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Adsorption and Oxidation of Thallium(I) by a Nanosized Manganese Dioxide

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Abstract The adsorption and oxidation of thallium(I) by nanosized manganese dioxide ($nMnO_2$) may have an impact on the removal of Tl from waters in engineered applications, as well as the fate and transport of Tl in natural waters. The fundamental data on the adsorption and oxidation of Tl(I) by $nMnO_2$ were obtained here. The results show that Tl was adsorbed by $nMnO_2$ within 15 min at pH 7.0. Moreover, Langmuir fitting indicated a maximum adsorption capacity of ~58.48 mg/mmol (i.e., ~672 $mgTl/gMnO_2$). The presence of Ca^{2+}, Mg^{2+}, SiO_3^{2-}, PO_4^{3-}, and CO_3^{2-}decreased the removal of Tl(I) to a certain extent; however, it was increased by a pH from 4.0 to 9.0. The oxidation of Tl(I) was proposed at pH 4.0 based on the observation of Mn release and $nMnO_2$ aggregation, while the oxidation of Tl(I) might not be favored at neutral and basic conditions. The presence of 3 mg/L humic acid hindered the adsorption of Tl(I) on $nMnO_2$. These results indicate that $nMnO_2$ could help to remove Tl from water in engineered applications and might deepen our understanding of the transport of Tl in natural waters.

Keywords Thallium · Nanosized manganese dioxide · Adsorption · Oxidation

1 Introduction

The presence of heavy metals in the aquatic environment attracts great attention from both environmental scientists and engineers due to their toxicity and accumulation in organisms. Toxicity studies have revealed that thallium is more toxic than many heavy metals including Hg, Cu, Zn, Pb, and Cd (Zitko 1975). Tl is an environmentally widespread element and can be found in natural environments including continental and oceanic crusts, rivers, oceans, and lake and marine (Baker et al. 2009; Lin and Nriagu 1999; Nielsen et al. 2009; Rehkämper et al. 2004; Rehkämper and Nielsen 2004). For example, Tl concentrations range from 0.08 to 5 ppm in marine and 2.1 to 23.1 ppm in lake sediments (Mathis and Kevern 1975; Matthews and Riley 1970). Discovered by William Crookes in 1861, Tl has traditionally been used as a medical agent and rodenticide, before more recently being incorporated into high-technology industries such as alloys, gamma radiation detection devices, low-temperature thermometers, and high-temperature superconductors (Cvjetko et al. 2010; Galvan-Arzate and Santamaria 1998). The environmental release of Tl from various industrial uses is inevitable, including ore processing, metal mining, and

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smelting (Pua et al. 2013). In fact, water pollution by Tl is really happening in some cases (Law and Turner 2011; Xiao et al. 2012). To date, little study reported the removal of Tl in engineered applications. Although adsorption has been recognized as an effective way to remove Tl from the water matrix, there has been little research into its application. Of the adsorbents reported, polyacrylamide had a maximum adsorption capacity of ~377.4 mg/g (Senol and Ulusoy 2010), sawdust investigated as a green and economic adsorbent, with a max adsorption capacity of 13.18 mg/g (Memon et al. 2008), and multi-walled carbon nanotubes (MWCNTs) about a max adsorption capacity of 0.4–0.6 mg/g (Pua et al. 2013). Nevertheless, compared with other toxic heavy metals, very limited attention has been paid to Tl in engineered aquatic systems and natural aquatic waters.

The occurrence of nanosized manganese dioxide ($nMnO_2$) in both engineered and natural waters has been widely reported (Ferreira et al. 1997; Herszage et al. 2003; Lienemann et al. 1997). In natural systems, $nMnO_2$ is a common product of processes such as biological catalysis of dissolved manganese(II) and weathering of minerals (Buffle and Leppard 1995; Wigginton et al. 2007). Additionally, Mn oxides are stronger oxidants in natural systems compared with other minerals (Stone and Morgan 1984). Thus, the oxidation and adsorption of Tl by $nMnO_2$ might influence its fate and toxicity in the environment. Although the adsorption and oxidation of Tl by organisms and minerals under environmental conditions have been reported (Liu et al. 2011; Peacock and Moon 2012; Twining et al. 2003), the analogous effects from $nMnO_2$ have not been explored. More importantly, in engineered waters, $nMnO_2$ is commonly formed during processes including permanganate (Mn(VII)) reduction and dissolved manganese(II) oxidation (Ma and Graham 1996). In addition, adsorption is an effective way to remove the trace heavy metals from aqueous solutions in engineered application (Johnson 1990; Posselt et al. 1968). Manganese oxides have been proposed as strong, economical, and easily available adsorbent with higher adsorption capacity and selectivity than many other adsorbents (Qin et al. 2011; Tripathy et al. 2006). Thus, $nMnO_2$, a manganese oxide with a high specific surface area, should intuitively perform well as a potential material for the removal of heavy metal such as Tl (Hua et al. 2012). However, the veracity of this hypothesis is yet to be confirmed.

