential equation ($R^2=0.972$), where A and B are 6.17 mg/g and 0.142d⁻¹, respectively. Moreover, a positive correlation between As concentration and ${
m TiO_2}$ concentration during the duration of exposure existed with a correlation coefficient greater than 0.975.



- △ TiO₂ concentration exposed to As and TiO₂
- □ Control
- Exponential regression of TiO, exposed to As and TiO,

Figure 5 The accumulation of TiO₂ nanoparticles in carp.

Grolimund, Borkovec, Barmettler, & Sticher (1996) demonstrated that mobilized colloids can provide a pathway for rapid transport of Pb. Flury, Mathison, & Harsh (2002) found that colloids mobilized in flow experiments with packed sediments carried Cs along. In another study, Maia, Mehnert, & Schafer-Korting (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. This study provides evidence of facilitated accumulation of the toxic contaminant by TiO₂ nanoparticles in the aquatic organisms. Carp accumulated more As in the presence of TiO₂ nanoparticles due to the facilitated transport. Hence, research should not be addressed only on the fate and toxicity of nanoparticles themselves, but also to the potential of the facilitated transport of other trace toxic pollutants when they co-exist, which is a significant step in better understanding of the potential exposure risks that nanoparticles might cause.

3.5 The distribution of As and TiO₂ in different tissues of carp

Carp taken on the 2nd, 5th, 10th, 20th day were dissected. Arsenic and ${\rm TiO_2}$ in different tissues were analyzed and the results are shown in Figure 6. Considerable As and ${\rm TiO_2}$ accumulated in intestine, stomach and gills of the fish, and the lowest level of accumulation was found in muscle. The presence of ${\rm TiO_2}$ nanoparticles did not change the distribution of As. The order of As and ${\rm TiO_2}$ accumulation in different parts of carp was intestine > stomach > gills > liver > skin and scales > muscle.

Comparing As concentration in the tissues of carp exposed to As-contaminated water in the absence of TiO₂ nanoparticles with those in the absence of TiO₂ nanoparticles, Arsenic concentration in stomach, intestine and gills in all exposure periods, arsenic concentration in liver and muscle on the 5th, 10th and 20th day and As concentration in skin and scales at the 10th day exposure are significantly higher.

Heavy metals enter the aquatic organism through direct consumption of water or food and through nondietary routes such as uptake through absorbing epithelia. The gills, skin, and digestive tract are potential sites of adsorption of waterborne chemicals



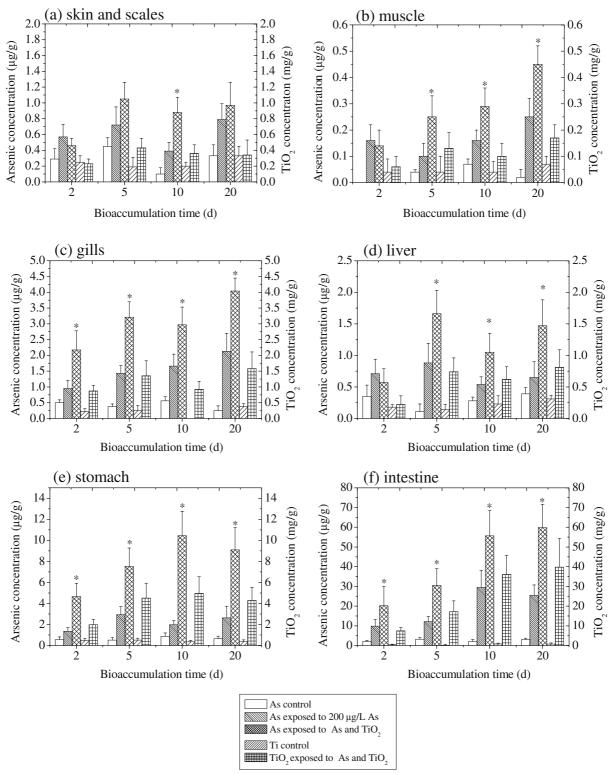


Figure 6 The accumulation of As and TiO_2 in tissues of carp exposed for 2, 5, 10 and 20 days: **a** skin and scales; **b** muscle; **c** gills; **d** liver; **e** stomach; **f** intestine. Data are expressed as

mean \pm SE. Asterisks denote means As concentrations, which are significantly different from those exposed to without TiO₂ nanoparticles at that duration (P < 0.05).



(Pedlar & Klaverkamp, 2002). Tan's study shows that TiO_2 nanoparticles used in sunscreen can get deep enough into the skin to be taken up into the lymphatic system, while larger particles (greater than 1 μ m in diameter) cannot (Tan et al., 1996). However, in our study there was no significant enhancement of As concentration in the skin and scales, with the exception of that on the 10th day, indicating that the facilitated transport of As by TiO_2 nanoparticles through skin negligible.

Accumulation of As and TiO₂ in stomach, intestine and gills are significant and accumulation of As in these tissues are enhanced by the presence of TiO₂ nanoparticles. As stated in the above, a large amount of As were adsorbed onto TiO₂ nanoparticles. The bound As was transported to carp as TiO₂ nanoparticles were consumed by the carp, thus resulting the enhancement of As concentration in the stomach and intestine. Gills are in direct contact with aquatic environment and are a physiologically complex and vulnerable structure, making them target organs for waterborne toxicants (Reid & McDonald, 1991). Moreover, the amount of mucus on the gill surface increases during metal exposure (Handy & Eddy, 1991), which may contribute to the adsorption of TiO₂ nanoparticles onto gill. Direct uptake of TiO₂ nanoparticles via gills and intestine may occur, and subsequently TiO₂ nanoparticles was rapidly transferred, distributed and accumulated, resulting the high concentration of TiO2 in liver and muscle. Facilitated transport of As may occur when TiO₂ nanoparticles transported via gills and intestine. As TiO₂ nanoparticles accumulated in intestine and gills, the adsorbed As on the surface of TiO₂ nanoparticles may be released and uptake by the body; while the residual As bound on TiO2 nanoparticles which cannot be released maybe transported by TiO₂ nanoparticles as they transferred in the body. As a result, after 20 days of exposure, Arsenic concentration in liver and muscle of carp exposed to As-contaminated water in the presence of TiO₂ nanoparticles increased by 80% and 126%, as compared with that in the absence of TiO₂ nanoparticles.

4 Conclusion

The small particle size and large specific surface area of P25 TiO₂ nanoparticles may account for their strong

adsorption capacity for As(V). Facilitated transport of As occurred when carp were exposed to As-contaminated water in the presence of TiO₂ nanoparticles, and the carp accumulated considerably more As in the presence of TiO₂. Accumulation of As and TiO₂ in stomach, intestine and gills are significant and accumulation of As in these tissues were enhanced by the presence of TiO₂ nanoparticles. As TiO₂ nanoparticles accumulated in intestine and gills, the adsorbed As on the surface of TiO₂ nanoparticles may be released and uptake by the body; while the residual As bound on TiO₂ nanoparticles which cannot be released maybe transported by TiO₂ nanoparticles as they transferred in the body. As a result, there are 80% and 126% enhancement of As concentration in liver and muscle after 20 days of exposure.

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