TiO_2 nanoparticles in aquatic environments: impact on heavy metals distribution in sediments and overlying water

Ali Marefat[1] · Abdolreza Karbassi[1] · Behzad Aghabarari[2]

Abstract The extensive application of TiO_2 nanoparticles (NPs) highlights the importance of investigating their influence on aquatic systems. In this work, the effect of TiO_2 NPs on heavy metals speciation was studied on a lab scale. For this goal, a series of aquaria containing water, sediment, and TiO_2 NPs with various concentrations were set up. The study results revealed that TiO_2 NPs caused (copper) Cu, (mercury) Hg, (titanium) Ti, and (zinc) Zn to be adsorbed by sediments in the forms of exchangeable and Fe–Mn species. According to measurements, 30 μg/L of TiO_2 NPs made Cu, Hg, Ti and Zn concentration in the water column decreased from 33, 1.14, 20, and 32 to 4, 0.58, 3, and 22.3 μg/L, respectively. Manganese (Mn) was also adsorbed by sediment, and in all experiments, its concentration in the water column reduced from 44 to about 20 μg/L. Due to the photocatalytic capacity of TiO_2 NPs, arsenic (As) concentration in the water column increased from 0 to 8.7 μg/L with the introduction of 30 μg/L of TiO_2 NPs. The sequential extraction results showed that in all experiments, concentrations of lead (Pb), nickel (Ni), and cobalt (Co) remained constant in different chemical species of sediment, which meant conservative behavior of them in presence of TiO_2 NPs. In addition, a remarkable change was observed in water quality parameters such as ORP, TDS, TOC, BOD, NO_3, and PO_4 after the introduction of TiO_2 NPs to aquaria. The reason behind these changes could be related to the decomposition of sediment organic content by TiO_2 NPs.

Keywords TiO_2 nanoparticles · Heavy metal speciation · Redox potential · Chemical extraction · Cluster analysis

1 Introduction

Titanium dioxide nanoparticles (HereafterabbreviatedasTiO2NPs) have proven advantages in diverse fields such as textile, medical, food additives, cosmetic and electronic products. It is estimated that TiO_2NPs production will reach 2.5×10^6 tons per year in the USA by 2025 (Robichaud et al. 2009). Intentional or accidental release of TiO_2NPs into aquatic environments might have detrimental impacts on flora, fauna, and human life (Gottschalk et al. 2011; Saratale et al. 2018). Studies estimate NPs to be the most abundant Engineered nanomaterial in aquatic environments ranging from 21 to 10,000 ng/L in surface water (Maurer-Jones et al. 2013). Also, studies confirm that aquatic sediments are the main sink for TiO_2NPs (Cross et al. 2015). For example, Fan et al (2018) reported that the level of TiO_2NPs in sediments was significantly higher than in water column. That's why the highest concentrations of TiO_2NPs are reported in aquatic sediments of the United States and Europe (Gottschalk et al. 2009).

On the other hand, TiO_2NPs have a significant potential to modify bioavailability, mobility, toxicity, and accumulation of co-existing pollutants (heavy metals and toxic organics) in sediment. Fan et al (2017) revealed that TiO_2NPs change concentrations of As, Pb, Cd, and Cu species in sediments. Small size, large surface area, and

✉ Ali Marefat
ali.marefat@ut.ac.ir

1 School of Environment, College of Engineering, University of Tehran, Tehran, Iran

2 Research Department of Nano-technology and Advanced Materials, Tehran, Iran

strong electrostatic attraction of TiO$_2$NPs are the main reasons for influencing on geochemical speciation of heavy metals (Zhang et al. 2007; Domingos et al. 2009; Luo et al. 2011). As a result, it is important to study the effect of TiO$_2$NPs on the geochemistry of heavy metals in sediment (Cai et al. 2019).

Photocatalytic activity of TiO$_2$NPs is another prominent feature, which influences heavy metals speciation, but not much research has been conducted in this field to date. Due to Photocatalytic ability, TiO$_2$NPs have the potential to cause a series of redox reactions in the water column (Liu et al. 2017) and produce strong oxidants like hydroxyl radicals, which degrade organic and inorganic compounds and also change heavy metals distribution (Kalyanasundaram et al. 2013). Numerous studies reported the degradation of organic and inorganic compounds by TiO$_2$NPs (Kang et al. 2019). It should be noted that photocatalytic activity of TiO$_2$NPs in an aquatic media is limited, because TiO$_2$NPs are only active in the presence of ultraviolet light, and on the other hand, only about 4% of the sun's light spectrum contains ultraviolet ray (Zhu et al. 2014; Chakhari et al. 2017).

In this study, to assess the role of heavy metals speciation in sediments, the contaminated sediments of the Anzali wetland were applied rather than spiking heavy metal ions in sediments (which is a common method to simulate heavy metal-contaminated sediments).

To our knowledge, few studies have considered the effect of TiO$_2$NPs on sediment geochemistry. Besides, the mobility of heavy metals in sediments under photocatalytic reactions of TiO$_2$NPs has not been investigated to date. The present study is one of the first studies to investigate the potential of photocatalytic activity of TiO$_2$NPs in aquatic environments. According to the abovementioned, the aims of this study are:

(1) To explore the impact of TiO$_2$NPs on various sedimentary phases (loosely bonded ions, Fe–Mn, organics).

(2) To investigate the effect of TiO$_2$NPs on the interaction of heavy metals between surface sediments and overlying water.

(3) To investigate the influence of TiO$_2$NPs on physicochemical parameters of the water column.

(4) To evaluate the impact of Photocatalytic activity of TiO$_2$NPs on aquatic systems.

2 Methodology

- Materials

In this study, titanium dioxide powder was purchased from Degussa (Degussa-P25). According to producer data, P25 contains 85% anatase and 15% rutile, particles size of 20 nm, and a specific surface area of 57 m^2/g. The chemicals applied during the experiments were analytical grade. Milli-Q water (18 MΩ-cm) was used to prepare all solutions.

- Sample collection and preparation

The sampling station (latitude of 37°24′46″N and longitude of 49°24′24″E) was located in the southern part of the Anzali wetland (Fig. 1). It is worth mentioning that the sampling zone was exposed to pollutants transferred from four main rivers named Siahdarvishan, Masouleh Rudkhan, Palang Ver, and Khalkaee.

Sediment Samples (depth of 0–10 cm) were collected by a Peterson Grab sampler in July 2020, kept in pre-cleaned packages, transported to the laboratory, and dried at room temperature. Then they were homogenized using a shaker instrument from RESTCH Company. To remove gravel and other large particles, a 63-μm sieve was used. The sieved samples were used for bulk digestion and sequential extraction analysis.

Also, water samples were taken with acid-washed polyethylene plastic bottles. After transporting to the laboratory, water samples were kept in a static state for 48 h (allowing particles to settle) and then filtered by a 0.22 μm Millipore AP and HA filter.

Setup test

All experiments were performed in a series of glass aquaria containing 10 cm of pre-dried and pre-sieved sediment, and 8 cm of the filtered water column. Thereafter, TiO$_2$NPs were added into aquaria at concentrations of 5, 10, 15, 20, 25, and 30 ug/L, respectively. These aquaria were aged outdoors for 60 days with closed mouths. Moreover, a control sample with no containing TiO$_2$NPs was applied simultaneously under the same conditions.