In the study described herein, the influence of contact time, initial Tl(I) concentration, presence of competing cations (Na^+, Ca^{2+}, and Mg^{2+}) and anions (SiO_3^{2-}, PO_4^{3-}, CO_3^{2-}) on the adsorption of Tl(I) by $nMnO_2$ were investigated. Subsequently, the adsorption of Tl(I) by $nMnO_2$ was studied at different pH conditions (i.e., pH 4.0, 7.0, and 9.0). Moreover, Tl(I) oxidation was also verified by the determination of Mn dissolution and the aggregation of $nMnO_2$. Finally, the adsorption and oxidation of Tl(I) by $nMnO_2$ were also studied in the presence of 3 mg/L humic acid (HA).

2 Materials and Methods

2.1 Materials

All solutions used in this study were prepared with double distilled water (>18.2 MΩ cm). $TlNO_3$ (99 %), acetic acid 3-(*N*-morpholino)-propanesulfonic acid (MOPS, p*Ka*=7.2), and HA were purchased from Sigma-Aldrich Company. $KMnO_4$, $Na_2S_2O_3$, NaOH, HNO_3, $NaNO_3$, $Mg(NO_3)_2$, $Ca(NO_3)_2$, and sodium borate ($Na_2B_4O_7 \cdot 10H_2O$) were obtained from Sinopharm Chemical Reagent Co., Ltd. These chemicals except HA were used as received.

The HA stocks were prepared following the procedure described by our previous work (Huangfu et al. 2013; Jiang et al. 2009). Briefly, HA stocks were purified by repeated centrifugation (4,000 rpm), pH adjustment, and precipitation to remove ash and humin. A separatory funnel was then used to separate HA from fulvic acid by precipitating for 48 h at about pH 3. The purified HA was characterized by UV-vis, FTIR, and 1H NMR spectroscopy and acid-base titration, and the results can be found in our previous work (Ma et al. 2007). High-temperature oxidation method (model Multi3100, Jena, Germany) was employed to measure the concentration of total organic carbon (TOC) of HA. The stocks were stored in the dark at 4 °C and used within a month.

2.2 Synthesis and Characterization of $nMnO_2$

The same method used in our previous study was used to synthesize $nMnO_2$ (Huangfu et al. 2013). The dark brown $nMnO_2$ stock suspensions were stored in the dark at 4 °C and used within 2 weeks. Their critical characteristics including average Mn oxidation state, size, and surface charge were determined. The iodimetric method was used to measure the average Mn oxidation state. Dynamic light scattering conducted on a Malvern instrument (Nano ZS90, Malvern, UK) was employed to obtain the size and surface charge of $nMnO_2$. The results showed that the average Mn oxidation state in $nMnO_2$ was about 4.0 and the average diameter was about 55.86 nm. The absolute zeta potential of these colloids was about −41.96 mV, and these colloids exhibited negative charge in a wide range of pH (i.e., pH 2–12) (Huangfu et al. 2013).

2.3 Batch Adsorption Experiments

Batch adsorption experiments were conducted through traditional bottle-point method employing polyethylene flasks. An aliquot of $nMnO_2$ suspension was added into polyethylene flasks containing predetermined amount of Tl(I), cations, or HA. Then the mixtures were stirred by a magnetic stirring apparatus at 25 °C. The pH was buffered at 4.0±0.1 by 2 mM acetate, 7.0±0.1 by 2 mM MOPS, or 9.0±0.1 by 1 mM sodium borate. After 2 h, samples were taken out and $nMnO_2$ was separated by centrifuging for 10 min at 4,000 rpm using Amicon centrifugal ultrafilters (Amicon Ultra-15 10K, Millipore, MA) containing porous cellulose membranes with a nominal pore size of 5~10 nm. At the same time, the size of $nMnO_2$ was measured using a Malvern instrument described later. For the kinetic experiments, the samples were taken at various time intervals. All polyethylene flasks were washed with concentrated nitric acid and deionized water. Each flask was used only once.

The hydrodynamic diameter of $nMnO_2$ in adsorption experiments was determined by using a Malvern instrument (Nano ZS90, Malvern, UK). Aliquots of the suspension were added into the dynamic light scattering (DLS) cuvette, and the measurements were immediately started. All DLS measurements were carried out at a scattering angle of 90, and each autocorrelation function was accumulated for 60 s. The concentration of Tl and Mn in the filtrates obtained from the centrifugal ultrafiltration of batch adsorption experiments was measured by an inductively coupled plasma mass spectrometer (NexION 300Q, PerkinElmer, USA) after 2 % HNO_3 (MOS grade) was added.

