Effects of calcium ions on surface characteristics and adsorptive properties of hydrous manganese dioxide

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ABSTRACT

The effects of calcium ions (Ca^{2+}) on the surface characteristics and adsorptive properties of hydrous manganese dioxide (δMnO_2), taking arsenic and humic acid as model pollutants, were systematically investigated. The FTIR spectra and SEM/EDX analyses indicate coordination between Ca^{2+} and the surface hydroxyls ($\equiv\text{Mn}-\text{OH}$) of δMnO_2 , which leads to an increase of the surface ζ potential. Ca^{2+} can facilitate δMnO_2 aggregation, as indicated by the particle size distribution (PSD) and on-line flocculating index (FI). The variation of δMnO_2 surface characteristics that is induced by Ca^{2+} enhances the adsorption of humic acid (HA) and arsenic onto δMnO_2 . The adsorption of HA is enhanced more significantly by Ca^{2+} than that of arsenic, which is positively related to the coordination strength between Ca^{2+} and individual pollutants. The SEM/EDX analysis shows the formation of Ca–HA complexes, which have a higher affinity for δMnO_2 than HA. The bridging effect of Ca^{2+} plays a major role in enhancing HA adsorption onto δMnO_2 . Due to different interactions between Ca^{2+} and pollutants, the adsorption mechanism is pollutant-dependent in the presence of Ca^{2+} .

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1. Introduction

The adsorption of different pollutants (e.g., natural organic matter, phosphate, arsenic, and hydroquinone) onto natural or synthetic manganese oxides has been investigated so far with interfacial reaction mechanisms, including adsorption, surface complex formation, heterogeneous oxidation, and reductive dissolution [1–3]. However, previous studies mainly focused on prepared adsorbents. Few studies have focused on the adsorptive behaviors of adsorbents formed in situ, such as hydrous manganese dioxide (δMnO_2), which is produced in situ through interactions between manganese sulfate (MnSO_4) and potassium permanganate (KMnO_4).

Calcium ions (Ca^{2+}), a common cation in natural water environment, could impact pollutant adsorption onto adsorbents and significantly affect the reaction mechanisms involved [4,5]. For example, Ca^{2+} changed the dominant reactions during natural organic polyelectrolyte adsorption onto tobermorite [5] and lessened the adverse effect of silicate inhibiting arsenic co-precipitation with ferric chloride [6]. These effects were mainly ascribed by the formation of complexes between Ca^{2+} and metal oxides, organics, and inorganics [2,3]. However, previous studies mainly employed

natural ores or preprepared metal oxides as adsorbents, rarely focusing on freshly formed δMnO_2 . Our earlier studies reported the positive effect of Ca^{2+} on humic acid (HA) and arsenic adsorption onto δMnO_2 [7,8], but did not reveal the mechanism by which Ca^{2+} affects the surface characteristics and adsorptive properties of δMnO_2 .

The objectives of this study were to (1) examine the effects of Ca^{2+} on the surface characteristics of δMnO_2 with FTIR, SEM/EDX, ζ potential, particle size distribution (PSD), on-line flocculating index (FI), and BET surface area (S_{BET}) analyses; (2) comparatively investigate the effects of Ca^{2+} on HA and arsenic adsorption onto δMnO_2 ; and (3) propose the dominant mechanisms of Ca^{2+} facilitating the adsorption of model pollutants onto δMnO_2 .

2. Materials and methods

2.1. Reagents and δMnO_2 preparation

Chemical grade HA consisting of 62.53% C, 32.34% O, and 4.80% H was obtained from Tianjin Chemical Reagents Company. To prepare a stock solution, HA ash was first dissolved in 2 M NaOH, sonicated for 30 min, and then kept in darkness airtight at 4 °C for 3 months for the dissolution of as much HA as possible. It was diluted and filtered through 0.45- μm cellulose acetate filters twice before use. The sodium arsenite (NaAsO_2) and sodium arse-

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nate (NaAsO_3) stock solutions were prepared in de-ionized water every 10 days.

δMnO_2 was prepared through a reaction between MnSO_4 and KMnO_4 following the procedures reported in our previous publication [7]. X-ray diffraction analysis (Shimadzu Co., Japan) showed a low degree of crystallinity, indicating its similarity to what others referred to as δMnO_2 .

