

Enhanced removal of organics by permanganate preoxidation using tannic acid as a model compound – Role of *in situ* formed manganese dioxide

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Abstract

The effect of permanganate preoxidation on organic matter removal during the coagulation with aluminum chloride was investigated using tannic acid as a model compound. Results showed that a small amount of KMnO_4 (0.75 mg/L) increased the removal efficiency of tannic acid up to 20%, as compared to the process of coagulation by aluminum chloride alone. The key factor enhancing the removal efficiency of tannic acid in preoxidation process was the *in situ* formation of a reductant manganese dioxide. The complexation model was used to describe the reaction between MnO_2 and tannic acid. Under weak pH condition, tannic acid was difficult to be adsorbed by MnO_2 due to the static electrical repulsive forces. The presence of Ca^{2+} served as a bridge to hold the negative charged MnO_2 and tannic acid together, which could be a crucial factor influencing tannic acid adsorption by *in-situ* manganese dioxide.

Key words: KMnO_4 ; MnO_2 ; adsorption; coagulation; oxidation; tannic acid

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Introduction

The removal of natural organic matter (NOM) has received increasing concern in light of the correlation with the formation of disinfection byproducts (DBPs). Preoxidation has been proved to be one of the effective methods to enhance coagulation and improve NOM removal. Traditionally, chlorine was used to enhance the coagulation of water with a high organic content. However, the negative effect of using chlorine is the formation of hazardous byproducts (THMs), which limits its use as a preoxidant (Singer and Chang, 1989). Ozone preoxidation had a positive effect on the coagulation of surface water by improving the removal of turbidity and by enhancing the availability of biodegradation, whilst a higher dosage of ozone will result in an increase of residual turbidity and the formation of some hazardous matters, such as aldehyde and ketone (Reckhow, 1986). Ma *et al.* (1997) reported that permanganate preoxidation substantially enhanced the coagulation of surface water as expressed in terms of residual turbidity and DBPs. It was speculated that KMnO_4 oxidized the organics and make them easier to be adsorbed by the hydrolysis products of coagulant. Furthermore, they indicated that the MnO_2 formed *in situ* as the reduction product of KMnO_4 could adsorb the organics in the process of coagulation.

Manganese dioxide has been used extensively as an oxidizing agent reacting with organic and inorganic

compounds, such as phenol (Stone, 1987), Mn^{2+} (Perez-Benito, 2002) and As(III) (Driehaus *et al.*, 1995) and so on. It is also available to adsorb some heavy metal ions, such as Co(II) (Murray, 1975), Cr(III) (Edmond and Dhanpat, 1987), Pb^{2+} (Al-Degs, 2001) and other inorganic compounds (Yao *et al.*, 1996). It was found that MnO_2 was an effective water treatment agent. But limited work has been done in *in situ* formation of MnO_2 and its effect on the process on coagulation.

The present study selected commercially available tannic acid as a surrogate of NOM to study the mechanism of KMnO_4 preoxidation and its function as a coagulant aid by using aluminum chloride to remove tannic acid. The mechanism of MnO_2 reacting with tannic acid was also studied.

1 Materials and methods

1.1 Chemicals

Commercial tannic acid was purchased from Tianjin Kermel Company, China. The empirical formula of tannic acid was $\text{C}_{76}\text{H}_{53}\text{O}_{46}$ with a mean molecular weight of about 1700 g/mol, an organic carbon content of about 50% as reported by other researchers (El-Rehaili and Weber, 1987; Summers *et al.*, 1989; Newcombe *et al.*, 1997).

The stock solutions used in this study are tannic acid (5 g/L), $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ (0.1 mol/L), KMnO_4 (0.7270 g/L), $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ (1.1680 g/L) and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (5 g/L). All

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chemicals were reagent grade and all solutions were made using distilled water.

1.2 Enhanced coagulation

For coagulation testing, a six-unit multiple stirrer system was employed. Each one contained about 1 L of distilled water with 25 mg/L tannic acid and 0.5 mmol/L $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ (0.1 mol/L). Varied volumes of 0.7270 g/L KMnO_4 solutions were injected, respectively, into the aqueous solutions. After rapid mixing at 200 r/min for 2 min, varied volumes of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (5 g/L) solutions were also injected and made up to 1 L with distilled water. The mixture was rapidly mixed for 3 min, followed by 30 min of flocculation at 40 r/min. Thirty minutes were allowed for the settling of flocs. Then the samples were filtered with a 0.45- μm membrane. The filtrates were subjected for total organic carbon (TOC) analysis (TOC-5000A, Shimadzu, Japan) and UV scanning (UV-2550, Shimadzu, Japan) at 276 nm to determine the efficiency of coagulation. Each experiment was performed in duplicates.