- Chemical analysis

LA-950 Laser Particle Size Analyzer was utilized to determine particle size distribution. ASTM-D7348-08 method was used to measure the loss of ignition (LOI). It must be mentioned that LOI is a common method to measure the organic contents of sediment. To analyze biological oxygen demand (BOD), the Winkler method was used. Also, the dichromate reflux method was applied to measure chemical oxygen demand (COD). Total organic carbon (TOC) was determined by oxidation and analyzed by IR gas measurement. The Brown ring test was applied to measure nitrate NO$_3$. After digestion with peroxodisulfade, the molybdenum blue method was used to determine phosphate PO$_4$ (APHA 1985). The detection limit for TOC, BOD, NO3, and PO4 was 0.01 mg/l. Bante900 Benchtop Multiparameter Water Quality Meter was utilized to

Fig. 1 Map of Anzali wetland and the sampling point
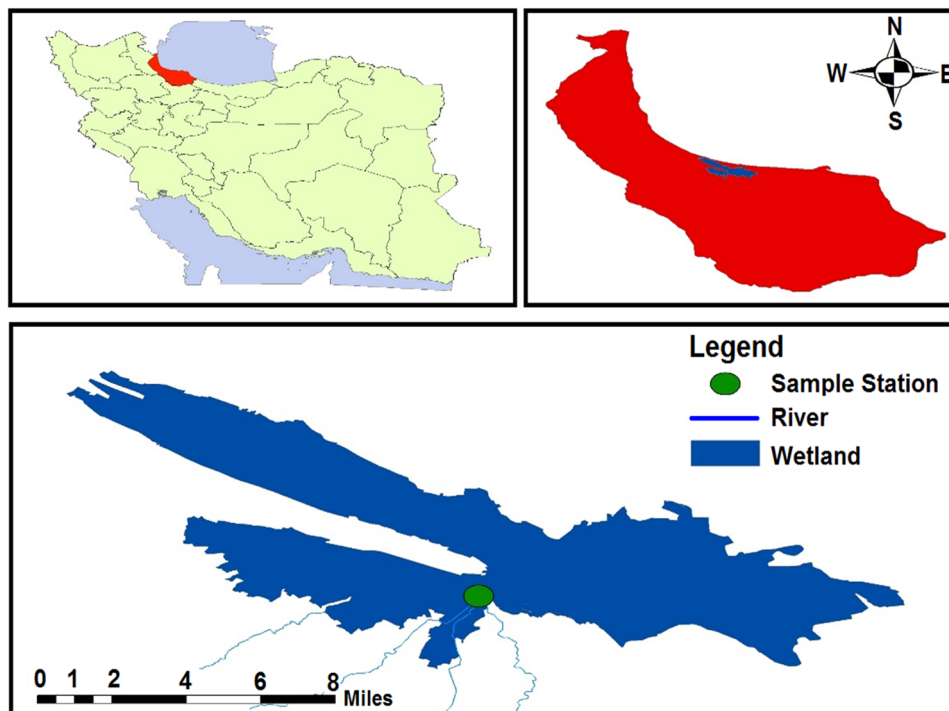
measure pH, Oxidation Reduction Potential (ORP), and Total Dissolved Solids (TDS).

To determine the total concentration of metals, 1 g of pre-died sample was digested by Aqua regia according to the 305B method (USEPA 1996) To evaluate mobility, bioavailability, and interaction of heavy metals in an aquatic environment, it is needed to determine their geochemical species in the sediments (Saleem et al. 2018; Chakraborty et al. 2019). For this purpose, European Union's standards, measurements, and testing scheme (SM and T, formerly BCR) was applied as a sequential extraction procedure to specify the geochemical speciation of heavy metals in sediment (Rauret et al. 1999). According to this method, metal species in sediment are divided into four fractions: exchangeable species (F1), Fe–Mn oxides species (F2), organic–metallic species (F3), and residual species (F4). Table 1 summarizes information on the extraction procedure. After each step of extraction, a centrifuge at 3000 rpm was used for 15 min to separate extraction achieving from sediment. Also, a pipette was used to remove supernatant.

- Measurement of heavy metals concentration

ICP-OES was used to analyze and measure the concentration of heavy metals in the digested samples mentioned above. Hydrochloric acid and potassium iodide were added to convert As (V) to As (III), Before analyzing samples. The concentration of Hg in the digested samples was measured by a VGA-77 connected to a Varian SpectrAA.200 spectrometer. Sodium borohydride solution, as a reducing agent was added to the samples prepared for Hg analysis.

- Risk sssessment code (RAC)

The geochemical distribution of heavy metals can give us a vision of sediment influence on an aquatic environment (Zhang et al. 2014). In general, the bioavailability order of heavy metals species in sediment is as follows: Exchangeable > Fe–Mn > Organic > Residual (Sungur et al. 2015). The risk assessment code (RAC), which is introduced by Perlin et al. (1985), is an index used to evaluate the mobility and bioavailability of heavy metals in

Table 1 SM and T sequential extraction method

Step	Fraction	Extractant	Experiment conditions
1	Exchangeable	40 mL of 0.11 M CH_3COOH	16 h, Room temperature, constant shaking
2	Fe–Mn	40 mL of 0.5 M Hydroxylamine HCl	16 h, Room temperature, constant shaking, pH = 1.5
3	Organic–metallic	10 mL of H_2O_2 (30% w/v) 10 mL of H_2O_2 (30% w/v) 50 mL of 1 M $NH_4CH_3CO_2$	1 h, Room temperature 1 h, 85 °C, Reduce to a low volume 16 h, Room temperature, constant shaking. pH = 2

sediment. RAC is based on sequential extraction results and is defined as follows:

$$RAC = \frac{F_1}{C_t} \times 100$$

where F_1 is concentration of a metal in exchangeable species, and C_t is total concentration of a metal (or sum of metal concentration in four species). The RAC indices can be classified into five levels (Table 2).

- QA/QC control

  To validate the analytical data:

1. All treatments were conducted in triplicate. The relative standard deviation was calculated (RSD < 5%).
2. Blank samples were applied to minimize the laboratory errors.
3. To assess the photocatalytic activity of TiO_2NPs in aquaria, a blank sample was used in dark conditions.
4. A referenced sediment sample (MESS-3), supplied by the National Research Council of Canada, was applied for assessing the accuracy of the bulk digestion method. Table 3 presents the analytical error between measured and published contents of metals in the referenced sediment. As shown in Table 3, the recovery ranges were between 96 and 102%.
5. The accuracy of sequential extraction was assessed by comparing the summation of 4 fractions with the total extraction as follows. The recovery ranges were between 96 and 105%.

$$Recovery = \frac{100 \times (F_1 + F_2 + F_3 + F_4)}{Total}$$

- Statistical analysis

Data were normalized and MVSP software (version 3.2) was utilized for clustering analysis. The clustering analysis was performed based on the Pearson coefficient and weighted pair group with arithmetic mean (WPGMA).