The adsorbed amount of $nMnO_2$ was calculated by the difference of the initial and final concentrations using the following equation:

$$Q_t = \frac{C_0 - C_t}{C_{nMnO_2}} \tag{1}$$

where C_0(mg/L) is the initial concentration of Tl, C_t(mg/L) is the concentration of Tl in solution at time t, and C_{nMnO2}(mmol/L) is the concentration of $nMnO_2$ added in the adsorption experiments (0.05 mmol/L).

3 Results and Discussion

3.1 The Effects of Contact Time, Initial Tl(I) Concentration, and Competing Cations

The effects of contact time were conducted in a system containing 3.5 mg/L of Tl(I) at pH 7.0 (Fig. 1). Under these conditions, the removal of Tl(I) by $nMnO_2$ was a fast process with an equilibrium adsorption attained within 15 min. Figure 1 also shows that the maximum adsorbed amount of $nMnO_2$ was ~32 mg/mmol (42.9 % removal). This quick adsorption onto the surface of manganese oxide has also been reported for various inorganic substituents, such as Pb, Ni, and Cd (Qin et al. 2011; Tripathy et al. 2006; Yao and Millero 1996). Similarly, data detailing the kinetics of Tl(I) adsorption onto sawdust, obtained by Memon et al., revealed that a maximum removal was achieved within 7 min (Memon et al. 2008). Additionally, a quick adsorption rate was also observed for MWCNTs (Pua et al. 2013).

The effect of Tl(I) concentration on uptake by $nMnO_2$ was also assessed in various systems at pH 7.0 (Fig. 2). The adsorbed amount of $nMnO_2$ increased with the increase of equilibrium Tl(I) concentration. The

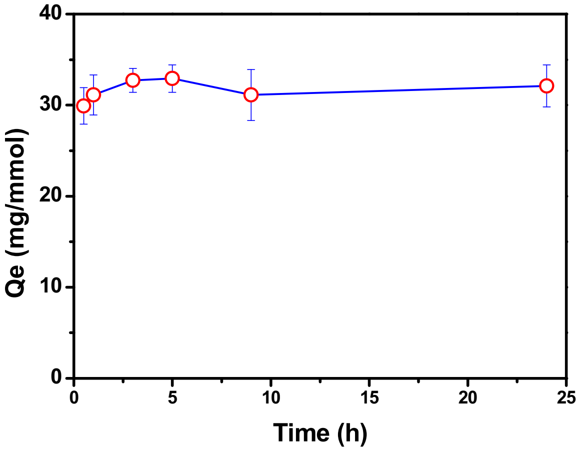

Fig. 1 The residual Tl in aqueous solution as a function of contact time. The adsorption experiments were conducted at 25 °C, pH=7.0. Initial dosage of $nMnO_2$, 0.05 mM

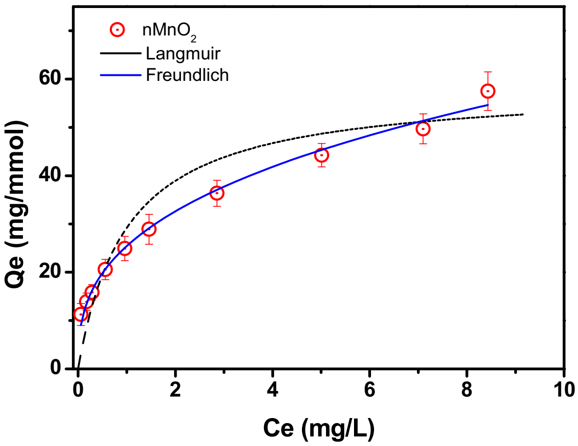

Fig. 2 Experimentally obtained Tl sorption onto nMnO$_2$ and its compatibility to Langmuir and Freundlich models. The adsorption experiments were conducted at 25 °C, pH=7.0. Initial dosage of nMnO$_2$, 0.05 mM

resulting adsorption isotherms were evaluated with reference to their compatibility to the Langmuir (Eq. 2) and Freundlich models (Eq. 3):

