EXAFS studies on adsorption irreversibility of Zn(II) on TiO₂: Temperature dependence

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Abstract

Adsorption irreversibility of Zn(II) on TiO₂ at various temperatures was studied using a combination of classical macroscopic methods and extended X-ray absorption fine structure (EXAFS) spectroscopy. When the temperature was increased from 5 to 40 °C, the Zn(II) adsorption capacity increased by 130%, and adsorbed Zn(II) became more reversible. The standard Gibbs free energy change (ΔG^0) of the adsorption reaction at 5, 20, and 40 °C was determined to be -19.58 ± 0.30 , -22.28 ± 0.10 , and -25.14 ± 0.21 kJ mol⁻¹, respectively. And the standard enthalpy (ΔH^0) and entropy (ΔS^0) were 24.55 ± 2.91 kJ mol⁻¹ and 159.13 ± 0.53 J mol⁻¹ K⁻¹, respectively. EXAFS spectra results showed that the hydrated Zn(II) was adsorbed through fourfold coordination with an average Zn–O bond distance of 1.98 ± 0.01 Å. Two Zn–Ti atomic distances of 3.25 ± 0.02 and 3.69 ± 0.03 Å were observed, which corresponded to an edge-sharing linkage mode (strong adsorption) and a corner-sharing linkage mode (weak adsorption), respectively. As the temperature increased from 5 to 40 °C, the number of strong adsorption sites (N_1) remained relatively constant while the number for the weak adsorption sites (N_2) increased by 31%. These results indicate that the net gain in adsorption capacity and the decreased adsorption irreversibility at elevated temperatures were due to the increase in available weak adsorption sites (N_2) or the decrease in the ratio of N_1/N_2 . Both the macroscopic sorption/desorption equilibrium data and the molecular level evidence of this study suggest that in a given environmental system (e.g., soils or natural waters) zinc and other similar heavy metals are likely more mobile at higher temperatures.

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1. Introduction

Adsorption and desorption are important processes governing the mobility and bioavailability of heavy metals in soils and groundwater [1]. Adsorption–desorption of Zn in soils and waters can be affected by many factors, such as aging [2,3], adsorbent properties [4–6], and concentration [7,8]. However, studies on the effect of temperature on the adsorption reversibility have been very limited [9].

Temperature in various environmental compartments can fluctuate diurnally, seasonally, and spatially. For example, tem-

perature in natural waters can vary seasonally by as much as 30 K [10], and water temperature in oceans and lakes changes considerably with the depth of the water column [11]. Temperature fluctuation can affect the adsorption capacity and irreversibility, and thus the fate and transport of heavy metals in the environment. Therefore, mechanistic and quantitative studies of the effect of temperature on the adsorption–desorption behavior will facilitate more accurate predictions of the fate and transport of heavy metals in the environment.

For many decades, studies on adsorption reversibility of heavy metals in soils and natural waters have been confined to macroscopic phenomenological studies because of the complexity of natural geosorbents and analytical constraints [12,13]. Although numerous hypotheses have been proposed to interpret the discrepancies between experimental observa-

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tions and ideal equilibrium adsorption theories, molecular-level evidence is often lacking for understanding the commonly observed adsorption phenomena such as nonequilibrium adsorption of metals, adsorption hysteresis, and effect of particle concentration on the adsorption/desorption equilibrium. In 1998, Pan and Liss [14] proposed a metastable equilibrium adsorption (MEA) theory and pointed out that the molecular orientation at the adsorbent–solution interface and the mode of adsorbate–adsorbent interactions can significantly impact the equilibrium adsorption of heavy metals. They proposed that adsorption reactions on solid surfaces generally end up in different metastable-equilibrium states, depending on the paths of the adsorption process, rather than in a unique ideal equilibrium state that is independent of the adsorption kinetics. The deviation of the real metastable-equilibrium states from the ideal equilibrium state results in the inconstancy of traditionally defined equilibrium constants. Equilibrium adsorption constants and adsorption isotherms, when they are expressed through the macroscopic parameter of adsorption density (mol m^{-2}), can thus be fundamentally affected by the reversibility of adsorption reactions. This behavior cannot be explained by classical adsorption thermodynamics. For more complex sorption processes where multiple surface reactions and partitioning processes occur simultaneously on the heterogeneous components of a soil/sediment sample, various semiempirical models have been proposed to interpret sorption hysteresis [15–18]. However, the fundamental principle pertaining to how the reversibility of the surface adsorption can lead to different metastable equilibrium states remains unknown. Since a change in temperature can alter the irreversibility of sorption pathways, the final MEA states are expected to be temperature dependent.