3 Results

According to Tables 4, 5, 6, TiO_2 NPs addition to the aqueous media causes changes in heavy metals concentration and organic content in both overlying water and the

Table 2 RAC (Risk Assessment Code) classification

Rac value	Class
< 1	No risk
1–10	Light risk
11–30	Medium risk
31–50	High risk
50 >	Very high risk

Table 3 The Published and measured contents of metals for MESS-3 (mg/Kg)

Metal	Published value	Measured value	Recovery efficiency
Cr	105	103.1	98.1
Co	14.40	14.7	102.4
Cu	33.90	32.9	97
Zn	159	154.2	97
Pb	21.10	20.8	98.5
Ni	46.90	47.9	102
Mn	324	332	102.4

surface sediment. Moreover, major variation in physicochemical parameters of the water column is observed. Full details are provided below:

- Physicochemical parameters of water column

As shown in Fig. 2, by increasing the TiO_2 NPs concentration in the aqueous media, TDS, nitrate, phosphate, TOC, BOD and COD have shown an increasing trend (Fig. 2c, d, e, f, g, and h), ORP has exhibited a declining trend (Fig. 2a) and pH has shown a steady trend (Fig. 2b) after the 60-day test period.

- Heavy metals concentration in water column

According to Table 5, after the addition of TiO_2 NPs, changes in heavy metals concentration in the water column are obvious. Measurements reveal that the concentration of Mn, Cr, and Ti has decreased from 44, 33, and 20 to 19, 4, and 3 ppb, respectively. Furthermore, a slighter reduction in the concentration of Zn, Co, and Hg in the water column is observed.

On the other hand, whereas the initial water sample does not contain arsenic, after a 60-day test period, arsenic has been identified in the water column with a concentration of 8.7 ppb. Moreover, a slight increase in Ni concentration is observed in the water column after the addition of TiO2 NPs.

As a result, except for Pb, whose concentration remains constant after the addition of TiO_2 NPs, the concentration of other heavy metals changes.

- Texture of sediment

The used sediment with 12% LOI contains 0.9% clay, 67.7% silt, and 31.6% sand. The obtained results in this study prove that TiO_2 NPs cause the decomposition of organic compounds in the sediment. Per Table 4, as the concentration of TiO_2 NPs increases from 0 to 35 μg/L in the water column, the LOI decreases from 12% to 8% in the sediment.

- Distribution of heavy metals in sediment

Table 4 Water column and sediment characteristics before and after the addition of TiO₂ NPs

TiO₂NPS(ppb)	ORP mV	pH ppm	TDS	TOC	NO₃	PO₄	COD	BOD	LOI %
0	251	7.8	320	3.5	10	0.2	42	9	12
5	236	7.7	345	5.9	16	0.5	44	13	10.3
10	225	7.8	362	6.5	19	0.8	53	15	9.8
15	212	7.9	387	7.2	24	0.9	60	18	9.3
20	186	7.8	401	7.8	28	1.1	75	20	8.9
25	163	7.9	432	8.2	34	1.3	87	21	8.6
30	152	7.7	450	8.6	39	1.5	99	23	8.1

The data reported in Table 6 show that, except for Pb, TiO₂ NPs affect the geochemistry distribution of other heavy metals in the sediment.

According to bulk digestion analysis, the presence of TiO₂ NPs leads to the desorption of As and also, to a lesser extent, Ni from the sediment. On the other hand, TiO₂ NPs cause the adsorption of Mn, Zn, Hg, Cu, and Ti in the sediment. However, Pb and Co show conservative behavior in the aquatic environment (Table 6).

Sequential extraction analysis helps us to acquire more understanding of the interaction mechanism of heavy metals between water and sediment. So, the behavioral mechanism of each heavy metal, based on a sequential extraction procedure, is described below.

4 Titanium

The presence of TiO₂ NPs in aqueous media influences Ti distribution. After adding TiO₂ NPs to the test environment, Ti concentration increases in the sediment and simultaneously decreases in the water column, indicating Ti adsorption by the sediment.

As shown in Fig. 3, Ti adsorption leads to the formation of exchangeable species and Fe–Mn species in the sediment. In the case of Ti, the formation process of exchangeable species is higher than that of the Fe–Mn species. Furthermore, Ti is not adsorbed by the sediment in the form of organometallic species.

On the other hand, contrary to Fe–Mn species, the exchangeable species content increases with increasing the concentration of TiO₂ NPs from 0 to 30 μg/L. Therefore, the formation process of Fe–Mn species is independent of TiO₂ NPs content in the water column.

5 Zinc

Due to the addition of TiO₂ NPs to the aqueous media, the concentration of Zn decreases in the water column and increases in the sediment, meaning that Zn is adsorbed by

the sediment. However, increasing TiO₂ NPs level has no significant effect on the zinc adsorption process.

Figure 4 illustrates that level of exchangeable species is in direct relation to the level of TiO₂ NPs. In contrast, the level of Fe–Mn species is negatively related to TiO₂ NPs level. However, organic–metallic species displays a relatively conservative behavior with changing TiO₂ NPs level.

6 Lead

TiO₂ NPs have no effects on Pb distribution in both overlying water and the sediment surface. However, according to Fig. 5, a slight change is observed in the level of exchangeable and organic–metallic species of Pb.

7 Nickel

Nickel exhibits a relatively conservative behavior against TiO₂ NPs content changes. To be more precise, a slight change in nickel concentration is observed in both the water column and sediment surface after adding TiO₂ NPs.

Figure 6 shows that organic–metallic species of nickel are significantly reduced upon arrival of TiO₂ NPs to the aqueous medium, although this reduction does not intensify with increasing TiO₂ NPs levels. Furthermore, a slight reduction of exchangeable species of nickel is observed with increasing TiO₂ NPs levels. However, Fe–Mn species of Ni display a completely conservative behavior in the presence of TiO₂ NPs.

8 Copper

The change of copper concentration indicates its adsorption by the sediment after adding TiO₂ NPs to the test environment. According to Fig. 7, copper is adsorbed mainly as Fe–Mn species and then as exchangeable species. However, organic–metallic species have no role in the copper adsorption process. The remarkable point is that the