2.2. Experimental methods

Sodium nitrate (NaNO_3) was used to adjust the background ionic strength when necessary. Calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) and model pollutants (e.g., HA and arsenic) were added into the reaction solution at desired concentrations and pH was adjusted thereafter. Batch experiments on adsorption were conducted in capped flasks with continuous rotary shaking (125 rpm) at $25 \pm 1^\circ\text{C}$ for 60 min. Samples were filtered through $0.45\text{-}\mu\text{m}$ membrane filters to analyze total organic carbon (TOC) and arsenic concentrations in the filtrate. The adsorption density of these two pollutants on δMnO_2 was calculated by the formula

adsorption density

$$= ([\text{pollutant}]_{\text{initial}} - [\text{pollutant}]_{\text{final}}) / \delta\text{MnO}_2 \text{ dosage},$$

where $[\text{pollutant}]_{\text{initial}}$ means the initial concentration of a pollutant, and $[\text{pollutant}]_{\text{final}}$ stands for the final concentration of a pollutant.

To examine the effect of Ca^{2+} on δMnO_2 aggregation, batch experiments were conducted in glass beakers with rapid mixing (150 rpm, 1 min) and subsequent slow mixing (50 rpm, 20 min). Samples were continuously withdrawn 10 mm below the water level with a peristaltic pump for on-line FI analysis.

While the interactions between Ca^{2+} and HA were investigated, 2 mM Ca^{2+} was added into the HA solution (17.1 mg/L DOC, dissolved organic carbon) and the reaction was allowed to proceed for 60 min. The solution was thereafter filtered through a $0.45\text{-}\mu\text{m}$ membrane filter, and the membrane residue was washed with de-ionized water and freeze-dried for SEM/EDX analysis.

2.3. Analytical methods

The elemental composition of HA was determined with a Vario-EL elemental analyzer (Elementar Co.) without pretreatment. FTIR spectra were recorded in KBr pellets using an FT-NIR Raman spectrometer (Perkin-Elmer Co.). Surface elemental ratio was analyzed by an S-3000N scanning electron microscope (SEM, Hitachi Co.) coupled with an energy-dispersive X-ray analyzer (EDX, EDAX Inc.). Samples were washed with de-ionized water, centrifuged, and freeze-dried before analysis.

S_{BET} was determined by the single-point Brunauer-Emmett-Teller (BET) N_2 adsorption method using an ASAP 2000 accelerated surface area and porosimetry analyzer (Micromeritics Co.). Suspensions were first centrifuged and freeze-dried under vacuum and then resuspended in acetone and freeze-dried again [7] for S_{BET} analysis.

The electrokinetic potential (ζ potential) of δMnO_2 was measured with a zeta potential analyzer, Model Zetasizer2000 (Malvern Co.), in triplicate. The average volumetric particle diameter (AVPD) and PSD were determined with a Mastersizer2000 laser particle size analyzer (Malvern Co.).

A PDA2000 photometric dispersion analyzer (Rank Bros Ltd.) was employed to monitor the on-line FI. The PDA monitors the turbidity fluctuation of particles in a flow-through cell, providing useful information on particle diameter variation and on-line aggregation [9].

Fig. 1. FTIR spectra of δMnO_2 in the presence or absence of Ca^{2+} .

TOC was determined by UV-persulfate oxidation with a Phoenix 8000 TOC analyzer (Tekmar-Dohrmann Co.). Arsenic concentrations were determined by the hydride generation-atomic fluorescence spectroscopy (HG-AFS) method with an AF-610A atomic fluorescence spectrometer (Rayleigh Analytical Instrument Co., China). The arsenic detection limit of the instrument was $2\text{ }\mu\text{g/L}$.

3. Results and discussion

3.1. Effects of Ca^{2+} on the surface characteristics of δMnO_2

3.1.1. Effect of Ca^{2+} on the surface functional groups of δMnO_2

The FTIR spectra of δMnO_2 (Fig. 1) showed quite similar trends between 1600 and 4000 cm^{-1} in the presence or absence of Ca^{2+} , and both spectra indicated the presence of physisorbed water molecules. The shoulder bands at 3380 cm^{-1} corresponded to the structural $-\text{OH}$ stretching vibration (ν_{OH}). The bands at 1624 cm^{-1} were related to the $\text{H}-\text{O}-\text{H}$ bending (δ_{OH}), indicating the deformation of adsorbed water molecules.