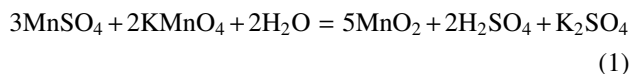
1.3 Reaction of KMnO_4 and MnO_2 with tannic acid

Manganese dioxide was prepared by reducing KMnO_4 with tannic acid and MnSO_4 , respectively. The experimental sequence is described as follows.

Sequence I: the coagulation method was adopted as mentioned in Section 1.2 without AlCl_3 addition in the process of KMnO_4 reaction with tannic acid. In the process of oxidation, KMnO_4 was reduced by tannic acid to MnO_2 which can adsorb tannic acid. $\text{NH}_2\text{OH} \cdot \text{HCl}$ was also used to reduce MnO_2 to eliminate the effect of *in situ* formed MnO_2 on the tannic acid removal in the process of preoxidation by KMnO_4 .

Sequence II: under the same reaction conditions as described in Sequence I, a certain amount of MnSO_4 was added to reduce KMnO_4 to MnO_2 before tannic acid was added. In this process, tannic acid was removed by the adsorption of *in situ* formed MnO_2 only.

KMnO_4 reacts with stoichiometric amount of MnSO_4 according to Reaction (1):



The microtopography of *in situ* formed MnO_2 had been characterized by atomic force microscope (AFM) in previous research (Zhang *et al.*, 2008). The aim of this study was to evaluate the function of *in situ* formed MnO_2 and the role of KMnO_4 in enhancing coagulation.

2 Results and discussion

2.1 Effect of KMnO_4 preoxidation on coagulation with aluminum chloride

As shown in Fig. 1, KMnO_4 preoxidation had an obvious effect on the coagulation of aluminum chloride for tannic acid removal. At any dosage of coagulant adopted in the test, tannic acid removal of KMnO_4 pretreated samples was higher than that without KMnO_4 pretreatment. The

increase of tannic acid removal efficiency was more than 20% for KMnO_4 dosage range 0.75–2.20 mg/L. The tannic acid removal efficiency did not increase significantly with further increase of KMnO_4 . The soluble manganese at all KMnO_4 dosages adopted in the test was lower than the drinking water quality standard (0.1 mg/L). This means that preoxidation by KMnO_4 is an effective method to enhance the coagulation by aluminum chloride.

2.2 Roles of KMnO_4 and MnO_2 on tannic acid removal

KMnO_4 preoxidation obviously increase the tannic acid removal in the process of coagulation by aluminum chloride. One reason might be that KMnO_4 oxidized the tannic acid and made it easier to be removed by coagulation. The other reason might be that *in situ* formed MnO_2 by reducing reaction between KMnO_4 with tannic acid under neutral condition, can adsorb tannic acid successively. In order to verify the hypothesis, the effects of KMnO_4 and MnO_2 on tannic acid removal were investigated individually. In the process of KMnO_4 oxidation, $\text{NH}_2\text{OH} \cdot \text{HCl}$ was used to reduce MnO_2 to eliminate its effect on tannic acid removal and the result is shown in Fig. 2 (curve marked with diamond). Tannic acid removal was attributed to the oxidation of KMnO_4 only. It can be seen that tannic acid could be removed only around 10% as MnO_2 was reduced by $\text{NH}_2\text{OH} \cdot \text{HCl}$, while the maximum removal efficiency of 50% was obtained as MnO_2 was not reduced, as seen from the curve marked with triangle. The higher tannic acid removal efficiency was obtained in the case of MnSO_4 being added to reduce KMnO_4 , as seen from the curve marked with square. The results suggested that the oxidation by KMnO_4 was not an essential factor for tannic acid removal. The adsorption of MnO_2 played the most important role in tannic acid removal. The increase of tannic acid removal efficiency in the process of enhancing coagulation by KMnO_4 originated from the adsorption of MnO_2 which is formed *in situ*.