Fig. 2 Changes in water quality parameters after the TiO$_2$ NPs addition; **a** ORP, **b** pH, **c** TDS, **d** NO$_3$, **e** PO$_3$, **f** TOC, **g** BOD, and **h** COD
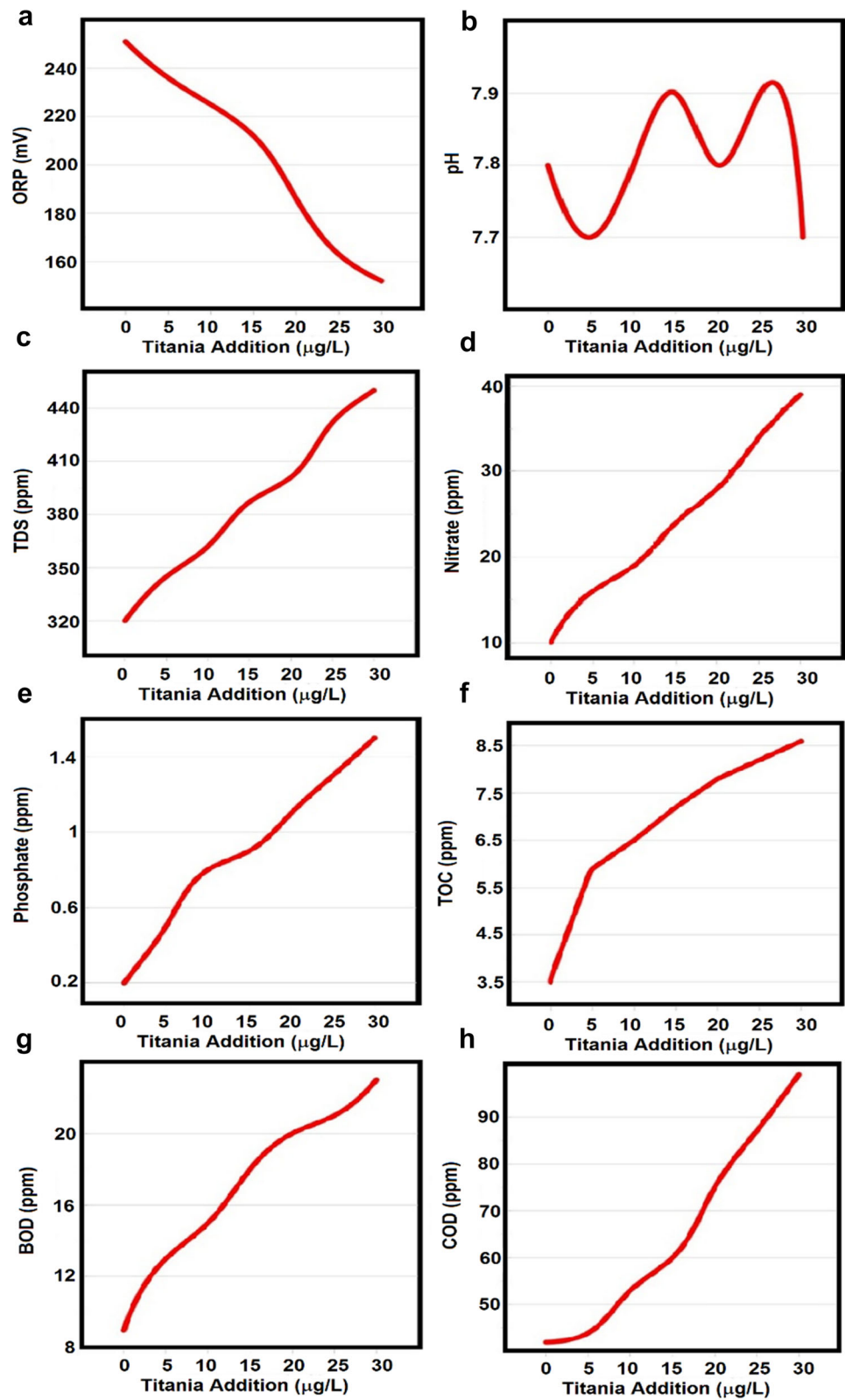
tendency for the formation of Fe–Mn species is reduced with increasing TiO$_2$ NPs levels.

Table 5 Heavy metals concentration in the water column before and after the addition of TiO$_2$ NPs

TiO$_2$ NPs (ppb)	Ti	Zn	Pb	Ni	Cu	Co	As	Hg	Mn
0	20	32	1.5	3	33	3	0	1.24	44
5	18	24	1.5	3.1	4	2.3	8	0.7	20
10	15	23.3	1.5	3.1	4	2.2	8.3	0.68	19.4
15	12	25	1.5	3.3	4	2.3	8.3	0.62	20.4
20	8	25	1.5	3.4	4	2.3	8.4	0.61	21
25	5	23.5	1.5	3.4	4	2.4	8.7	0.6	20.4
30	3	22.3	1.5	3.5	4	2.3	8.7	0.58	19.4

9 Cobalt

Cobalt concentration in the water column decreases after adding TiO$_2$ NPs. As shown in Fig. 8, except for a slight change in exchangeable species, no changes are observed in Fe–Mn and organic–metallic species of cobalt. Furthermore, no changes are also observed in the cobalt concentration in water and sediment with increasing species concentration from 5 to 30 μg/L. Thus, cobalt has a relatively conservative behavior upon the arrival of species in an aquatic environment.

10 Manganese

After the addition of TiO$_2$ NPs to aquaria, Mn concentration is reduced in the water column, so that at high levels of TiO$_2$ NPs, its concentration is halved. Figure 9 reveals that manganese adsorption as exchangeable species and Fe–Mn species is the reason for this reduction. In contrast,

Table 6 Distribution of heavy metals concentration in sedimentary phases before and after the addition of TiO$_2$ NPs

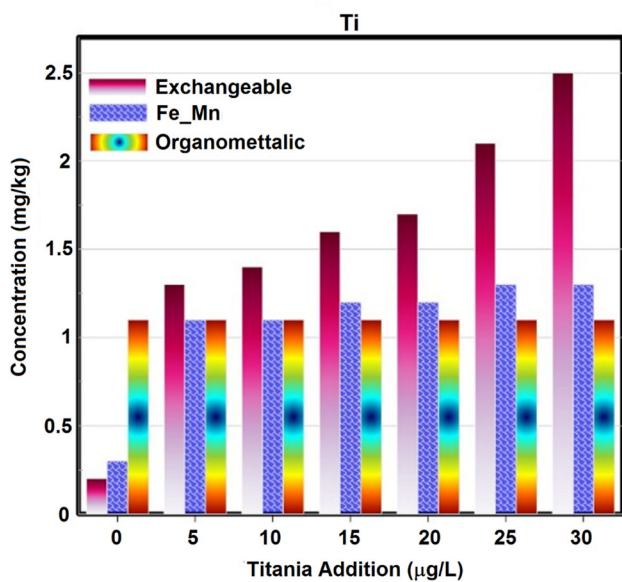| Metal Distribution (ppb)	TiO$_2$ NPs	Ti mg/Kg	Zn	Pb	Ni	Cu	Co	Mn	As	Hg
Total Concentration	0	2466	58	7.1	6.4	5.6	3.6	384	3.4	0.9
	5	2468	58.1	7.1	6.3	8.5	3.7	385	3.2	0.92
	10	2471	58.3	7.15	6.2	8.3	3.7	387	3.2	0.92
	15	2475	58.3	7.1	6.2	8.4	3.6	388	3.1	0.93
	20	2481	58.4	7.12	6.1	8.1	3.6	390	3	0.95
	25	2486	58.5	7.2	6.1	8	3.6	395	2.9	0.99
	30	2490	58.7	7.21	5.9	8.4	3.7	398	2.8	1
Exchangeable Bounds	0	0.2	0.8	0.52	0.09	0.4	0.05	7.9	3	0.04
	5	1.3	0.9	0.52	0.09	0.6	0.05	8	2.2	0.05
	10	1.4	1	0.52	0.08	0.6	0.06	8.2	1.8	0.05
	15	1.6	1.3	0.51	0.08	0.7	0.05	8.4	1.2	0.06
	20	1.7	1.5	0.51	0.08	0.6	0.05	8.8	0.7	0.06
	25	2.1	1.6	0.5	0.07	0.7	0.07	9.1	0.5	0.06
	30	2.5	1.8	0.5	0.07	0.6	0.06	9.5	0.3	0.07
Fe–Mn Bounds	0	0.3	0.6	0.3	0.1	0.3	0.04	6.5	0.06	0.05
	5	1.1	1	0.3	0.1	1	0.04	8.8	0.03	0.05
	10	1.1	0.9	0.3	0.1	1	0.04	8.9	0.03	0.05
	15	1.2	0.71	0.3	0.1	0.9	0.04	9.1	0.03	0.06
	20	1.2	0.7	0.3	0.1	0.8	0.04	9.4	0.03	0.05
	25	1.3	0.65	0.3	0.1	0.8	0.04	9.6	0.03	0.06
	30	1.3	0.6	0.3	0.1	0.9	0.03	10	0.02	0.05
Organic–metallic Bounds	0	1.1	0.7	0.25	0.2	0.3	0.1	7.4	0.12	0.04
	5	1.1	0.7	0.28	0.1	0.3	0.1	7.2	0.1	0.04
	10	1.1	0.8	0.27	0.09	0.3	0.1	7	0.09	0.04
	15	1.1	0.8	0.27	0.09	0.3	0.1	6.8	0.09	0.04
	20	1.1	0.86	0.27	0.06	0.3	0.1	6.6	0.07	0.04
	25	1.1	0.9	0.25	0.05	0.3	0.1	6.2	0.05	0.04
	30	1.1	0.93	0.25	0.04	0.3	0.1	5.7	0.05	0.04