In the absence of Ca^{2+} , the shoulder band at 1034 cm^{-1} was assigned to the vibration of surface hydroxyl groups (e.g., $\equiv\text{Mn}-\text{OH}$) within metal oxides [10]. In the presence of Ca^{2+} , this band disappeared, due to the formation of complexes between Ca^{2+} and $\equiv\text{Mn}-\text{OH}$. The pH_{PZC} (point of zero charge) of δMnO_2 was reported to be about pH 3.0 [7]. In different pH ranges, δMnO_2 exhibits different surface charges through surface dissolution and hydrolysis reactions as follows:

Ca^{2+} is able to form complexes with $\equiv\text{Mn}-\text{OH}$ and contributes to the disappearance of $\equiv\text{Mn}-\text{OH}$ through the following reactions:

Our SEM/EDX analysis indicated the presence of elemental Ca on the δMnO_2 surface, confirming the occurrence of reactions between Ca^{2+} and $\equiv\text{Mn}-\text{OH}$.

3.1.2. Effect of Ca^{2+} concentration on the surface charge of δMnO_2

The effect of Ca^{2+} concentration on the ζ potential of δMnO_2 is shown in Fig. 2. Results indicate that at pH 7.0, δMnO_2 had a low ζ potential of -23.4 mV , which increased to -12.4 mV at 0.2 mM Ca^{2+} and -1.5 mV at 0.6 mM Ca^{2+} . Further increasing the Ca^{2+} concentration did not notably increase the ζ potential. In the presence of HA (4.76 mg/L as DOC), the addition of Ca^{2+} ,

Fig. 2. Effect of Ca^{2+} concentration on the ζ potential of δMnO_2 (pH 7.0). Experimental conditions: open symbols—in the absence of HA; solid symbols—in the presence of 4.76 mg/L HA as TOC.

either before or after HA addition also led to a ζ potential increase. For example, Ca^{2+} increased the ζ potential of δMnO_2 from -29.0 mV (no Ca^{2+}) to -14.1 mV (0.8 mM Ca^{2+}) when HA was predissolved in the reaction solution. δMnO_2 , with pH_{PZC} about 3.0, was a highly acidic oxide and showed a high adsorbing potential for Ca^{2+} . Ca^{2+} could compress the diffuse double electrical layer of δMnO_2 . Additionally, the interactions between Ca^{2+} and $\equiv\text{Mn}-\text{OH}$ could increase the surface potential through ion exchange and surface complexation reactions [11].

Comparatively, greater ζ -potential increase was observed when Ca^{2+} was added after HA, especially at lower Ca^{2+} concentrations. The presence of HA decreased the amount of Ca^{2+} available for the diffuse double electrical layer compression, owing to competitive complexation between Ca^{2+} and the acidic functional groups within HA. When HA was added after Ca^{2+} , the positive charge of $\equiv\text{Mn}-\text{O}-\text{Ca}^+$ species was largely decreased due to the electrical interaction between $\equiv\text{Mn}-\text{O}-\text{Ca}^+$ and HA. However, if HA was added before Ca^{2+} , the $\equiv\text{Mn}-\text{OH}$ first interacted with the hydrogen bonds within HA through the hydrogen-bonding effect. This effect decreased the required Ca^{2+} amount for surface $\equiv\text{Mn}-\text{OH}$ complexation, providing more Ca^{2+} to compress the diffuse double electric layer.

3.1.3. Effect of Ca^{2+} concentration on the stability and aggregation of δMnO_2

The effect of Ca^{2+} concentration on the stability and aggregation of δMnO_2 is shown in Fig. 3. Results in Fig. 3a indicate that more than 99% of δMnO_2 particles were below 0.5 μm in the absence of Ca^{2+} . However, about 95% of δMnO_2 particles were larger than 3.6 μm after 1.0 mM Ca^{2+} was added. It is clearly seen that Ca^{2+} significantly promoted the aggregation of δMnO_2 particles.

