Adsorption/Desorption of Cd by Titanium Dioxide Nanoparticles and Sediment Particles as well as Their Facilitated Bioaccumulation of Cd into Carp

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ABSTRACT

There are increasing concerns nowadays about the health and environmental impact of nanomaterials. In this study, the adsorption/desorption abilities of Cd onto TiO_2 nanoparticles and on natural sediment particles (SP) were examined and the difference in facilitated transport ability were assessed. The results showed that TiO_2 nanoparticles had a significantly stronger adsorption capacity for Cd than SP. The isotherm data followed Freundlich isotherm and the constants K_F and n were found to be 32.8 mg/g and 0.956 for P25 and 3.25 mg/g and 1.03 for SP. After 144 hour's desorption, Cd desorption percentage from P25 was approximately 6% lower than that from SP. However, the desorbed amount of Cd from P25 was much higher than those from SP. Facilitated transport abilities of toxic pollutants by particles are related with the adsorption/desorption capability of the particles. The large adsorption and desorption amount of P25 indicates that the adsoprtin/desorption from nanoparticles has a significant influence on the mobility and bioavailability of Cd in aquatic environments. The results of bioaccumulation tests showed that the presence of SP did not have significant influence on the accumulation of Cd in carp during the 25 day's of exposure. However, the presence of TiO_2 nanoparticles greatly enhanced the accumulation of Cd in carp. After 25 day's of exposure, Cd concentration in carp increased by 146%.

Keywords: TiO_2 nanoparticles, sediment particles, Cd, adsorption, bioaccumulation

1 INTRODUCTION

Nanometer-scale materials possibly exhibit different physical, chemical, and biological properties that may not be predictable from observations on larger-sized materials. Extensive researches on the applications of nanomaterials have been carried out recently[1-4]. As common nanomaterials, TiO_2 nanoparticles are now becoming increasingly popular. The opacity and whitening properties of TiO_2 nanoparticles have made this pigment desirable for a variety of industrial applications, including the manufacture of paints, textiles, papers, plastics, sunscreens, cosmetics, and food products[5]. In the near future the release of TiO_2 nanoparticles into aquatic systems is inevitable as more and more industrial applications are found for this nanomaterial. An important process through which nanomaterials can affect living organisms is bioaccumulation. The bioaccumulation of nanoparticles may have harmful effects on an individual's health, enhance the persistence of nanoparticles in the ecosystem and pose further risks to human health and the environment through the food chain. The study of Sun et. al provided the evidence of facilitated bioaccumulation of As(V) in carp in the presence of titanium dioxide nanoparticles[6]. Adsorption and desorption of toxic pollutants by nanoparticles may dramatically affect the facilitated transport ability of nanoparticles. In this study the adsorption/desorption abilities of Cd onto TiO_2 nanoparticles and natural sediment particles (SP) were examined and their different facilitated transport abilities were assessed.

2 EXPERIMENT

2.1 Adsorption and desorption of Cd onto TiO_2 nanoparticles and SP

Surficial sediment particles (SP) were collected from a non-contaminated reservoir. After collection the sample was dried and sieved through 400 meshes. TiO_2 nanoparticles (Degussa P25) were used as received.

Sorption kinetics and isotherm were performed using batch experiments. In each experiment, 100 mL 10 mg/L suspension of TiO_2 or SP were prepared and added to a series of 250 mL Erlenmeyer flasks. Required amount of Cd standard solution was added to initiate the adsorption. The initial Cd concentration was 100 μg/L.

Adsorption isotherms were studied by varying initial Cd concentration under a fixed TiO_2 or SP suspensions of 10 mg/L. Isotherm tests were conducted for 2 h and then residual aqueous Cd concentration was analyzed. The amount of Cd adsorbed was calculated by mass balance between the initial and final solution concentrations.