2.3 Reaction of tannic acid with KMnO_4 and MnO_2

The oxidation of tannic acid by KMnO_4 may cause the change of its structure and thus influence its performance

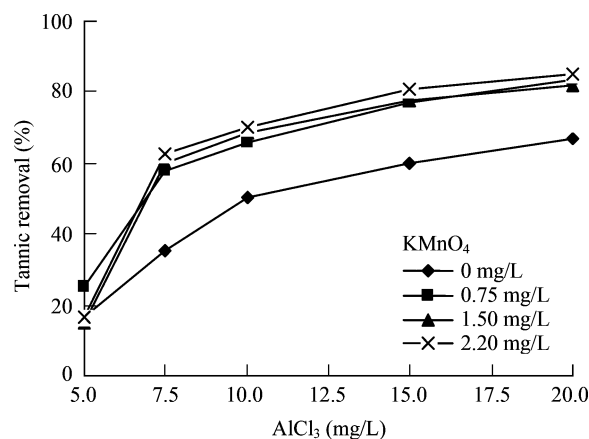


Fig. 1 Effect of KMnO_4 preoxidation on tannic acid removal by coagulation. Raw water quality: tannic acid 25 mg/L; CaCl_2 0.5 mmol/L; pH 5.5–5.7; temperature 18–20°C.

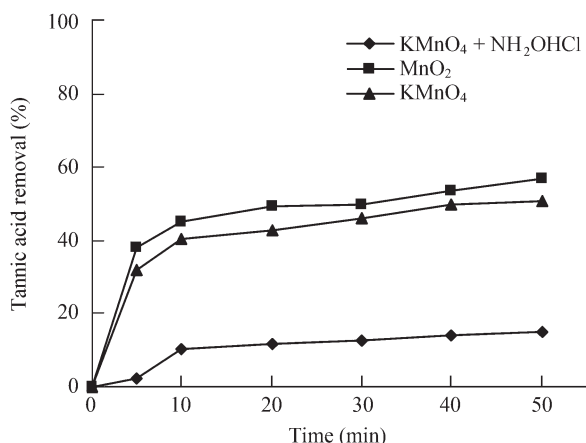


Fig. 2 Comparison of KMnO_4 and the *in situ* formed MnO_2 on tannic acid removal. Preoxidation time: 5 min. Raw water quality: tannic acid 25 mg/L; pH 5.5–5.7; temperature 18–20°C; KMnO_4 2.20 mg/L; AlCl_3 0 mg/L.

on coagulation. The spectrum of tannic acid was measured in the presence of KMnO_4 and MnO_2 to investigate the reactions between them.

Figure 3 shows that KMnO_4 in the solution was completely reduced to form MnO_2 as the dosage of MnSO_4 was increased to 5.85 mg/L which was calculated according to the Eq. (1). While at lower concentrations of MnSO_4 (1.17–4.68 mg/L), KMnO_4 was partially reduced by MnSO_4 and the residual KMnO_4 coexisted with MnO_2 . The low dosage of MnSO_4 , led to the high residual concentration of KMnO_4 and the low concentration of MnO_2 .

The absorbance spectrum of the tannic acid solution in the UV range has two broad bands with maximum absorption wavelength at 210 and 276 nm (Fig. 3). The oxidation of KMnO_4 caused a perceptible change in the spectrum of tannic acid as seen from the curve marked with a circle. The maximum absorbance at 276 nm shifted to 269 nm, while the maximum absorbance at 210 nm did not change during the oxidation. The variation of absorbance at 276 nm may be caused by the partial oxidation of tannic acid by KMnO_4 .