Ca^{2+} could significantly increase the AVPD of δMnO_2 . In the absence of Ca^{2+} , the AVPD value of δMnO_2 was approximately 0.1 μm . When the Ca^{2+} concentration was increased to 0.2 and 0.4 mM, the AVPD value remarkably increased to 15.0 and 24.2 μm , respectively. Further increasing the Ca^{2+} concentrations to 0.6 and 0.8 mM did not increase the AVPD notably. Since 0.6 mM Ca^{2+} was enough to increase the ζ potential (Fig. 2), it is inferred that Ca^{2+} promoted the aggregation of δMnO_2 particles through decreasing the electrostatic repulsive forces.

The S_{BET} analysis of δMnO_2 was in good accordance with the PSD analysis. The S_{BET} of δMnO_2 was determined to be 117.4

Fig. 3. Effect of Ca^{2+} concentration on (a) the particle size distribution and (b) the FI of δMnO_2 .

m^2/g , which was much higher than that of commercial βMnO_2 (29.3 m^2/g). The high S_{BET} value was ascribed to the amorphous status of δMnO_2 , whose XRD pattern revealed no obvious crystalline peaks. The addition of 1 mM Ca^{2+} decreased the S_{BET} to 80.5 m^2/g due to the aggregation of δMnO_2 particles.

It is noted that the δMnO_2 aggregation was significantly enhanced even at a Ca^{2+} concentration as low as 0.2 mM. Thus, it can be inferred that the Ca^{2+} concentration in most natural water environments [12] is enough to promote δMnO_2 aggregation.

Ca^{2+} also impacted the dynamic δMnO_2 aggregation at different Ca^{2+} concentrations (Fig. 3b). Results indicate that the FI value of δMnO_2 continuously increased with increasing Ca^{2+} concentration. In contrast, the FI value stayed consistently zero in the absence of Ca^{2+} , indicating the tiny and dispersed δMnO_2 particles. A low Ca^{2+} concentration of 0.2 mM could increase the FI to a maximal value of 7.5% . At 0.6 mM Ca^{2+} , the maximal FI value was further increased to 9.2% , with a correspondingly shortened critical time. No distinct difference was observed between 0.6 and 1.0 mM Ca^{2+} , which was in agreement with PSD data.

This result is of practical interest. Aqueous Mn(II) should be minimized in drinking water treatment due to its unfavorable effect on taste, color, and turbidity. Mn(II) is generally oxidized to δMnO_2 , which can be readily removed through subsequent filtration. Our result shows that Ca^{2+} , which is commonly present in drinking water resources, can notably enhance δMnO_2 removal by promoting δMnO_2 aggregation.

Fig. 4. Effect of Ca^{2+} on HA adsorption onto δMnO_2 at different pH values: open symbols—in the absence of 1 mM Ca^{2+} ; solid symbols—in the presence of Ca^{2+} .

3.2. Effects of Ca^{2+} on HA and arsenic adsorption onto δMnO_2 and their mechanisms

3.2.1. Effect of Ca^{2+} on HA adsorption onto δMnO_2

The effect of Ca^{2+} on HA adsorption onto δMnO_2 at different pH values is shown in Fig. 4. Results indicate that little HA was adsorbed by δMnO_2 in the absence of Ca^{2+} . However, 1.0 mM Ca^{2+} significantly increased HA adsorption, with a maximal removal efficiency of 77.0% at pH 7.0. The corresponding adsorption density was calculated to be 0.97 mg-TOC/mg- δMnO_2 under this condition. Similar trends were observed at pH 5.5 and 8.5, and more HA could be removed as the pH increased.

The mechanisms of humic substance adsorption onto metal oxides generally include anion exchange (electrostatic interaction), ligand exchange (surface complexation), hydrophobic interaction, entropic effects, hydrogen bonding, and cation bridging [13]. In the absence of Ca^{2+} , δMnO_2 adsorbs HA mainly through the reactions:

Table 1

Effect of Ca^{2+} concentration on arsenic removal by δMnO_2 (0.63 mg/L $[\text{As(III)}]_0$, 6 mg/L δMnO_2).