In recent years, the EXAFS technique has been increasingly employed for providing structural and compositional information of surface complexes [19,20], which often offers critical insights into the underlying adsorption/desorption mechanisms [21–23]. This facilitates our understanding of commonly observed phenomena such as sorption hysteresis and slow sorption/desorption processes. For instance, prior EXAFS results revealed that the adsorption reversibility of heavy metal Zn was closely related to the molecular structures of the surface complexes and the mode of surface complexation [24–27]. Since temperature is expected to affect both sorption thermodynamics and kinetics, the adsorption–desorption behavior of heavy metals may be temperature dependent. Furthermore, coupling the macroscopic phenomenological sorption studies with microscopic EXAFS investigation into the surface molecular orientation of sorbed metal ions may reveal important insights into the underlying sorption and desorption mechanisms. From an environmental remediation viewpoint, such information is of great significance in assessing the mobility and toxicity of heavy metals in the environment.

Titanium dioxide (TiO_2) has been intensively studied as an adsorbent for heavy metals owing to its high chemical stability in acidic and alkaline solutions and reasonably fast rate of adsorption and desorption [28–30]. TiO_2 exists in two major

polymorphic forms, anatase and rutile. Because of its greater surface area, anatase is often a preferred adsorbent in many applications [31,32]. The EXAFS signal–noise ratio in the Zn– TiO_2 system is much higher than that in many other Zn–metal oxide systems, making the mechanism analysis at atomic levels more reliable.

The present study aims to investigate the fundamental mechanisms on the Zn(II) adsorption–desorption and its impacts on the mobility of Zn. Specifically, the effect of temperature on the sorption mode, irreversibility, and their relationships to metastable equilibrium states of sorbed Zn(II) ions will be studied through both macroscopic adsorption–desorption equilibrium experiments and microscopic EXAFS analyses.

2. Experimental

2.1. Materials

TiO_2 was purchased from the Beijing Chemical Reagents Company (Beijing, China). X-ray diffraction analyses showed that the TiO_2 was pure anatase. The specific surface area was measured to be $201.3 \text{ m}^2 \text{ g}^{-1}$ following the standard N_2 -BET method. The particle-size distribution, measured with a Mastersizer 2000 analyzer (Malvern, UK), ranged from 0.3 to $2.5 \mu\text{m}$. The average particle size was $0.95 \mu\text{m}$.

2.2. Methods

2.2.1. Adsorption–desorption isotherms

Following the method by Pan and Liss [33], adsorption isotherms were measured at 5, 20, and 40°C , respectively. In brief, 30 mL of a solution containing 0.1 M NaNO_3 and a range of initial concentrations of Zn(II) (from 7.65×10^{-6} to $3.82 \times 10^{-4} \text{ mol L}^{-1}$) was mixed with 0.03 g TiO_2 in 50-mL PP centrifuge tubes. The tubes were then capped and shaken in an incubator set at a given temperature for 24 h, which proved to be sufficient to reach equilibrium. During the course of the adsorption experiment, the solution pH was kept constant at 6.30 ± 0.03 through intermittent addition of 0.1 M NaOH or 0.1 M HNO_3 . On equilibrium, solids were removed by centrifugation at 3200g force. Then the supernatants were filtered with $0.22\text{-}\mu\text{m}$ membrane and analyzed for Zn(II) concentration by differential pulse voltammetry (797 VA Computrace, Metrohm, Switzerland). At the Zn concentration levels tested here, the loss of Zn on the filters is negligible compared to the standard deviations of the experiment [33]. The zinc adsorption density was calculated from the difference between the initial and the final concentrations of Zn(II) in the solution phase. For EXAFS measurements, the separated Zn-laden TiO_2 solids of selected samples were placed in 2-mm-thick sample holders and sealed with adhesive PVC tapes. All adsorption experiments were duplicated to assure data quality.