$$Q_e = \frac{K_L Q_m C_e}{1 + K_L C_e} \tag{2}$$

$$Q_e = K_F {C_e}^n \tag{3}$$

where Q_e (mg/mmol) is the adsorbed amount of Tl(I) ions; C_e (mg/L) is the equilibrium concentration of Tl(I) ions in aqueous matrix; Q_m (mg/mmol) is the estimated maximum adsorption capacity; K_L (L/mg) is the Langmuir adsorption equilibrium constant; K_F is Freundlich constant related to adsorption capacity; n is Freundlich constant (surface heterogeneity) related to adsorption intensity. The fitting parameters (Table 1) showed that the maximum adsorption capacity was 58.48 mg/mmol (i.e., ~672 mg(Tl)/g(MnO$_2$)), indicating that nMnO$_2$ could adsorb large amounts of Tl(I). A comparison with the Tl(I) removal capacity of various previously used adsorbents was shown in Table 2. Though direct comparison of maximum adsorption capacities of nMnO$_2$ with those of other adsorbents is difficult because of different experimental conditions applied, it is clear that nMnO$_2$ is the most effective absorbent. While both models fit the experimental data well (Fig. 2), the Freundlich fit was better, agreeing with a similar study performed with zeolites (Senol and Ulusoy 2010).

Table 1 Langmuir and Freundlich parameters for Tl(I) adsorption onto nMnO$_2$

Langmuir			Freundlich		
Q_m (mg/mmol)	K_L(L/mg)	R^2	K_F	n	R^2
58.48	1	0.9678	25.44	0.36	0.9912

Table 2 Comparison of the maximum Tl(I) adsorption capacity on various adsorbents

Adsorbent	pH	Q_m (mg/g)	Reference
Sawdust (untreated)	7.0	2.71	(Memon et al. 2008)
Sawdust (caustic treated)	7.0	13.18	(Memon et al. 2008)
PAAm–Z	~5	377.4	(Senol and Ulusoy 2010)
PAAm–B	~5	73.44	(Senol and Ulusoy 2010)
MWCNTs	~9.5	0.417	(Pua et al. 2013)
H_2SO_4-MWCNTs	~9.5	0.426	(Pua et al. 2013)
$Na_2S_2O_8$-MWCNTs	~9.5	0.658	(Pua et al. 2013)
nMnO$_2$	7.0	672	This study

The influence of three common cations in the water matrix (Na$^+$, Ca^{2+}, and Mg^{2+}) on Tl adsorption were also investigated at pH 7.0 (Fig. 3). In the presence of the monovalent Na$^+$ (i.e., NaNO$_3$), the change in Tl(I) adsorption capacity by nMnO$_2$ was negligible even at the largest concentration tested (10 mM), 200 times higher than the Tl present (~0.049 mM). This suggests good selectivity for Tl(I) from a water matrix containing Na$^+$. In the presence of the divalent cations, Ca^{2+} and

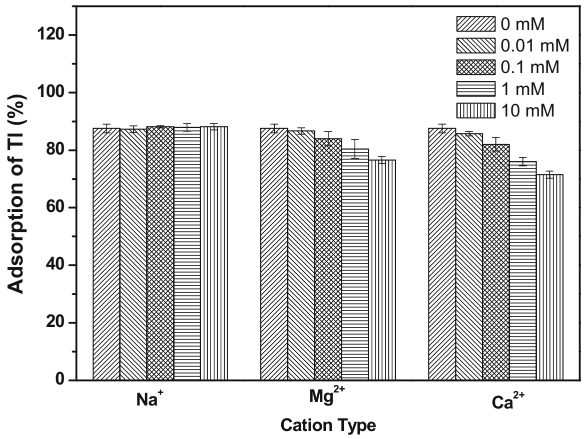

Fig. 3 The influence of cation ions on the adsorption of Tl(I) by nMnO$_2$. The adsorption experiments were conducted at 25 °C, pH=7.0. Initial dosage of nMnO$_2$, 0.24 mM. Initial Tl(I), 10 mg/L

Mg^{2+} (i.e., $Ca(NO_3)_2$ and $Mg(NO_3)_2$), decreasing amounts of adsorbed Tl by $nMnO_2$ were observed with increasing cation concentrations (Fig. 3). Ca^{2+} was more effective than Mg^{2+} in reducing the uptake of Tl at equivalent concentrations. Competing adsorption (Memon et al. 2008) or a reduction in $nMnO_2$ surface area due to aggregation might be responsible for the observed decrease of Tl uptake. A previous study has shown that the aggregation of $nMnO_2$ was most prevalent in the presence of Ca^{2+}, followed by Mg^{2+} and Na^+ (Huangfu et al. 2013), matching the disrupting power of Tl adsorption.

To obtain the influence of anions on the Tl adsorption, SiO_3^{2-}, PO_4^{3-}, and CO_3^{2-} were selected. As can be seen in Table 3, the existence of anions decreased the Tl adsorption by $nMnO_2$. When the concentration of SiO_3^{2-} increased from 0.01 to 10 mM, the Tl(I) removal rate decreased from 73 to 50 %. Similarly, the removal rate reduced from 73 to 53 % and from 73 to 45 % in the presence of PO_4^{3-} and CO_3^{2-}, respectively.