Under acidic condition, KMnO_4 exhibited a strong

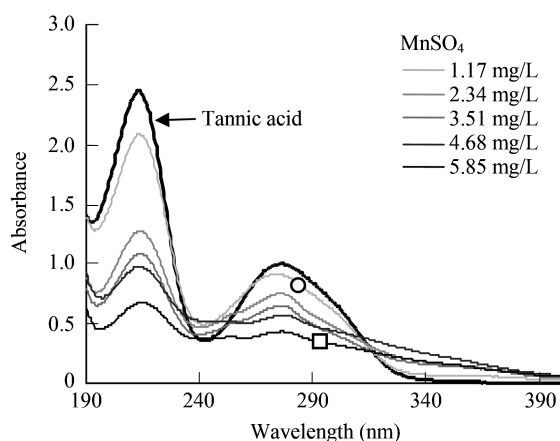
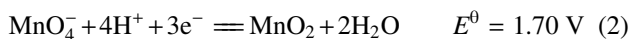


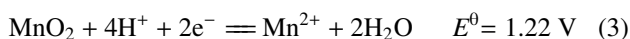
Fig. 3 Effect of KMnO_4 and MnO_2 on absorbency spectrum of tannic acid. Reaction time 35 min; KMnO_4 3.63 mg/L; AlCl_3 0 mg/L. Raw water condition: tannic acid 25 mg/L; pH 5.5–5.7; temperature 18–20°C.

oxidative characteristics and the semi-reaction is shown as Reaction (2).



While at pH 5.5 as adopted in this experiment, the oxidation potential of KMnO_4 decreased to 1.28 V which was calculated according to Nernst formula with an assumption that other ions being at thermodynamic normal state. The decrease of oxidation potential of KMnO_4 at high pH caused the partial oxidation of tannic acid and induced a slight variation in its structure.

The addition of MnO_2 did not cause the shift of maximum absorbance of tannic acid at 210 and 276 nm, as seen from the curve marked with a square. While the base line of the spectrum is increased. It is speculated that MnO_2 can not oxidize tannic acid because the normal oxidation potential of MnO_2 is lower compared with KMnO_4 . The semi-reaction is shown as Reaction (3).



At pH 5.5, the oxidation potential of MnO_2 is 0.57 V, calculated according to Nernst formula which assumed that other ions being at thermodynamic normal state. The variation of spectrum correlated with the reaction of tannic acid with MnO_2 may be attributed to the complex reaction occurred between the two reactants. The issue was further inferred from the low concentration of the soluble manganese (0.56 mg/L) in the filtered solution at the point of MnSO_4 being added up to 5.85 mg/L.

In order to further verify the speculation mentioned above, tannic acid removal and TOC removal were analyzed and the results are shown in Fig. 4. The additive ratio of MnSO_4 and KMnO_4 is similar to Fig. 3. It can be seen that the same trend for tannic acid and TOC removal was observed. This means that KMnO_4 can not oxidize tannic acid to form some new molecules because the new oxidative products of tannic acid do not have the same adsorptive properties with tannic acid. The divergence may be emerged for both TOC and tannic acid removal if the tannic acid was broken down to small molecules during the process of oxidation by KMnO_4 .

With low MnSO_4 concentration and high residual KMnO_4 , tannic acid and TOC removal efficiencies were low. However, tannic acid and TOC removal efficiency increased with the increase of MnO_2 concentration. This is further verified that the oxidation of KMnO_4 is not the only factor for tannic acid removal, while the adsorption by MnO_2 formed *in situ* may play the most important role in tannic acid removal.

2.4 Complexation model of tannic acid with MnO_2

KMnO_4 oxidation of tannic acid or MnO_2 reacting with tannic acid usually accompany the variation of pH. As seen in Fig. 5, the pH value increases with the increase of KMnO_4 . The presence of Ca^{2+} has no effect on the variation of pH. When KMnO_4 was completely reduced by MnSO_4 to form MnO_2 , a similar trend was observed. But the pH value of the solution is higher than tannic acid solution in the case of KMnO_4 oxidation. The increase of pH

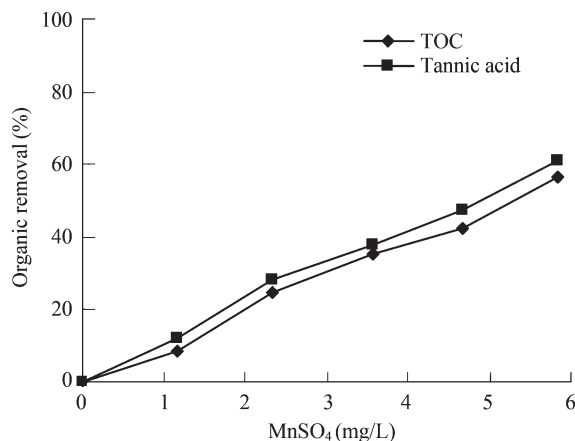


Fig. 4 Effect of KMnO_4 and MnO_2 on organic removal. Reaction time: 35 min; AlCl_3 0 mg/L; KMnO_4 3.63 mg/L. Raw water conditions: tannic acid 25 mg/L; pH 5.5–5.7; temperature 18–20°C.