Following the adsorption experiments, the points on different isotherms corresponding to the same solution-phase Zn(II) concentration of $\sim 0.090\text{--}0.092 \text{ mmol L}^{-1}$ were selected for

further desorption experiments. The desorption tests were initiated by replacing a fraction (20 mL) of the equilibrium supernatants (after centrifuging) with an equal volume of a solution containing the same background compositions (0.1 M NaNO₃ and pH 6.3) but free of Zn(II). The mixtures were then reequilibrated on a shaker for 24 h. The equilibrium distribution of Zn(II) between the solution and the adsorbent was then determined following the same procedures as for the adsorption experiments. The dilution–reequilibration steps were carried out in three consecutive steps to obtain the desorption isotherms. Separate kinetic experiments indicated that adsorption and desorption equilibrium was reached in 2 and 12 h, respectively (data not shown here). The experiments were performed in duplicate to assure data quality.

2.2.2. EXAFS measurements and analysis

EXAFS data were collected at the BL-12C XAFS experimental station of the Photon Factory (PF) of the KEK in Japan. The storage ring was operated at 2.5 GeV with a beam current of 300 mA. A fixed-exit double-crystal monochromator (Si(111)) and a focusing bent cylindrical mirror were installed. A double mirror was installed to reduce the higher order reflections. The incident and output beam intensities were recorded using ionization chambers filled with nitrogen gas and a 15% argon-doped nitrogen mixture, respectively. All adsorption samples were recorded using a 19-element SSD at the *K*-edge of Zn in the fluorescence mode. The reference compounds of ZnO(s) powders and Zn²⁺(aq) solutions were recorded in the transmission mode. Energy calibration was conducted with a Zn metal foil.

The EXAFS fitting was performed using the program WinXAS3.1 following the standard procedures [34]. A linear function for the preedge region and a second-order polynomial in the postedge region were used for normalization. The $\chi(k)$ functions were extracted using a cubic spline and were Fourier-transformed with k^3 weighting over the approximate k range 2.2–10.8 Å^{−1}. This procedure resulted in radial distribution functions (RDFs) which displayed a set of structural peaks at distances from the central Zn atom. Then the first and second peaks were selected, respectively, using a Hanning window, and then Fourier-backtransformed and processed with window widths of 0.8–2.1 and 2.35–3.75 Å for the two peaks, respectively. Amplitude and phase-shift functions were calculated with FEFF8.0 [35]. The amplitude reduction factor (S_0^2) was fixed at 0.87 for data fitting. The crystallographic structures of ZnO [36] were used as the input structures to obtain the Zn–O and Zn–Zn pair correlation functions, and the structure of Zn₂TiO₄, which is similar to anatase [37], was used for obtaining the Zn–Ti functions. EXAFS fittings were carried out by systematically refining the bond lengths, R , Debye–Waller factors, σ^2 , and inner potential corrections, ΔE_0 , for the models considered. The edge shifts (E_0) for all shells were constrained to be equal. R_f is a measure of the agreement between experimental and theoretical EXAFS curves. $R_f < 20\%$ indicates a very good fit whereas $R_f \leq 40\%$ is acceptable [23].

Fig. 1. Adsorption and desorption isotherms of Zn(II) on TiO₂ at various temperatures. Symbols, experimental data; solid lines, model-fitted adsorption isotherms; dashed lines, model-fitted desorption isotherms. S₅, S₂₀, and S₄₀ indicate where desorption was initiated and samples selected for subsequent EXAFS analyses. Data given as mean of duplicates and errors refer to the difference between the duplicated samples.