Ca^{2+} (mM)	HA as DOC (mg/L)	As removal (%)	As adsorption density (mg-As/g- δMnO_2)
0	0	2.1	2.1
1.0	0	18.3	19.3
0	4.62	2.0	4.3
0.4	4.62	14.0	14.8
1.0	4.62	16.9	17.9
0	8.62	0.8	4.0
0.1	8.62	7.4	7.8
1.0	8.62	21.1	17.9

where L^- and HL' respectively represent the acidic and neutral forms of HA ligands, and $\equiv\text{MnOH} + \text{OH}^-$ stands for the hydrolyzed $\equiv\text{Mn}-\text{O}^-$.

However, HA was negatively charged around neutral pH due to the deprotonation of its surface acidic groups, such as carboxylic ($-\text{COOH}$) and phenolic ($-\text{ArOH}$) groups. δMnO_2 was also negatively charged, with a ζ potential of -23.4 mV at pH 7.0 (Fig. 2). The repulsive force between HA and δMnO_2 inhibited the electrostatic and hydrogen bonding reactions, thus leading to limited HA removal.

Ca^{2+} acted as a cation bridge between HA and δMnO_2 to facilitate HA adsorption. First, Ca^{2+} could increase the ζ potential of δMnO_2 , thus decreasing the repulsive force between δMnO_2 and HA. Yao and Millero reported that Ca^{2+} could enhance phosphate adsorption onto δMnO_2 by reversing the surface charge of δMnO_2 from negative to positive [14]. In addition, Ca^{2+} could coordinate with the $-\text{COO}^-$ and $-\text{ArO}^-$ groups to form more easily adsorbed metal/humic complexes. Our SEM/EDX analysis showed an elemental ratio (C/Ca) of 38:1, which demonstrated the occurrence of the complexation between Ca^{2+} and HA. Kaneco et al. reported that Cu^{2+} and Al^{3+} enhanced fuvic acid adsorption onto metal oxides [3]. Schulthess and Huang reported that metal/humic complexes exhibited a higher adsorption density on metal oxides than humic substances alone [15].

3.2.2. Effect of Ca^{2+} on arsenic adsorption onto δMnO_2

Ca^{2+} also exerted a positive effect on arsenic adsorption onto δMnO_2 , as shown in Table 1. Quantitatively, 1.0 mM Ca^{2+} could increase the adsorption density of As from 2.1 to 19.3 mg As/g δMnO_2 . In the presence of HA (4.62 mg/L DOC), the removal efficiency of As was increased from 2.0% (no Ca^{2+}) to 14.0% (0.4 mM Ca^{2+}) and 16.9% (1.0 mM Ca^{2+}). Our former study also indicated the limited potential of Ca^{2+} to facilitate the adsorption of arsenic onto δMnO_2 [16]. Generally, in comparison with HA removal, the enhancement of arsenic removal by Ca^{2+} was not so significant.

In the neutral pH range, As(V) exists in the forms of H_2AsO_4^- and HAsO_4^{2-} , whereas H_3AsO_3 is the predominant As(III) species and less than 10% of As(III) is in the form of H_2AsO_3^- . As(V) was adsorbed onto manganese oxides through complexation between As(V) and surface $\text{Mn}-\text{OH}$ [1]. However, As(III) adsorption involved additional oxidation of As(III) to As(V) [1].

As mentioned above, Ca^{2+} could enhance δMnO_2 aggregation, thus decreasing the amount of δMnO_2 passing through the filtration process. As a result, more arsenic was removed through adsorption by δMnO_2 and subsequent filtration.

However, Ca^{2+} and arsenic species could only form weak complexes. Swash and Monhemius reported that CaHAsO_4 , $\text{CaHAsO}_4 \cdot \text{H}_2\text{O}$, and $\text{CaHAsO}_4 \cdot 2\text{H}_2\text{O}$ were the main species formed from the interactions between arsenate and Ca^{2+} , with their water solubility varying from 2.9×10^{-2} to 5.8×10^{-2} M [17]. Qiu and Liu reported that the water solubility of $\text{Ca}(\text{AsO}_2)_2$ was 3.5×10^{-3} M [18]. In this study, the concentration product of Ca^{2+} and arsenic

Fig. 5. FTIR analysis of δMnO_2 with adsorbed arsenic species: (a) initial As(V), 0 mM Ca^{2+} ; (b) initial As(V), 1 mM Ca^{2+} ; (c) initial As(III), 0 mM Ca^{2+} ; and (d) initial As(III), 1 mM Ca^{2+} . Experimental conditions: initial arsenic concentration was 10 mg/L, 100 mg/L δMnO_2 , 50 mM NaNO_3 .

species was much lower than the water solubility of corresponding species, implying weak complexation between Ca^{2+} and arsenic species.