Fig. 3 Chemical species of titanium in different levels of TiO$_2$ NPs
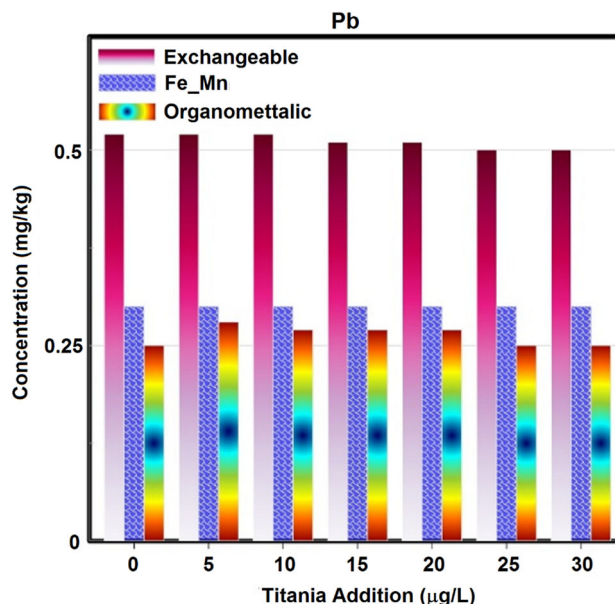

Fig. 5 Chemical species of lead in different levels of TiO$_2$ NPs
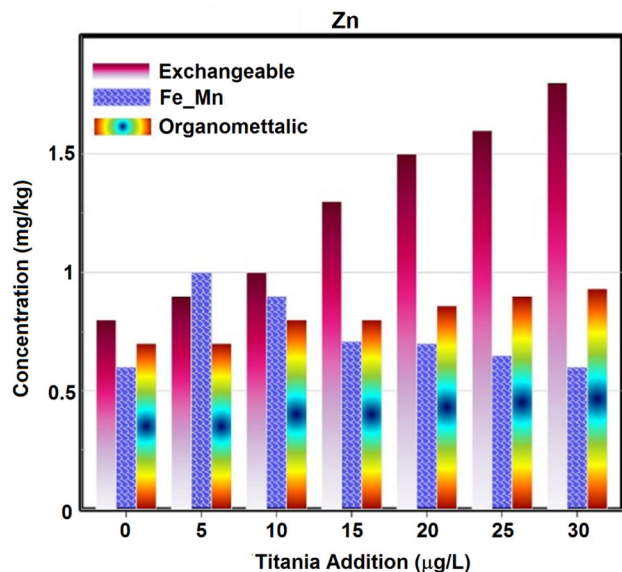

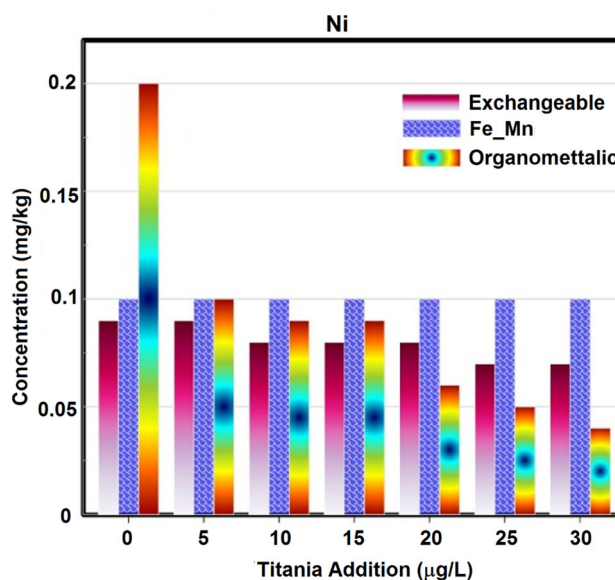Fig. 4 Chemical species of zinc in different levels of TiO$_2$ NPs

Fig. 6 Chemical species of nickel in different levels of TiO$_2$ NPs

manganese reduction in organic–metallic species is observed. Therefore, it can be concluded that TiO$_2$ NPs affect manganese interactions with water and sediment through two opposite mechanisms. However, the effect of TiO$_2$ NPs on the adsorption mechanism is stronger than the desorption one. In consequence, TiO$_2$ NPs finally lead to the reduction of manganese concentration in the water column.