3. Results and discussion

3.1. Adsorption–desorption isotherms and hysteresis

Fig. 1 shows the adsorption and desorption isotherms of Zn(II) on TiO₂ at three fixed temperatures. The adsorption and desorption isotherm data were fitted with the Freundlich model,

$$q_{\text{eq}} = K_F C_{\text{eq}}^n, \quad (1)$$

where C_{eq} is the equilibrium concentration of Zn(II) in solution (mmol L^{−1}), q_{eq} is the equilibrium adsorption density of Zn(II) (mmol g^{−1}), K_F is the Freundlich capacity coefficient, and n the Freundlich exponent. Equation (1) can be conveniently linearized by taking the logarithm on both sides, leading to

$$\log q_{\text{eq}} = n \log C_{\text{eq}} + \log K_F. \quad (2)$$

Thus, K_F and n for each adsorption and desorption isotherm were then determined by fitting Eq. (2) to the respective isotherm data. Table 1 summarizes the model-fitted adsorption and desorption parameters.

The results indicate that the equilibrium adsorption density of Zn(II) increased substantially with increasing temperature. When the temperature was increased from 5 to 20 and 40 °C, the Freundlich capacity coefficient was increased by a factor of 1.7 and 2.3, respectively. On the other hand, the desorption isotherms significantly deviate from the corresponding adsorption isotherms, indicating that adsorption of Zn(II) onto TiO₂ was not fully reversible. The thermodynamic index of irreversibility (TII) proposed by Sander et al. [38] was used to quantify the adsorption irreversibility. The TII was defined as the ratio of the observed free energy loss to the maximum possible free energy loss due to sorption hysteresis, which was given by

$$\text{TII} = \frac{\ln C_{\text{eq}}^{\text{A}} - \ln C_{\text{eq}}^{\text{D}}}{\ln C_{\text{eq}}^{\text{S}} - \ln C_{\text{eq}}^{\text{D}}}, \quad (3)$$

Table 1
Freundlich isotherm parameters for Zn(II) adsorption and desorption and calculated values of thermodynamic index of irreversibility (TII) of Zn(II) on TiO₂ at various temperatures

T (°C)	Adsorption				Desorption				TII
	R ²	log K _F	K _F	n	R ²	log K _F	K _F	n	
5	0.99	−0.285 ± 0.08	0.52	0.65 ± 0.04	0.99	−0.87 ± 0.08	0.14	0.16 ± 0.06	0.63
20	0.99	−0.013 ± 0.05	0.97	0.60 ± 0.03	0.95	−0.32 ± 0.04	0.48	0.34 ± 0.11	0.34
40	0.99	0.073 ± 0.04	1.18	0.59 ± 0.02	0.94	−0.12 ± 0.07	0.76	0.41 ± 0.06	0.20

Fig. 2. (a) Plots of $\ln(q_{eq}/C_{eq})$ vs q_{eq} for determination of the equilibrium adsorption constant (K), and (b) Van't Hoff plot for the adsorption of Zn(II) on TiO₂ at 5, 20, and 40 °C.

where C_{eq}^S is the solution concentration of the adsorption state S (C_{eq}^S, q_{eq}^S) from which desorption is initiated; C_{eq}^D is the solution concentration of the desorption state D (C_{eq}^D, q_{eq}^D); C_{eq}^γ is the solution concentration of hypothetical reversible desorption state γ ($C_{eq}^\gamma, q_{eq}^\gamma$). C_{eq}^S and C_{eq}^D are determined based on the experimental adsorption and desorption isotherms, and are easily obtained from the adsorption branch where the solid-phase concentration is equal to q_{eq}^D .

Based on the definition, the TII value lies in the range of 0 to 1, with 1 indicating the maximum irreversibility. The TII value (Table 1) decreased by a factor of >3 when the temperature increased from 5 to 40 °C. Evidently, the adsorption of Zn(II) on the TiO₂ surface becomes much more reversible with increasing temperature.