Desorption of Cd from P25 and SP were accomplished through sequential replacement of the aqueous phase with pure water to induce Cd release. Firtly, 10 mL P25 and SP suspensions (100 mg/L) were allowed to contact with 100 and 200 μg/L Cd respectively in 15 mL PTEE tubes in dark for 12 h to reach adsorption equilibrium. Then the suspensions were centrifuged and the supernatant solution was replaced with 5 mL pure water to start desorption. At 1, 3, 6, 12, 24, 48, 72, 96 and 144 h the replacement of the supernatant with 5 mL pure water was repeated. The

fraction of Cd desorbed from the particles was calculated based on the change in aqueous phase concentration before and after desorption.

2.2 Bioaccumulation experiment

Carp (*Cyprinus carpio*) were used for the bioaccumulation tests. The initial body weight and length of the fish were 6.1 ± 1.2 g and 4.0 ± 0.7 cm respectively. For the accumulation tests, 16.0 mL 100 mg/L Cd solutions were added into three glass tanks containing 16 L dechlorinated tap water respectively and the initial concentration of Cd was 97.3 ± 6.9 μg/L. In two of the three tanks abovementioned, 0.160 g TiO_2 nanoparticles and 0.160 g SP were added respectively. Two h later, 30 carp were placed into the tanks. The fish were fed with a commercial food twice a day during the experiment. The tanks were aerated slightly throughout the tests. Fish were transferred to freshly made solution every day. During the tests, the temperature of water was maintained at 23 ± 2 °C for each exposure. The pH in the exposure water was 7.8. Three fish were removed and sacrificed at 2, 5, 10, 15, 20 and 25th day, and on the 20th day, 6 carp from each of the four treatments were dissected into skin and scales, muscle, gills, and viscera. After pretreatment, Cd and TiO_2 concentrations in carp or different parts of carp were analyzed respectively.

3 RESULTS AND DISCUSSION

3.1 Adsorption kinetics of Cd onto P25 and SP

Adsorption kinetics was observed for 6 h. The adsorption process of Cd onto P25 and SP was fast, reaching equilibrium within 30 min. After equilibrium, the amount of Cd adsorbed by P25 was approximately 72%, which is much higher than that adsorbed onto SP (20%), indicating that P25 has a stronger adsorption capability for Cd than SP. The zeta potential of P25 and SP at the experimental pH (7.8) was found to be about -20.5 mV and −14.4 mV. At this level of pH, Cd remains as Cd^{2+} cations in the solution [7]. Cd could be readily adsorbed onto the surface of P25 and SP due to electrostatic attraction, thus giving less time to reach equilibrium.

Isotherm was determined using 2 h of equilibrium time. Experimental data of Cd adsorption onto P25 and SP are plotted in Fig. 1. The data fit Freundlich isotherm well and the parameters are shown in Table 1.

Table 1 Parameters for Freundlich isotherm

	R^2	K_F (mg/g)	n
P25	0.975	32.8	0.956
SP	0.978	3.25	1.03

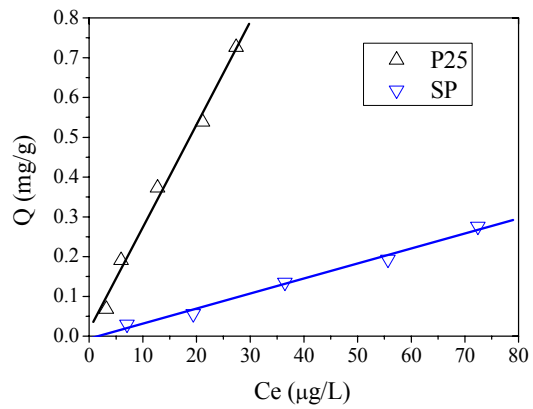

Fig. 1 Freundlich isotherm plots for adsorption of Cd onto P25 and SP.