3.2 The Influences of pH on the Adsorption and Oxidation of Tl(I)

Ambient pH is a critical condition for the removal of Tl from a water matrix. To observe the influence of pH, the adsorption of Tl(I) by $nMnO_2$ was investigated under various pH conditions (pH 4.0, 7.0, and 9.0) (Fig. 4a). Generally, at low initial Tl(I) concentration, i.e., 0.5 mg/L, all the added Tl was adsorbed on $nMnO_2$ and therefore the same adsorption capacity was obtained at all pHs. As the initial Tl(I) increased, the total amount of the Tl adsorbed also increased until the maximum adsorption was reached at all pHs tested. More importantly, the uptake of Tl(I) increased with the increase of pH (Fig. 4a). Interestingly, an increase of dissolved Mn was also observed at pH 4.0 with the increase of initial Tl(I) concentrations (Fig. 4b), a phenomenon which was not observed at neutral and basic conditions.

Table 3 The influence of anions on the Tl(I) adsorption by $nMnO_2$ (removal efficiency,)

Anion type	0[a] (%)	0.01[a] (%)	0.1[a] (%)	1[a] (%)	10[a] (%)
SiO_3^{2-}	74	73	70	65	50
CO_3^{2-}	74	73	71	67	53
PO_4^{3-}	74	73	68	62	45

[a] Concentration of anions

It is widely known that the redox reactions between heavy metals and manganese oxides at different pH conditions play a critical role in the adsorption of these components and the passivation of manganese oxides themselves (Lockwood and Chen 1973; Murray 1974b). Thus, these redox reactions might be responsible for the discrepancy of Tl uptake by $nMnO_2$ under different pH conditions. The coupled redox reaction for the reductive dissolution of MnO_2 and oxidation of aqueous Tl(I) is recognized as (Lin and Nriagu 1998)

$$MnO_2(s) + 4H^+(aq) + 2e^- \Leftrightarrow Mn^{2+}(aq) + 2H_2O \quad \log K = 43.4 \tag{4}$$

$$Tl^+(aq) \Leftrightarrow Tl^{3+}(aq) + 2e^- \quad \log K = -42.3 \tag{5}$$

$$MnO_2(s) + Tl^+(aq) + 4H^+(aq) \Leftrightarrow Tl^{3+}(aq) + Mn^{2+}(aq) + 2H_2O \quad \log K = 1.1 \tag{6}$$

The reaction is thermodynamically unfavorable at standard states. Previous investigations, reporting evidence of Tl(I) oxidation on the hexagonal birnessite surface by X-ray adsorption spectroscopy (XAS) analysis (Peacock and Moon 2012), argued that the surface complex oxidation might promote this oxidation. In the present study, the fact that little dissolved Mn was detected might confirm that the oxidation of Tl(I) was negligible during the adsorption of Tl by $nMnO_2$ at pH 7.0 and 9.0, indicating that the oxidation is a slower process compared to adsorption. Additionally, Eq. 6 also shows that decreasing pH favors redox reactions. Experimentally, compared with pH 7.0 and 9.0, the obvious release of Mn (i.e., Mn(II)) to bulk at pH 4.0 might demonstrate that the redox reactions between Tl(I) and $nMnO_2$ were occurring. Correspondingly, the increase of initial Tl(I) should result in increased Mn leaching due to more MnO_2 being reduced to Mn(II) (Fig. 4b). Additionally, many heavy metals including As(III), U(VI), and Cr(III) can be oxidized by manganese oxides under acidic conditions (Lafferty et al. 2010; Landrot et al. 2012; Wang et al. 2013).

Figure 4a also showed that the adsorption amount of Tl by $nMnO_2$ was higher at pH 9.0, compared to pH 7.0. The larger amount of Tl adsorption by $nMnO_2$ might be mainly attributed to two aspects: (i) the surface properties of $nMnO_2$ and (ii) Tl speciation. Tl speciation of Tl(I) and Tl(III) as functions of pH is presented in Fig. 5a, b, respectively. The hydrolysis constant was