3.2. Adsorption thermodynamics

Equilibrium adsorption constant (K) was obtained following a method used by Khan and Singh [39]. First, the adsorption isotherm data were plotted as $\ln(q_{eq}/C_{eq})$ versus q_{eq} and extrapolated to zero q_{eq} . Then, a linear regression was performed on the experimental data based on least-squares analyses, and the intercept on the y-axis gives the value of $\ln K$ (Fig. 2a and Table 2). Based on the $\ln K$ values for the three temperatures, the standard free energy changes (ΔG^0) for the reaction were then calculated from the relationship

$$\Delta G^0 = -RT \times \ln K, \quad (4)$$

where R is the universal gas constant (8.314 J mol^{−1} K^{−1}) and T is the temperature in Kelvin.

The resultant ΔG^0 values are given in Table 2. The increased negative values of ΔG^0 with increasing temperature indicate that the adsorption reactions are thermodynamically more favorable at higher temperatures.

The corresponding enthalpy change (ΔH^0) and entropy change (ΔS^0) can be obtained from the slope and intercept from the Van't Hoff plot (Fig. 2b) [40] according to the equation:

$$\ln K = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}. \quad (5)$$

The observed positive enthalpy change ($\Delta H^0 = 24.55$ kJ mol^{−1}) confirms that the adsorption process was endothermic. Furthermore, the observed enthalpy change was greater than that for typical ion-exchange reactions (typically less than 8.4 kJ mol^{−1}) [41], suggesting that specific interactions other than outer-sphere electrostatic interactions are operative in the Zn(II)–TiO₂ adsorption system.

The much greater and positive ΔS^0 value (159.13 J mol^{−1} K^{−1}) indicates that the adsorption is driven by entropy changes. This implies that structural changes in zinc ions and TiO₂ units occur during the adsorption process. At the prevailing solution pH of 6.3, Zn(II) is present in the form of octahedral hydrated Zn(II) ions ($Zn(H_2O)_6^{2+}$) [42]. As a result of adsorption the number of the water molecules surrounding Zn decreased and thus the degree of the freedom of the water molecules increased [43].

3.3. The microscopic structure of adsorbed Zn(II)

The three samples corresponding to S₅, S₂₀, and S₄₀ in Fig. 1 were selected for EXAFS measurements. Note that the equilibrium Zn(II) concentration in the solution phase was about the

Table 2
Thermodynamic parameters for adsorption of Zn(II) onto TiO₂ at various temperatures

<i>T</i> (°C)	<i>R</i> ²	ln <i>K</i>	Δ <i>G</i> ⁰ (kJ mol ^{−1})	Δ <i>S</i> ⁰ (J mol ^{−1} K ^{−1})	Δ <i>H</i> ⁰ (kJ mol ^{−1})
5	0.96	8.47 ± 0.13	−19.58 ± 0.30	159.13 ± 0.53	24.55 ± 2.91
20	0.99	9.14 ± 0.04	−22.28 ± 0.10		
40	0.98	9.66 ± 0.08	−25.14 ± 0.21

Fig. 3. (a) Normalized, background-subtracted k^3 -weighted EXAFS spectrum and (b) the corresponding Fourier transform spectrum of Zn(II) *K*-edge EXAFS of reference samples and adsorption samples (—, EXAFS data; ---, model fittings).

same (~ 0.090 – 0.092 mmol L^{−1}) for the three samples; however, the adsorption density increased from 0.093 to 0.213, and 0.290 mmol g^{−1} as temperature increased from 5 to 20 and 40 °C, respectively.

Fig. 3 compares the normalized, k^3 -weighted EXAFS spectra (a) and corresponding Fourier transforms (b) of the references of Zn²⁺(aq) and ZnO(s). The lack of higher coordination spheres in the Zn²⁺(aq) spectrum indicates the absence of a Zn–Zn interaction for the reference Zn²⁺(aq) sample. In contrast, the second neighboring peak of higher magnitude indicates a strong Zn–Zn interaction for ZnO(s).