The average particle size of Degussa P25 nanoparticles is 21 nm, which is much smaller than that of SP (2 to 5 μm). The specific surface area of Degussa P25 nanoparticles is much larger than that of SP (50 m^2/g for P25 and 30 m^2/g for SP). The small particle size and large specific surface area of P25 are expected to account for their strong adsorption ability. Furthermore, the zeta potential of P25 at this level of pH was more negative than that of SP, indicating more Cd adsorbed onto P25.

3.2 Desorption of Cd from P25 and SP

Desorption results of Cd from P25 and SP are presented in Fig. 2. Release curves demonstrate that for both particles, desorption of Cd was quite rapid in the first 24 h. After the initial rapid desorption, only a small amount of additional desorption occurred at longer times. Cd desorption percentage from SP is a slightly higher than that from P25, and about 54% and 48% of the initially adsorbed Cd desorbed from SP and P25 after 144 h of desorption.

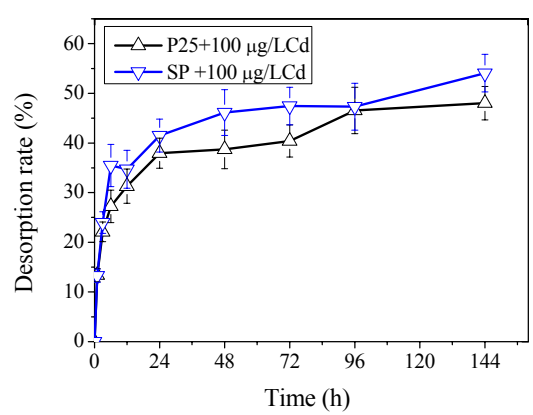

Fig. 2 Desorption of Cd from P25 and SP.

Table 2 Adsorption and desorption amount (percentage) of Cd by P25 and SP

Particles	Initial Concentration (μg/L)	Adsorption Amount (μg/mg)	Adsorption Percentage (%)	Retention Amount (μg/mg)	Retention Percentage (%)	Desorption Amount (μg/mg)	Desorption Percentage (%)
P25	100	0.74	74.40	0.39	51.99	0.36	48.01
SPM	100	0.20	20.35	0.09	45.94	0.11	54.06

P25 have smaller particles size, larger surface area, and more negative surface than SP, thus they have higher adsorption capability and stronger affinity for Cd. As shown in Table 2, about 74% of initially input Cd was adsorbed on P25, in contrast, only 20% of initially input Cd was adsorbed on SP. After 144 h desorption, despite that Cd desorption percentage from P25 is about 6% lower than that form SP, both the adsorbed amount of Cd onto P25 and desorbed amount of Cd from P25 are much higher than those from SP due to the high adsorption capability and strong affinity of P25 for Cd (Table 2).

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[8, 9]. In our study, both the adsorbed amount of Cd onto P25 and desorbed amount of Cd from P25 are much higher than those from SP, indicating that P25 may have a significantly stronger influence on the mobility and bioavailability of Cd in aquatic environments. Hence, more researches should be conducted to address the potential of the facilitated transport of other trace toxic pollutants by nanomaterials when they co-exist. Such researches could shed significant light on the potential exposure risks that nanoparticles might cause.

3.3 The facilitated bioaccumulation of Cd into carp

When TiO_2 nanoparticles and SP were added into the tanks, dissolved Cd concentration decreased due to the adsorption onto the particles. As a result, dissolved Cd concentrations were 34.4 ± 4.8 μg/L for the tank in the presence of TiO_2 and 81.3 ± 7.3 μg/L for the tank in the presence of SP. For the tank spiked with Cd only, the soluble Cd concentration was 97.3 ± 6.9 μg/L. TiO_2 concentration was 10.0 ± 1.3 mg/L when TiO_2 nanoparticles were added into the tank.

The accumulations of Cd in carp exposed to Cd, Cd + TiO_2 nanoparticles and Cd + SP as a function of exposure time are shown in Fig. 3. In this figure, the accumulation of Cd was described using the following standard exponential equation [10]:

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

where C_t is the Cd concentration in whole fish (μg/g dry weight), A is the Cd concentration at equilibrium (μg/g dry weight), B is the first-order rate constant (d^{-1}), and *t* is the exposure time.