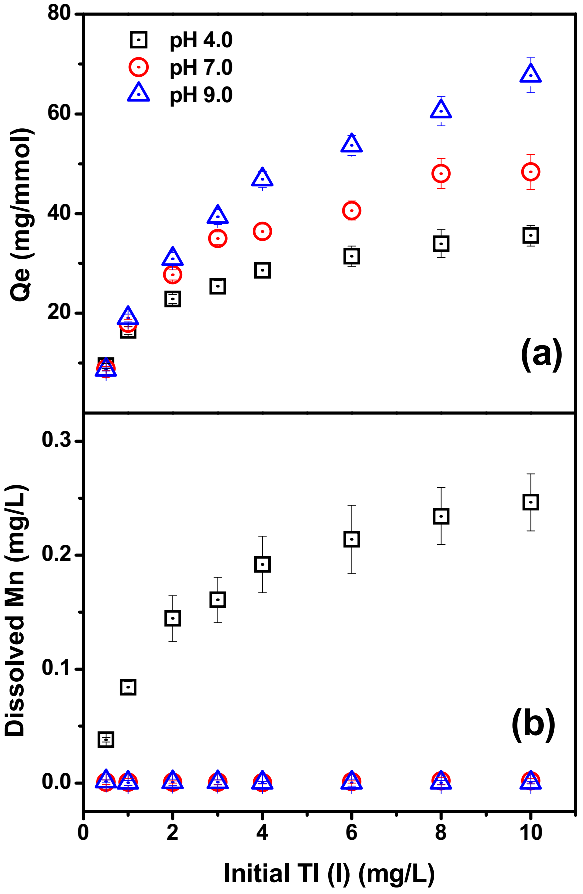

Fig. 4 Adsorption of Tl by $nMnO_2$ (**a**) and dissolved Mn as a function of initial Tl(I) (**b**) at different pH conditions. The adsorption experiments were conducted at 25 °C. Initial dosage of $nMnO_2$, 0.05 mM

reported by Nriagu and coworkers (Eqs. 7–11) (Lin and Nriagu 1998):

$$Tl^{+} + OH^{-} \Leftrightarrow TlOH \quad pKa = 11.7 \tag{7}$$

$$Tl^{3+} + OH^{-} \Leftrightarrow TlOH^{2+} \quad pKa = 2.69 \tag{8}$$

$$TlOH^{2+} + OH^{-} \Leftrightarrow Tl(OH)_2{}^{+} \quad pKa = 6.36 \tag{9}$$

$$Tl(OH)_2{}^{+} + OH^{-} \Leftrightarrow Tl(OH)_3 \quad pKa = 7.42 \tag{10}$$

$$Tl(OH)_3 + OH^{-} \Leftrightarrow Tl(OH)_4{}^{-} \quad pKa = 8.78 \tag{11}$$

As can be seen, Tl^{+} is the predominant species of Tl(I) at a wide pH range (Fig. 5a), including both pH 7.0 and 9.0. Additionally, the negative surface charge increases with pH from 4.0 to 9.0 (Huangfu et al. 2013). Therefore, increased negative surface charge on $nMnO_2$ might be mainly responsible for its higher Tl adsorption capacity at pH 9.0. In contrast, under acidic condition (i.e., pH 4.0), less negative charge on their surface might result in lower removal of Tl by $nMnO_2$ compared with that at pH 7.0 (Huangfu et al. 2013). Moreover, the oxidation of Tl(I) might lead to the coexistence of Tl(III) and Mn(II) at pH 4.0, where $TlOH^{2+}$ is the predominant species (Fig. 5b). Although this species might increase the amount of adsorbed Tl, the generation of Mn(II) might occupy the adsorption sites, reducing the adsorption capacity of this species. Previously, the notable uptake of Mn^{2+} onto MnO_2 was reported compared with many other divalent ions (e.g., Ca(II), Mg(II), Sr(II), Ni(II), Cd(II), Ba(II), and Zn(II)) (Fu et al. 1991; Murray 1974a). Therefore, the decrease of negative surface charge and surface passivation might be the predominant reason for the lower capacity at acidic conditions. Additionally, at pH 4.0, the reduction of $nMnO_2$ to Mn(II) might decrease the amount of adsorbent $nMnO_2$ and the resulting absorption. It should be noted that the aggregation of $nMnO_2$ might also be responsible for the reduction of Tl adsorption capacity at pH 4.0 due to the decrease in surface area. Nevertheless, this was not very clear and further studies are required.