value in tannic acid solution with the presence of KMnO_4 and MnO_2 may be originated from the complex reaction of MnO_2 with tannic acid. Mainly surface complex-ligand exchange reactions are considered by many researchers as the mechanism of NOM adsorption on iron oxide or aluminum oxide surfaces (Tipping, 1981; Gu *et al.*, 1994; Lai *et al.*, 2002). An increase of pH usually accompanies the adsorption reaction, indicating that NOM replaces hydroxyls on iron oxide surfaces. The same complex model was used to describe the complex reaction occurred between MnO_2 and tannic acid. In aqueous systems, the hydrated manganese oxide surface sites behave like diprotic acids, with three potential species: $\equiv\text{MnOH}_2^+$, $\equiv\text{MnOH}$ and $\equiv\text{MnO}^-$. The replacement of surface-coordinated H_2O or OH^- groups from MnOH_2^+ or MnOH by anionic functional groups of tannic acid (i.e., carboxyl and hydroxyl groups) results in the site-specific tannic acid adsorption onto oxide surfaces, as shown in the following Reactions (4) and (5) (Gu *et al.*, 1994; Edwards *et al.*, 1996; Chang *et al.*, 1997):



Therefore, it can be inferred that some organics in natural water which can be oxidized by KMnO_4 to form

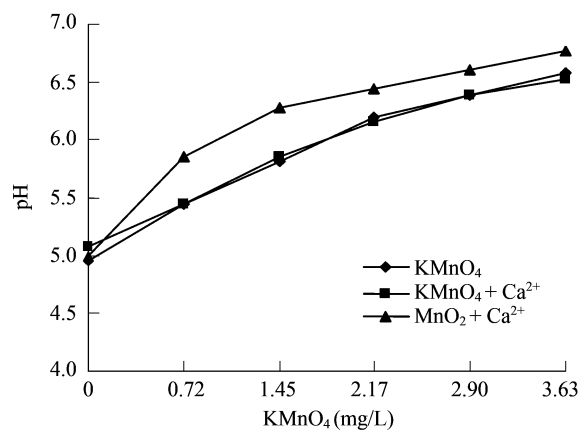


Fig. 5 Effect of KMnO_4 and MnO_2 on pH variation of tannic acid solution. Reaction time: 35 min; AlCl_3 0 mg/L. Raw water quality: tannic acid 25 mg/L; pH 5.5–5.7; temperature 18–20°C.

organic acid may be beneficial for further adsorption by MnO_2 as shown in Reactions (4) and (5).

The complex reaction between MnO^- and RCOO^- may be impossible because of the electrostatic repulsion. While under weak acid or neutral pH condition, MnO_2 mainly existed in the form of $\equiv\text{MnO}^-$ (Ulrich and Stone, 1989) and tannic acid is in the form of RCOO^- . In the presence of cations such as Ca^{2+} , it may serve as a bridge between MnO^- and RCOO^- . Colthurst and Singer (1982) reported that due to the negative charge of both manganese dioxide and humic substances, manganese dioxide did not appreciably adsorb humic substances, except when Ca^{2+} was present. Chena and Yehb (2005) obtained similar results that algae removal efficiency was increased in the presence of Ca^{2+} compared to MnO_2 system without Ca^{2+} . The influence of Ca^{2+} on tannic acid removal was investigated and the results are shown in Fig. 6.

It can be seen that Ca^{2+} played an important role on tannic acid removal in the process of adsorption by MnO_2 formed *in situ*. The presence of Ca^{2+} significantly enhanced tannic acid removal, whilst the oxidation of tannic acid by KMnO_4 was not affected by the presence of Ca^{2+} .