11 Arsenic

Observations confirm the unique behavior of arsenic compared to other metals. Before adding TiO$_2$ NPs, the exchangeable level of arsenic species is extremely high, and arsenic has an anthropogenic source in the sediment. The results of the bulk digestion and the chemical extraction analysis indicate that TiO$_2$ NPs have a substantial impact on exchangeable species of arsenic and cause their interaction with water and sediment. In comparison to other heavy metals, except for Ni, arsenic is desorbed from the
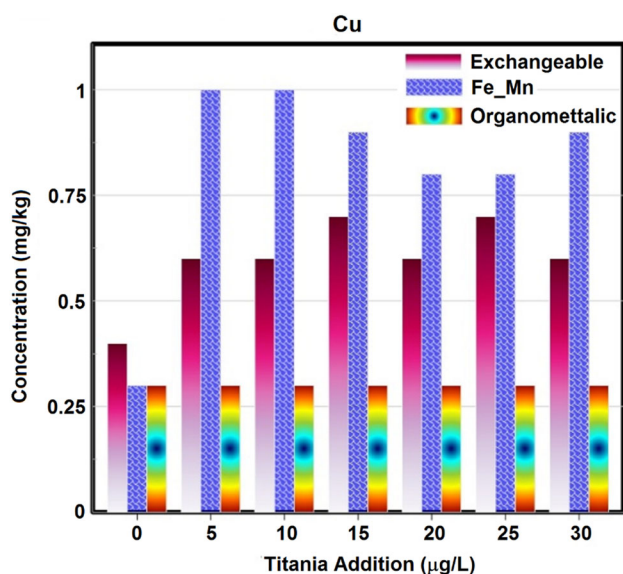
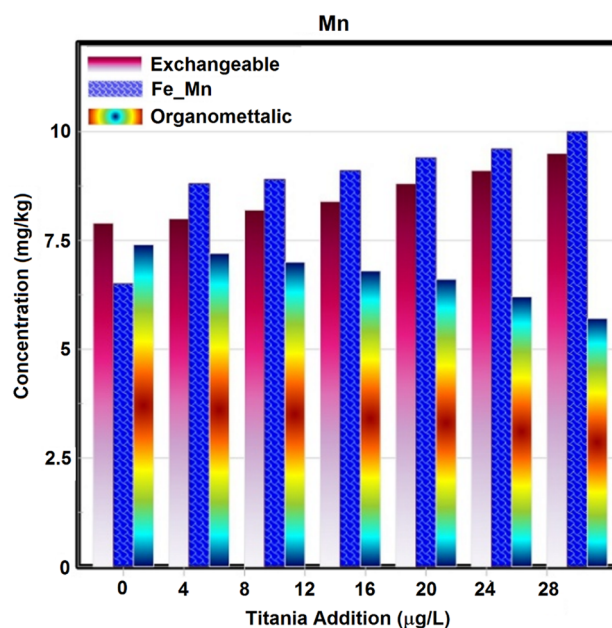Fig. 7 Chemical species of copper in different levels of TiO₂ NPs

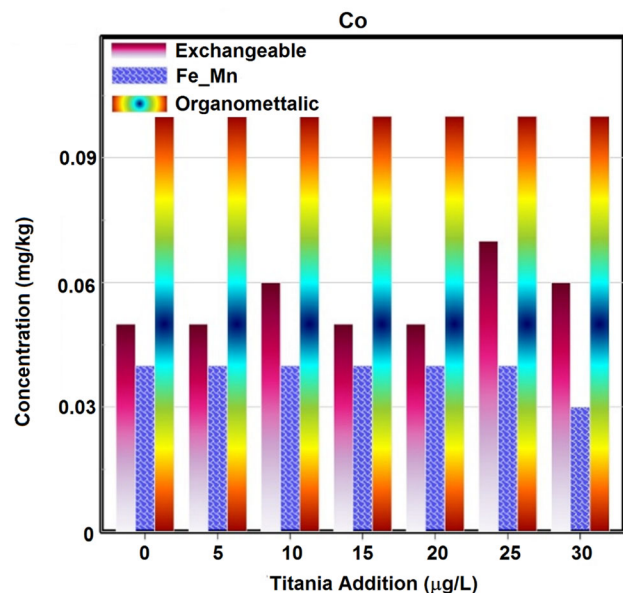Fig. 8 Chemical species of cobalt in different levels of TiO₂ NPs

Fig. 9 Chemical species of manganese in different levels of TiO₂ NPs
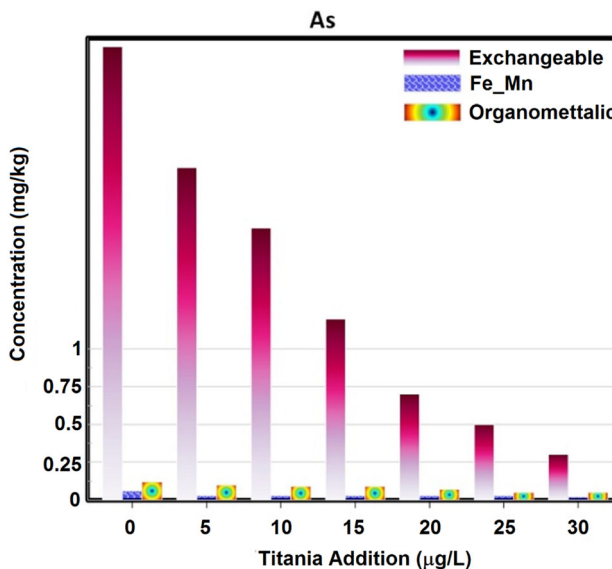
Fig.10 Chemical species of arsenic in different levels of TiO₂ NPs

sediment and enters the water column due to the presence of TiO₂ NPs in the test environment.

Figure 10 proves that the addition of TiO₂ NPs leads to a drastic reduction of exchangeable species of arsenic in the sediment. In addition, organic–metallic and Fe–Mn species of arsenic are slightly reduced in response to TiO₂ NPs in the aqueous media. More exactly, organic–metallic and Fe–Mn species of arsenic show a relatively conservative behavior.

12 Mercury

After the arrival of TiO₂ NPs to the aqueous media, Hg concentration in the water column is almost halved. The bulk digestion analysis reveals that reduced mercury is adsorbed by the sediment. According to Fig. 11, mercury adsorption occurs mainly in the form of exchangeable species and Fe–Mn ones. In addition, with increasing TiO₂ NPs levels in the environment, more exchangeable species are formed, although this amount is very low. Generally,

Fig. 11 Chemical species of mercury in different levels of TiO$_2$ NPs

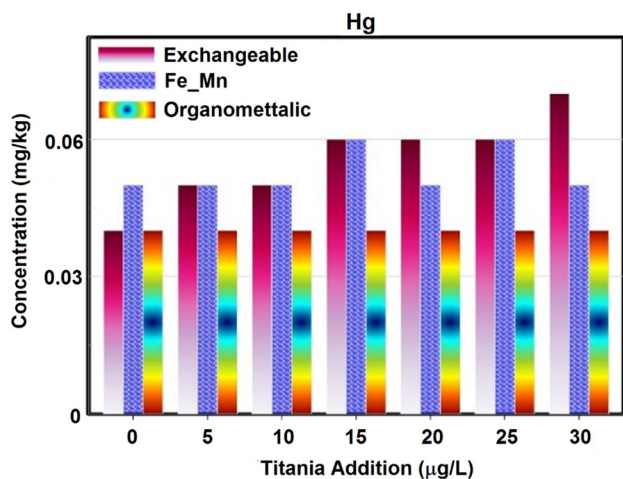increasing TiO$_2$ NPs raises the Hg accumulation in the sediment. Organic–metallic species do not play any role in the mercury interaction with water and the sediment in response to TiO$_2$ NPs.

13 Discussion

As shown in Fig. 12, after the addition of TiO$_2$ NPs, the ORP of the test medium decreases. The trend of change in ORP indicates the aquatic environment transition from aerobic to anaerobic conditions (Yavar et al. 2019). Moreover, according to the ORP classification by Bohn (1971), as TiO$_2$ NPs concentration increases, the water column degrades from moderately reduced conditions to highly reduced conditions.