FTIR analysis was employed to investigate the bridging effect of Ca^{2+} on the adsorption of arsenic species by δMnO_2 (Fig. 5). Samples a and b denoted the δMnO_2 with adsorbed As species in the presence of initial As(V). Samples c and d signified the δMnO_2 when As(III) was predissolved in the reaction solution. Additionally, no Ca^{2+} was added in experimental systems of samples a and c, and 1 mM Ca^{2+} was present for samples b and d. In the FTIR spectra, the peaks at 1639 cm^{-1} were ascribed to the deformation of water molecules, while the peaks between 1390 and 1432 cm^{-1} were attributed to the vibration of NO_3^- , which was used for ionic strength adjustment. The peaks at 1053 and 1093 cm^{-1} could be assigned to the vibration of $\equiv\text{Mn}-\text{OH}$, which was weakened in the presence of Ca^{2+} (Figs. 5b and 5d). Sample b showed a more obvious decrease in the $\equiv\text{Mn}-\text{OH}$ peak (e.g., 1053 cm^{-1}) than sample d, probably due to a higher degree of complexation between

Ca^{2+} and $\equiv\text{Mn}-\text{OH}$. Our SEM/EDX analysis substantiated that sample b had a higher Ca content (1.98%) than sample d (0.37%).

The 885 cm^{-1} peak was assigned to the As–O collision within the adsorbed As species, rather than to the As–O surface complex. Goldberg and Johnston reported that the As–O bands in the 0.1 M As(V) solution at pH 5 appeared at 878 and 907 cm^{-1} due to the As–O collision of $\text{AsO}_2(\text{OH})_2^-$ [19]. However, after As(V) adsorption onto amorphous iron oxides, two new bands at 824 and 861 cm^{-1} were observed, which were respectively assigned to the Fe–O–As complex and the adsorbed arsenic species in uncomplexed As species [19]. In this work, the slight shift of the As–O band indicated that the formation of surface complexes (e.g., Ca–O–As, Mn–O–As) was negligible. Therefore, the bridging effect of Ca^{2+} was weak in arsenic adsorption by δMnO_2 .

It should be noted that the As(V) absorption peak at 885 cm^{-1} also appeared in sample c and sample d (Fig. 5) even when only As(III) was present in the reaction solution, implying the interfacial oxidation of As(III) to As(V) during As(III) adsorption onto δMnO_2 .

3.2.3. Mechanism of enhanced pollutant adsorption onto δMnO_2 by Ca^{2+} ions

As mentioned above, Ca^{2+} could enhance pollutant removal by increasing the surface potential of δMnO_2 and reducing the repulsive force, as well as promoting δMnO_2 aggregation to increase the filtration efficiency of δMnO_2 particles. In addition, if the model pollutants could form complexes with Ca^{2+} and the solution pH was higher than the pH_{PZC} of δMnO_2 , the bridging effect of Ca^{2+} ,

where P^- represents the deprotonated model pollutant, would also boost pollutant removal.

Based on the experimental results discussed above, the mechanisms of Ca^{2+} facilitating the adsorption of different pollutants onto δMnO_2 are proposed in Fig. 6.

4. Summary

Ca^{2+} could significantly impact the surface characteristics of δMnO_2 through its complexation with Mn–OH. The presence of

Fig. 6. Proposed mechanisms for Ca^{2+} facilitation of pollutant adsorption onto δMnO_2 .

Ca^{2+} increased the ζ potential of δMnO_2 and promoted δMnO_2 aggregation, which was beneficial for the removal of negatively charged pollutants. However, the positive effect of Ca^{2+} on pollutant adsorption onto δMnO_2 was pollutant-dependent. In general, Ca^{2+} would exert a more positive effect on pollutants that can complex with Ca^{2+} (e.g., HA) than on pollutants that cannot complex with Ca^{2+} (e.g., arsenic species). The bridging effect of Ca^{2+} dominated its effect on pollutant adsorption onto δMnO_2 .

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