The effect of Ca^{2+} on tannic acid removal can, first, be attributed to the decrease of surface charge of MnO_2 . The zeta potential of aqueous MnO_2 with and without the presence of 0.3 mmol/L Ca^{2+} was measured to be -4.90 mV and -13.58 mV, respectively. At pH 5.5, manganese oxide carried negative charge and existed with the potential species of $\equiv\text{MnO}^-$ as mentioned above (Ulrich and Stone, 1989). Tannic acid also carried negative charge. Ca^{2+} may serve as bridge to bind the two negatively charged surfaces together (Perez-Benito, 2003). In addition, the particles of MnO_2 which produced by KMnO_4 *in situ* reduction are very small and the average diameter of particles is less than 100 nm. Ca^{2+} can accelerate the coagulation of manganese dioxide formed *in situ* and to form the precipitate. This can be supported by the AFM picture of MnO_2 formed *in situ* (Fig. 7) (Zhang *et al.*, 2008). Then tannic acid was wrapped in the precipitation of manganese dioxide and co-precipitated with it. This can be further supported

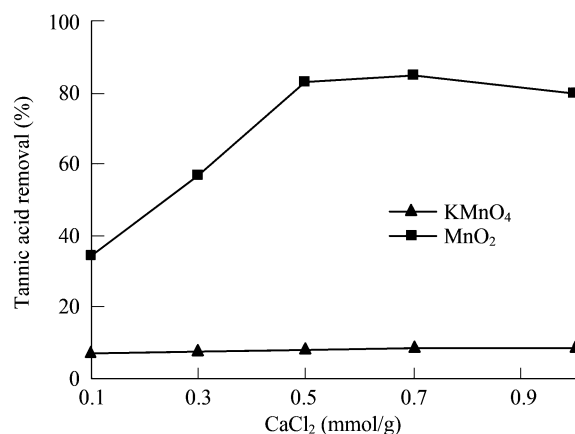


Fig. 6 Effect of Ca^{2+} on tannic acid removal. Conditions: extraction time: 35 min; KMnO_4 3.63 mg/L; AlCl_3 0 mg/L. Raw water quality: tannic acid 25 mg/L; pH 5.5–5.7; temperature 18–20°C.

by the correlation of tannic acid removal with the dosage of Ca^{2+} . When the concentration of Ca^{2+} is low, the influence of compressing double electric layer of colloid caused by Ca^{2+} is limited, MnO_2 formed *in situ* can not be coagulated to form precipitate, and tannic acid removal efficiency is low (Fig. 6). When Ca^{2+} concentration was 0.5 mmol/L, the coagulation with particles of MnO_2 formed *in situ* happened and the tannic acid removal efficiency is increased notably.

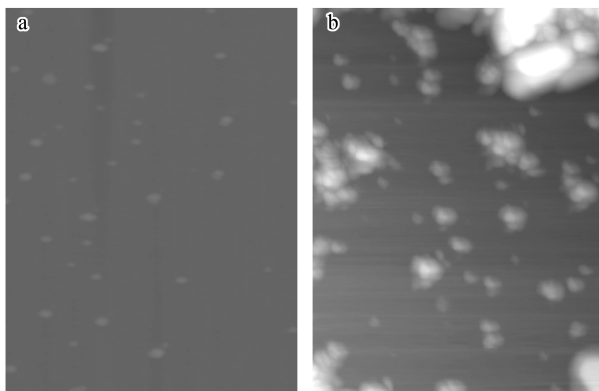


Fig. 7 Microtopography of *in situ* formed MnO_2 prepared with different co-ions. (a) image of MnO_2 formed *in situ* with CO_3^{2-} ; (b) Image of *in situ* formed MnO_2 with Ca^{2+} . CO_3^{2-} : 0.1 mol/L; Ca^{2+} : 0.1 mol/L; scan range: $1.5 \mu\text{m} \times 1.5 \mu\text{m}$ (Zhang *et al.*, 2008).

3 Conclusions

Preoxidation by KMnO_4 in the coagulation process of aluminum can significantly enhance the tannic acid removal. The oxidation of KMnO_4 alone is not the essential factor for tannic acid removal, but its reduction product (*in situ* formed MnO_2) under weak acid condition played an important role for tannic acid removal.

Complex reaction occurred between MnO_2 and tannic acid. Under weak acid condition, Ca^{2+} can serve as a bridge to bind the two negatively charged surfaces of MnO_2 and tannic acid together, and play an important role in tannic acid adsorption by MnO_2 .

Acknowledgments

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