After the addition of TiO$_2$ NPs, TDS increases in the water column as a result of the mineralization of the
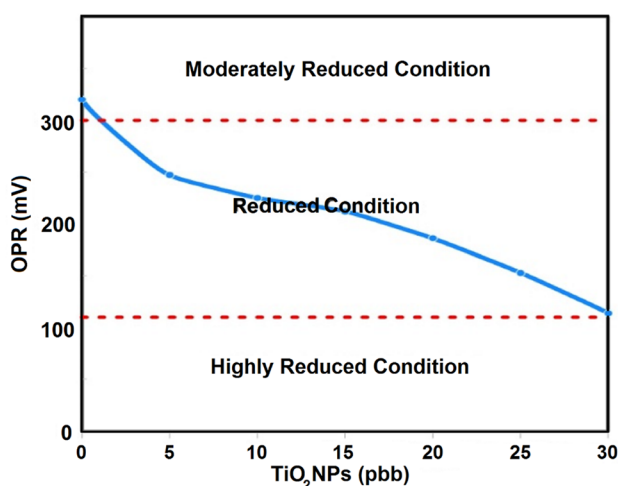

Fig. 12 The impact of TiO$_2$ NPs on ORP

sediment organic matter. Organic compounds, which often contain carbon, nitrogen, and phosphorus structures, are converted to other compounds, such as carbonate, nitrate, and phosphate, in the mineralization process. During this process, TDS in the water column will increase (Rezaei Tavabe et al. 2018). Numerous researchers have reported that after organic matter mineralization, TDS will increase in the water column (Konstas et al. 2019). In addition, as organic content in the sediment decreases, PO$_4$, NO$_3$, and TDS in the water column increase. Hence, it can be inferred that a low concentration of TiO$_2$ NPs in an aquatic environment can lead to the decomposition of organic compounds in the sediment. Increasing TOC in the overlying water provides another proof of organic compound decomposition in the sediment. Another noteworthy point is that the clustering analysis reflects a significant relationship between ORP and PO$_4$, NO$_3$, TOC, and TDS (Fig. 13). It implies that ORP reduction is due to organic matter decomposition. Thus, TiO$_2$ NPs reduce the water quality by degrading organic compounds, thereby transforming the test medium into an anaerobic condition. It should be noted that TiO$_2$ NPs can only degrade organic compounds by absorbing UV light (Nguyan et al. 2003).

On the other hand, the findings reveal that TiO$_2$ NPs not only lead to the decomposition of the sediment organic matter or degradation of water qualitative parameters but also affect the geochemical distribution of heavy metals in the sediment. A very limited number of studies have considered the impact of TiO$_2$ NPs on heavy metals distribution in the sediment (Fan et al. 2018). This study proves that TiO$_2$ NPs are capable of affecting the distribution of heavy metals in the sediment directly and indirectly. On the one hand, the large adsorption capacity of TiO$_2$ NPs changes heavy metal species in the sediment. On the other hand, due to their photocatalytic properties, TiO$_2$ NPs alter water quality parameters (especially ORP as mentioned earlier), and thus, indirectly affect the distribution of the heavy metals in the sediment. It is widely believed that ORP governs the chemical species of heavy metals in the sediment (Zhang et al. 2014; Karbassi and Marefat 2017) in
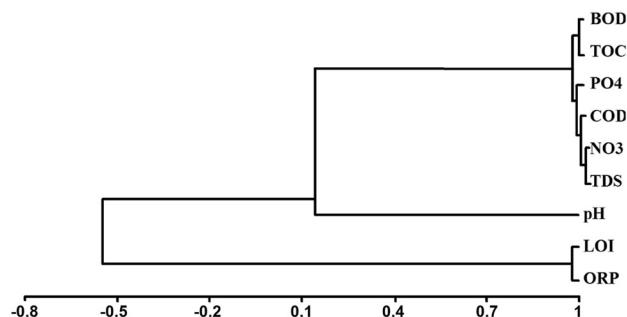

Fig. 13 The cluster analysis of physicochemical parameters of the water column

addition, it must be mentioned that no change in heavy metals species was observed in the blank sample used in dark condition.

According to Table 6, TiO$_2$ NPs cause some heavy metals to be adsorbed and others to be desorbed by sediments. The change in geochemical species provides more or less detailed information concerning the adsorption and desorption process of heavy metals in sediments (Marefat et al. 2019). The data analysis in Table 6 reveals that heavy metals might be classified into 5 general groups based on their adsorption and desorption mechanisms in sediments, as follows:

- Group 1: Heavy metals, desorbed from exchangeable and organic–metallic bounds, enter the aquatic environment (As and Ni).
- Group 2: Heavy metals, adsorbed as exchangeable species and iron-manganese ones in the sediment (Zn, Cu, and Ti).
- Group 3: Heavy metals, adsorbed only as exchangeable species in the sediment (Hg).
- Group 4: Heavy metals, adsorbed as iron-manganese species and exchangeable species while desorbed from organic–metallic species (Mn).
- Group 5: Heavy metals, having no interaction with sediment and water and showing a conservative behavior in an aquatic system (Pb and Co).

According to the cluster analysis (Fig. 14), there is a direct relationship between the concentration of Mn, Ti, Zn, and Hg in the sediment and the level of TiO$_2$ NPs added to the water column. It is concluded that after the accumulation of TiO$_2$ NPs in the sediment, they cause the adsorption of some heavy metals by the sediment surface. In confirmation of this conclusion, several investigators have reported that TiO$_2$ NPs have a high adsorption capacity for heavy metals (Zhang et al. 2007; Sun et al. 2009; Fan et al. 2017, 2018).

Fan et al. (2017) Proved that TiO$_2$ NPs in sediments play a substantial role in reducing water pollution. They demonstrated that heavy metals released from the sediment toward overlying water were re-adsorbed by TiO$_2$ NPs in the sediment surface. However, the findings of this study are in some respects inconsistent with the results of the study done by Fan et al. (2018). They claimed that the reduction of heavy metals concentration in exchangeable species and Fe–Mn ones stemmed from the fact that these species, desorbed from sediments, were re-adsorbed by TiO$_2$ NPs. On the contrary, the present study shows that neither the concentration of heavy metals decreases in exchangeable species and Fe–Mn ones nor they are adsorbed by TiO$_2$ NPs in the sediment. The potential reason for inconsistent results is that TiO$_2$ NPs do not necessarily adsorb heavy metals on their surface and may cause heavy metals adsorption on the sediment surface.

Among heavy metals adsorbed to the sediment, Cu showed different behavior. According to the cluster analysis (Fig. 12), unlike Zn, Hg, Mn, and Ti, no relation existed between the adsorption rate of Cu and the change in the level of TiO$_2$ NPs. As observed in the chemical fractionation experiment (Table 6), although adding TiO$_2$ NPs to the aqueous media leads Cu to be adsorbed by the sediment, the greater level of TiO$_2$ NPs does not cause the higher adsorption of Cu. Yin et al. (2020) showed that TiO$_2$ NPs in the sediment had a significant role in adsorbing Cu from the water column. However, unlike the present study, where Cu is adsorbed as Fe–Mn species and exchangeable species, in the study reported by Yin et al., Cu adsorption was mainly as residual species. The synthesis of TiO$_2$ NPs in activated carbon granules by Yin et al. may be the reason for conflicting results.