The spectra of the three adsorption samples at the three temperature levels appear comparable (Fig. 3b), but differ from either of the references, Zn²⁺(aq) or ZnO(s). For all adsorption samples, the first peak at about 1.6 Å dominated the Fourier transforms, which corresponded to the contribution of the Zn–O

Fig. 4. EXAFS data (—) and model-fitted results (---) for the Zn–O sphere (a) and Zn–Ti sphere (b).

Table 3
EXAFS results of the Zn–O sphere analysis for the reference samples and the adsorption samples

Samples	Zn–O sphere			
	<i>R</i> (Å)	<i>N</i>	σ ² (Å ²)	<i>R</i> _f
Zn ²⁺ (aq)	2.07	6.3	0.009	8.73
ZnO(s)	1.95	4.0	0.002	9.96
S ₅	1.99	4.3	0.007	11.31
S ₂₀	1.99	4.4	0.008	10.63
S ₄₀	1.98	4.5	0.008	10.14

Note. *N*, coordination numbers; *R*, atomic distance; σ, Debye–Waller factor; *R*_f, a measure of the agreement between experimental and theoretical EXAFS curves. Typical window width for the backtransform step was 0.80–2.10 Å.

coordination sphere, and there was no significant difference in the first peak for the three samples. Further, a broader peak extending from 2.1 to 3.7 Å, which reflects the second coordination sphere, was also observed for all the three samples. For all the adsorption samples and references, the first peak was

Table 4
EXAFS results of the Zn–Ti sphere analysis for the adsorption samples

Samples	First Zn–Ti shell		Second Zn–Ti shell		σ^2 ($\text{\AA}^2$)	R_f	N_1/N_2
	R_1 ($\text{\AA}$)	N_1	R_2 ($\text{\AA}$)	N_2			
S ₅	3.26	1.1	3.70	1.6	0.008	31.46	0.69
S ₂₀	3.24	1.1	3.68	1.8		30.10	0.61
S ₄₀	3.25	1.2	3.69	2.2		29.09	0.54

Note. Typical window width for this backtransform step was 2.35–3.75 $\text{\AA}$.

well fitted with the one-shell model (Fig. 4a). The fluctuation trend of three samples was comparable to the reference ZnO, but shifted to the higher κ ($\text{\AA}^{-1}$) than that of $\text{Zn}^{2+}(\text{aq})$. This result indicates that the three adsorption samples have similar coordination structures with the reference ZnO. A two-shell fit was used to fit the second peak for all the adsorption samples (Fig. 4b), which resulted in smaller errors than a single-shell fit. Tables 3 and 4 summarize the results of the quantitative analysis for the first and second spheres of samples S₅, S₂₀, and S₄₀.

Table 3 shows that for the reference $\text{Zn}^{2+}(\text{aq})$ the average Zn–O bond length was 2.07 $\text{\AA}$ and the coordination number was 6.3, compared to 1.95 $\text{\AA}$ and 4.0, respectively, for ZnO(s). Therefore, $\text{Zn}^{2+}(\text{aq})$ is sixfold coordinated with oxygen, whereas ZnO(s) is fourfold coordinated, which agrees with previous work [25,26,44]. It has been reported that the most common coordination geometries of hydrous Zn(II) are octahedron (i.e., $\text{Zn}(\text{H}_2\text{O})_6^{2+}$) with a Zn–O bond length of 2.07–2.18 $\text{\AA}$ and tetrahedron (i.e., $\text{ZnO}(\text{s})$, $\text{Zn}(\text{OH})_4^{2-}$) with a Zn–O bond length of 1.92–1.99 $\text{\AA}$ [45]. Zhu and Pan [46] reported that in acidic solutions ($\text{pH} \leq 6.9$) $\text{Zn}^{2+}(\text{aq})$ is present in the form of octahedron with an average Zn–O bond length of 2.08 $\text{\AA}$. As shown in Table 3, the average Zn–O bond length of the three samples is 1.98 ± 0.01 $\text{\AA}$, and the average coordination number is 4.3 ± 0.02 . Therefore, Zn(II) is adsorbed on the TiO₂ surface in the mode of tetrahedral coordination at pH 6.3. The sixfold coordination ($\text{Zn}(\text{H}_2\text{O})_6^{2+}$) to fourfold coordination change should also be favored entropically because release of H₂O from cation coordination results in positive ΔS value [47].