The hydrodynamic diameter of $nMnO_2$ increased with the increase of initial concentration of Tl(I) at pH 4.0 (Fig. 6), demonstrating that aggregation was increased by increasing initial concentrations above 0.5 mg/L. According to the Derjguin-Landau-Verwey-

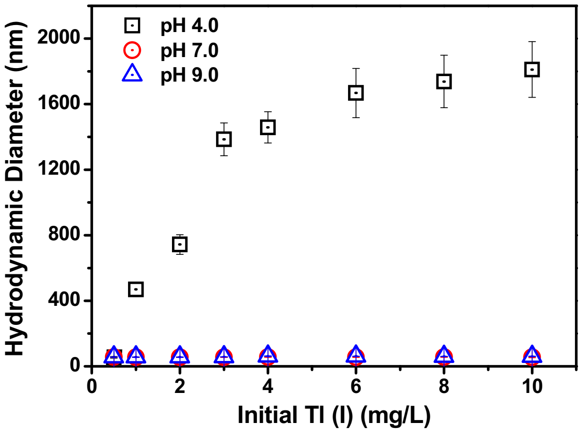

Fig. 5 The influence of initial Tl(I) on the aggregation of $nMnO_2$. The adsorption experiments were conducted at 25 °C. Initial dosage of $nMnO_2$, 0.05 mM

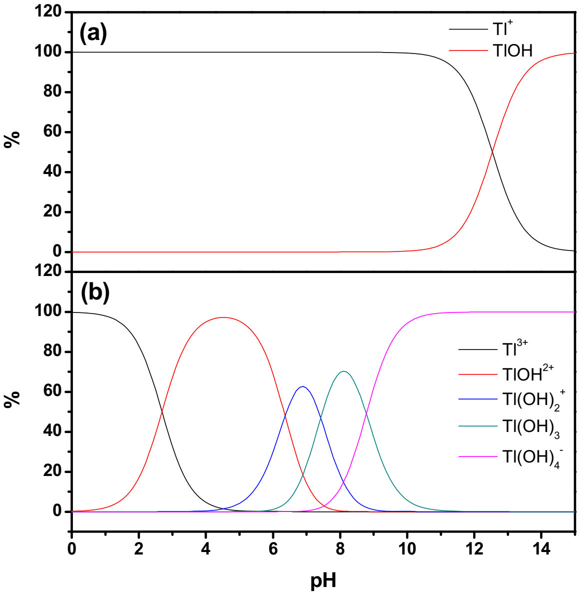

Fig. 6 Distribution of Tl(III) hydroxyl species as a function of pH. Tl(I) (**a**) and Tl(III) (**b**)

Overbeek (DLVO) theory, the aggregation of colloids cannot be obtained until the electrostatic repulsion was too small to hinder the approach of two particles (Chen and Elimelech 2006). Our present work shows that the aggregation of $nMnO_2$ occurs when the cation concentration was high enough ($[Na^+]>10$ mM, $[Mg^{2+}]>0.2$ mM, or $[Ca^{2+}]>0.05$ mM) (Huangfu et al. 2013). The maximum concentration Tl(I) added to the adsorption experiments (0.049 mM) was much lower than the concentration of the monovalent cation (10 mM Na^+) at which $nMnO_2$ aggregation occurred. Thus, the aggregation of $nMnO_2$ might not result from the added Tl(I) but some higher valent cations produced by the redox reactions between Tl(I) and $nMnO_2$ (e.g., Mn(II) or Tl(III)) due to their previously observed aggregation effects (Huangfu et al. 2013). When the initial concentration of Tl(I) was 0.5 mg/L (0.0025 mM), the cations originating from the redox reactions might not reach the critical concentration for aggregation. As the concentration of initial Tl(I) rose from 1 to 10 mg/L, large sizes of $nMnO_2$ were also observed, indicating increases in the produced high-valent cations. These results are consistent with our recent publications, in which increased aggregation rates were obtained with increased cation concentrations in the reaction-limit region (Huangfu et al. 2013). Thus, the aggregation of $nMnO_2$ might also confirm the oxidation of Tl(I) at pH 4.0. In contrast, no size change was observed for $nMnO_2$ at pH 7.0 and 9.0, consistent with the measurements of dissolved the Mn as shown above.

3.3 The Adsorption of Tl(I) in the Presence of HA

The influence of HA on the adsorption of Tl(I) by $nMnO_2$ was also explored (Fig. 7a). The introduction