Figure 14 illustrates a strong correlation coefficient between concentrations of As and Ni in the sediment with a change in OPR and sediment organic content. This relationship is mainly attributed to the photocatalytic properties of TiO$_2$ NPs, enabling them to cause a series of redox reactions in the aqueous media (Kang et al. 2019). Hence, organic compound degradation occurs, and Ni and As enter the aqueous phase. This hypothesis could be supported by the reduction of Ni and As organic species in the sediment. Therefore, it can be concluded that the photocatalytic properties of TiO$_2$ NPs affect the geochemical distribution of some heavy metals, and this mechanism should not be ignored in future studies. In comparison to other heavy metals, TiO$_2$ NPs have a much greater effect on arsenic. According to Fig. 15, before the addition of TiO$_2$ NPs to the aquatic environment, arsenic proportion in exchangeable species was extremely high in the sediment. In other words, the external environment was at high risk of As contamination. Furthermore, with increasing the TiO$_2$ NPs content in the water column, the quantity of arsenic in exchangeable species gradually decreases until at very high concentrations of TiO$_2$ NPs, the arsenic exchangeable species approach zero in the sediment. In other words, at
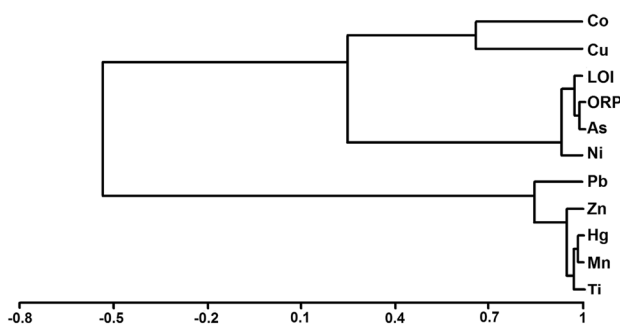
Fig. 14 The cluster analysis of heavy metals in the aqueous solution
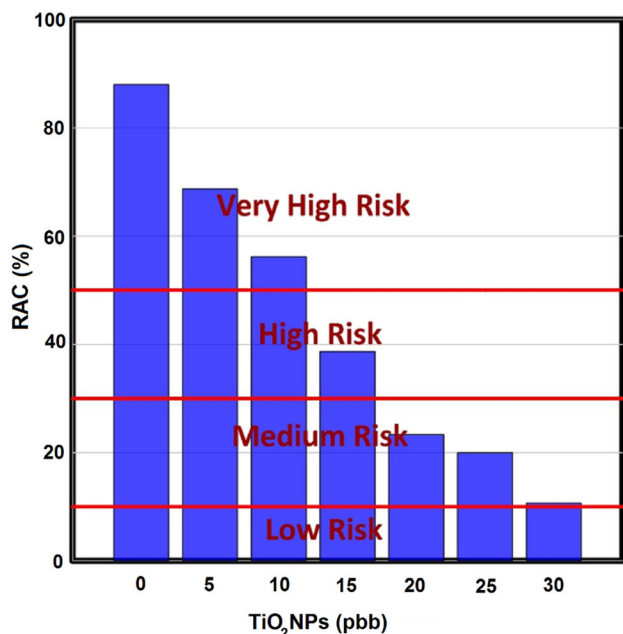
Fig. 15 The impact of TiO$_2$ NPs on RAC value for arsenic

high concentrations of TiO$_2$ NPs, the sediment potential for further contamination of aqueous media with arsenic disappears. It is worth noting that more than 230 million people worldwide are affected by arsenic-contaminated water. Alluvial sediments are the main source of arsenic contamination (Shaji et al. 2021). Heavy metal-contaminated sediments could be remediated using nanomaterials, including TiO$_2$ NPs. However, just a few studies have examined the potential of TiO$_2$ NPs for contaminated-sediment remediation (Duncan et al. 2019; Cai et al. 2019; Debnath et al. 2021). For example, Yin et al. (2020) demonstrated that TiO$_2$ NPs could be applied to remediate sediments contaminated by copper. High reactivity and strong adsorption capacity make TiO$_2$ NPs appropriate for remediating contaminated soil and sediments (Akcil et al. 2015; Peng et al. 2018).

However, unlike other studies that recognize the large adsorption capacity of TiO$_2$ NPs as an effective factor in the remediation process, the present study knows the photocatalytic capability of TiO$_2$ NPs as the main factor in remediating arsenic-contaminated sediment. To be more precise, TiO$_2$ NPs remediate the arsenic-contaminated sediment indirectly. Redox reactions, balanced by TiO$_2$ NPs cause the water column parameters to be changed, followed by releasing arsenic from its exchangeable and weak bounds in the sediment (Peng et al. 2009; Tandon and Singh 2016). Thus, TiO$_2$ NPs lead to sediment remediation from exchangeable and hazardous species of arsenic.

As mentioned, manganese exhibits two distinct adsorption–desorption behavior in the presence of TiO$_2$ NPs. Its exchangeable species and Fe–Mn ones decrease while its

organic–metallic species increase. The results illustrate that manganese desorption is in direct relation with the sediment organic content reduction. Therefore, TiO$_2$ NPs affect the geochemical distribution of manganese in two different ways: (1) The adsorption properties of TiO$_2$ NPs, resulting in the increase of exchangeable species and Fe–Mn ones; and (2) Photocatalytic properties of TiO$_2$ NPs, which causes reduction of organic–metallic species.

No changes in the Pb and Co species content are observed before and after the addition of TiO$_2$ NPs. It is while Pb adsorption by TiO$_2$ NPs has been reported by fan et al. (2018). It might be because, contrary to the present study, in which TiO$_2$ NPs are added into the water column, in the Fan et al. (2018) study, both Pb and TiO$_2$ NPs were spiked into the sediment.

Concerning the above-mentioned results, however, the study outcomes confirm that TiO$_2$ NPs have a major impact on heavy metals distribution in the sediment, considering the geochemical species of heavy metals, are still not comprehensive. Other factors such as ultraviolet intensity, TiO$_2$ NPs distribution in the sediment, TiO$_2$ NPs size and surface, external environment conditions, initial concentration of heavy metals in the sediment and water column, and aquatic organisms might also have a crucial role. So, further studies are required in the future.

14 Conclusions

In the present study, the influence of TiO$_2$ nanoparticles (NPs) on heavy metals speciation is investigated experimentally. According to our observation, strong adsorption capacity and photocatalytic capability are two prominent features of TiO$_2$ NPs in aquatic systems, affecting the distribution of heavy metals in sediments.

The results show that TiO$_2$ NPs make Cu, Hg, Ti and Zn be adsorbed by sediments as exchangeable and Fe–Mn species, while As and Mn be desorbed as exchangeable and organometallic species.

The photocatalytic degradation of sediments' organic content leads to significant changes in the water quality parameter. According to measurements, ORP sharply decreases after the introduction of TiO$_2$ NPs to the water environment. On the other hand, TOC, BOD, NO$_3$ and PO$_4$ increase due to the introduction of TiO$_2$ NPs.

Declarations

Conflict of interest The authors have no relevant financial or non-financial interests to disclose.

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