Edge-sharing linkage and corner-sharing linkage are the two most common modes of binding between the polyhedron of hydrated metal ions and the octahedral of metal oxides [25,26,48]. Typically, the interatomic distance of edge-sharing linkage is shorter than that of corner-sharing linkage [49]. The EXAFS analysis results (Table 4) show that there are two detectable linkage modes between the adsorbed Zn(II) ions and the neighboring atom Ti, corresponding to two average Zn–Ti bond lengths of 3.24 ± 0.01 $\text{\AA}$ ($n = 3$) and 3.69 ± 0.01 $\text{\AA}$ ($n = 3$), respectively. The shorter linkage corresponds to an edge-sharing linkage between the ZnO₄ tetrahedron and the TiO₆ octahedron, whereas the longer linkage reflects the corner-sharing mode.

3.4. Effect of linkage mode on adsorption irreversibility

Generally, edge-sharing adsorption is energetically more favorable than corner-sharing adsorption [20]. Consequently, the edge-sharing adsorption mode is more difficult to be desorbed than that of corner-sharing mode. Our previous work revealed

that adsorption of Zn(II) onto γ -MnOOH was dominated by edge-sharing linkage, and thus, the adsorption was rather irreversible due to the formation of surface complexes on the high-energy edge sites [25]. In contrast, Zn(II) adsorption onto δ -MnO₂ was dominated by corner-sharing linkage, and the adsorption was highly reversible [26]. The adsorption of Zn on TiO₂ was involved in both edge-sharing and corner-sharing linkage, and thus, the adsorption irreversibility falls between the two extreme cases.

The EXAFS results in Table 4 indicate that the number of stronger adsorption (i.e., edge-sharing) sites (N_1) remained relatively stable, while the number of weaker adsorption (i.e., corner-sharing) sites increased as the adsorption temperature increased from 5 to 40 °C. As a result, the ratio of N_1/N_2 dropped from 0.69 to 0.54. This observation revealed that the decreased irreversibility at higher temperatures was attributed to the increase in N_2 , or the decrease in N_1/N_2 . On the other hand, the increase in N_2 results in a net gain in overall sorption capacity, which accounts for the observed increase in Zn(II) sorption capacity at higher temperatures (Fig. 1). From a practical standpoint, this result indicates that in a given environmental compartment (soil or water bodies), the mobility and bioavailability of zinc and likely other similar heavy metals may be greater at elevated temperatures.

4. Summary and conclusions

Adsorption–desorption equilibrium experiments and EXAFS measurements were carried out to assess the relationship between temperature and adsorption irreversibility of Zn(II) on TiO₂. At pH 6.3, the hydrous Zn(II) was adsorbed on TiO₂ surface by sharing the oxygen atoms in the TiO₆ unit on the solid surface, with an average Zn–O distance of 1.98 ± 0.01 $\text{\AA}$. Two distinct Zn–Ti distances, 3.25 ± 0.01 and 3.69 ± 0.01 $\text{\AA}$, were measured, which correspond to two different linkage modes: corner-sharing linkage and edge-sharing linkage, respectively. The edge-sharing linkage offered a greater Zn(II) affinity than the corner-sharing linkage. The coordination structures and adsorption modes of Zn(II) ions are strongly temperature dependent. At lower temperatures (e.g., 5 °C), Zn(II) ions are adsorbed primarily in the form of edge-sharing, which is less reversible. At elevated temperatures (e.g., 40 °C), corner-sharing becomes the more prevailing adsorption mode, and the adsorption becomes more reversible. EXAFS results revealed that a rise in temperature results in a net gain in the number of weak binding sites, which in turn leads to an increase in Zn(II) sorption capacity and reversibility. This result implicates that in a given environmental system (e.g., soils or natural waters) zinc and other similar heavy metals are likely more mobile at elevated temperatures.

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