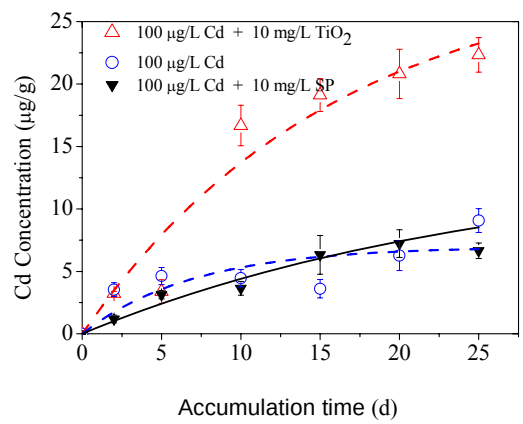

Fig. 3 Bioaccumulation of Cd in carp exposed to Cd, Cd + TiO_2 nanoparticles and Cd + SP

Cd concentration in carp of control was undetected. Cd concentrations in carp exposed to Cd contaminated water increased gradually and after 25 d of exposure it reached 9.07 μg/g. When exposed to Cd-contaminated water in the presence of TiO_2 nanoparticles, the carp accumulated considerably more Cd. As can be seen from Fig. 3, Cd concentration in the carp increased sharply, and reached 22.3 μg/g at the 25th day, which increased by 146% than that without TiO_2 nanoparticles, suggesting that the presence of TiO_2 nanoparticles greatly enhanced the accumulation of Cd in carp. However, Cd concentrations in carp exposed to Cd + SP increased slowly and it was not so much different from those in carp exposed to Cd only. The presence of SP did not have much influence on the accumulation of Cd in carp during the 25 d exposure.

The regression analysis results of the experimental data using Eq. (1) are presented in Table 3. Cd concentration in carp at equilibrium (A value) in the presence of SP is a little higher than that exposed to Cd only. However in the presence of TiO_2 nanoparticles, carp accumulated significantly more Cd, resulting in an A value that is 3-fold higher than that exposed to Cd without TiO_2 nanoparticles.

Table 3. The exponential accumulation parameters.

Exposed media	A (μg/g)	B (d^{-1})	R^2
Cd	6.98	0.143	0.631
Cd and SP	8.25	0.081	0.960
Cd and TiO_2 nanoparticles	29.3	0.063	0.942

Facilitated transport abilities of toxic pollutants by particles are related with the adsorption/desorption capability of the particles. The large adsorption and desorption amount of Cd onto P25 indicated that the presence of nanoparticles has a significant influence on the mobility and bioavailability of Cd in aquatic environments.

4 CONCLUSION

Due to their small particle size, large specific surface area and strong electrostatic attraction, TiO_2 nanoparticles have a stronger adsorption capacity for Cd than SP. Both the adsorbed amount of Cd onto P25 and desorbed amount of Cd from P25 are much higher than those from SP. Facilitated transport abilities of toxic pollutants by particles are related with the adsorption/desorption capability of the particles. The presence of SP did not have significant influence on the accumulation of Cd in carp during the 25 d of exposure. However, the presence of TiO_2 nanoparticles greatly enhanced the accumulation of Cd in carp. After 25 d of exposure Cd concentration in carp increased by 146%.

Nearly 3 million tons of submicron TiO_2 is produced annually worldwide and demand is increasing[11, 12]. In the near future the release of nanoparticles into aquatic systems is inevitable as more and more industrial applications are found for these nanomaterials. It's important to consider the ecological implications of nanomaterials and take a proactive approach to reducing unnecessary risks and unwanted consequences.

Tbis study provides some fundamental information about the fate of nanomaterials in aquatic environment. Such information would shed light on the potential environmental impact of nanoparticles, and provide useful information for policy and decision-making regarding handling, disposal and management of nanomaterials.

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