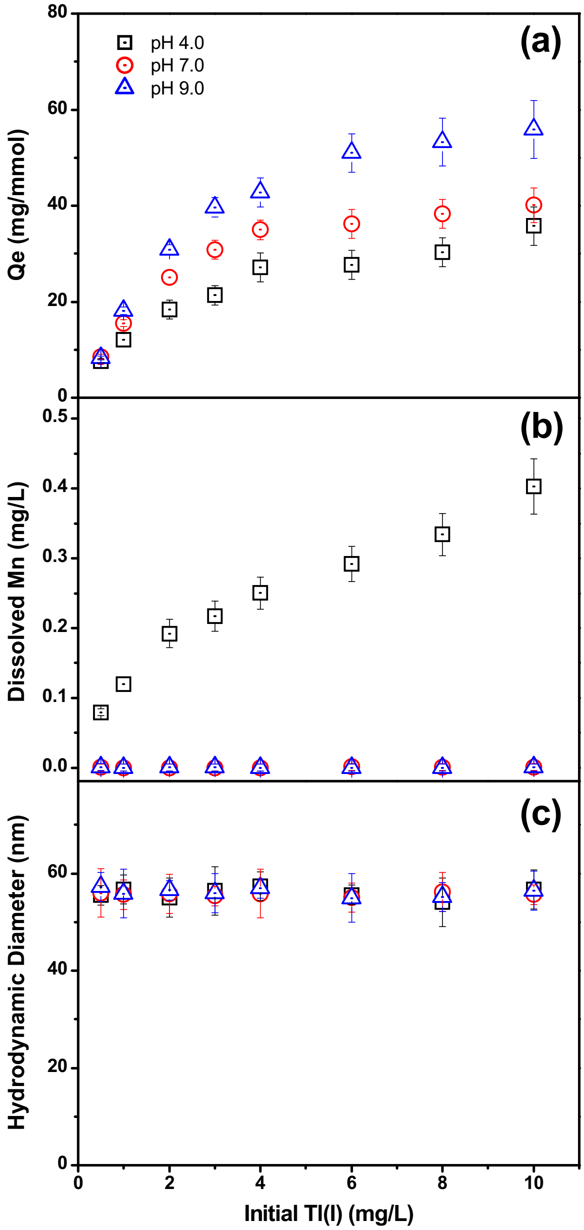

Fig. 7 Adsorption amount of Tl by $nMnO_2$ (**a**), dissolved Mn (**b**), and hydrodynamic diameters of $nMnO_2$ (**c**) as a function of initial Tl(I) at different pHs. The adsorption experiments were conducted at 25 °C. Initial dosage of $nMnO_2$, 0.05 mM. [HA], 3 mg/L of TOC

of HA slightly decreased the adsorption capacity of Tl at all pHs tested. The decrease of Tl adsorption amount might result from the passivation of the $nMnO_2$, originating from the adsorption of HA onto their surface (Huangfu et al. 2013). At present, the accurate mechanism is not yet clear. Figure 7b shows that a higher dissolution of $nMnO_2$ at the same initial Tl(I) concentration was observed than in the absence of HA. This might result from a reduction and dissolution of $nMnO_2$ by HA as a reduction of Mn oxides by natural organic matter which has been reported previously (Waite et al. 1988). The presence of HA hindered the aggregation of $nMnO_2$ at pH 4.0 (Fig. 7c), indicating that the aggregation of $nMnO_2$ might not be the predominant reason for the decrease of Tl uptake. Our previous study agrees that the increase of steric repulsion originating from the adsorption of HA may be responsible for the lower efficiency of $nMnO_2$ aggregation in the presence of HA (Huangfu et al. 2013).

4 Conclusions

Nanosized manganese dioxide was prepared, and the adsorption capacity of Tl(I) was investigated. The kinetic study showed that $nMnO_2$ could remove Tl(I) from aqueous solutions quickly under neutral conditions, and the adsorption equilibrium of Tl(I) was about 32 mg/mmol (i.e., ~368 mg(Tl)/g(MnO_2)). Moreover, the adsorption isotherms followed the Langmuir and Freundlich models, with the latter the more successful. The maximum adsorption capacity of Tl(I) by $nMnO_2$ was ~58.48 mg/mmol (i.e., ~672 mg(Tl)/g(MnO_2)), much higher than various previously reported adsorbents.

We also show that water conditions impact Tl(I) adsorption and oxidation. In the presence of Ca^{2+} and Mg^{2+}, the amount of adsorbed Tl(I) was decreased to a certain extent; however, only a negligible effect was found in the presence of Na^+. The increase of ambient pH enhanced the uptake of Tl(I) by $nMnO_2$. At acidic conditions (pH 4.0), both the release of Mn and the aggregation of $nMnO_2$ were observed, but $nMnO_2$ aggregation did not occur and Mn did not leach to the bulk at pH 7.0 and 9.0. More importantly, aggregation and Mn leaching were enhanced by the increase of initial Tl(I) concentration at pH 4.0, indicating the oxidation of Tl(I) by $nMnO_2$. Lower Tl(I) uptake was observed in the presence of 3 mg/L HA for all pHs tested, i.e., pH 4.0, 7.0, and 9.0. Moreover, at pH 4.0, the introduction of HA hindered the aggregation of $nMnO_2$ but enhances their dissolution.

Based on these results, $nMnO_2$ should be considered as a potential adsorbent to remove Tl from engineered systems. Moreover, the presence of $nMnO_2$ could influence the fate, transport, and mobility of Tl(I) to a certain extent in related natural waters.

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