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Analysis of the Causes of Excessive Manganese and Discussion on Treatment Measures in a Waterworks in Cangnan County

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Abstract

Excessive manganese in the effluent of a waterworks in Cangnan County not only leads to sensory abnormalities of drinking water but also poses a potential threat to human health, which has become an urgent water quality problem to be solved. In this study, flame atomic absorption spectrophotometry was adopted to determine the manganese concentration in water samples at each treatment stage, so as to evaluate the actual effect of different manganese removal processes. Aiming at the problem of excessive manganese in raw water, the waterworks optimized the conventional water treatment process by taking measures such as strengthening pre-chlorination and adding potassium permanganate composite salt. The results showed that both measures could effectively oxidize soluble divalent manganese into insoluble tetravalent manganese, which was then intercepted and removed by the filter, and the manganese content in the final effluent was stably controlled below the limit value of 0.1mg/L specified in GB 5749-2022. This study not only effectively solved the problem of excessive manganese in the waterworks but also provided a practical and feasible technical reference for the treatment of excessive manganese in reservoir water sources of similar waterworks in southern China.

Keywords: Excessive Manganese in Water; Reservoir Water Source; Pre-Chlorination; Potassium Permanganate Composite Salt; Manganese Removal Technology

1. Introduction

The "Sanitary Standards for Drinking Water" (GB 5749-2022) implemented in China clearly stipulates that the limit value of manganese in drinking water is 0.1mg/L (State Administration for Market Regulation of the People's Republic of China, 2022). Manganese is a trace element necessary for the human body, but long-term intake of water with excessive manganese content will cause serious harm to the human body, and also lead to sensory quality problems of water body. In terms of human health hazards, excessive manganese mainly damages the nervous system, blood system, respiratory system and digestive system of the human body, and even causes manganese poisoning in severe cases, showing symptoms such as muscle spasm, tremor, bradykinesia, anemia, bronchitis, and emotional instability (Cheng et al., 2021; Li, 2022). In terms of water body sensory quality, excessive manganese will cause color, odor and taste abnormalities of tap water, and even form brown precipitates in the water pipeline, which affects the normal use of water by residents. Therefore, effective control of manganese content in drinking water is an important part of waterworks to ensure water supply safety.

A waterworks in Cangnan County, Wenzhou City, with a daily water supply capacity of 20,000 tons, is an important urban water supply facility in the southern part of Cangnan County. The water treatment process adopted by the waterworks is a conventional process of folded plate-inclined tube coagulation and sedimentation + valveless filter filtration + sodium hypochlorite disinfection. The raw water is taken from Tiechang Reservoir and Yunzhe Reservoir in the jurisdiction. Since the summer of 2023, the water quality monitoring data of the waterworks showed that the manganese content in the effluent exceeded the standard seriously, which directly threatened the water supply safety of the residents in the water supply area. Through on-site investigation and sampling analysis, it was found that the main reason for the excessive manganese in the effluent was the serious manganese pollution of the two reservoir water sources, which was closely related to the local geological conditions and seasonal environmental changes.

Aiming at the problem of excessive manganese in the raw water of the reservoir, this study carried out a systematic analysis on the causes of excessive manganese in the water source, and tested and optimized different manganese removal processes on the basis of the original water treatment process of the waterworks. By determining the manganese concentration in water samples at each treatment stage with flame atomic absorption spectrophotometry, the optimal manganese removal process parameters were screened out, and practical and feasible treatment measures were formulated, which realized the stable up-to-standard of manganese content in the effluent of the waterworks. The research results can provide technical reference for the treatment of excessive manganese in similar reservoir water sources in coastal areas of southern China.

2. Test Materials and Methods

2.1. Main Reagents and Materials

Manganese standard sample (1000mg/L, National Institute of Metrology, China, No.: GBW(E) 080157, Batch No.: 21011); Nitric acid (guaranteed reagent, Changshu Zhitang Fine Chemical Co., Ltd.); Experimental water was ultrapure water (18.2MΩ·cm, Sichuan Youpu Purification Equipment Co., Ltd.). All glassware used in the test was soaked in nitric acid solution (1:9, V/V) for 24h, and rinsed with ultrapure water for 3 times before use to avoid manganese contamination.

2.2. Main Instruments and Equipment

AA-6880 flame atomic absorption spectrophotometer (Shimadzu Instruments (Suzhou) Co., Ltd.); Manganese hollow cathode lamp (Shimadzu Corporation); 0.45μm microporous filter membrane (Shanghai Xinya Purification Materials Co., Ltd.); Polyethylene sampling bottle

(500mL, Nanjing Xiangrui Experimental Equipment Co., Ltd.); Digital pH meter (Shanghai Leici Instrument Factory).

2.3. Instrument Working Parameters

In order to ensure the accuracy and precision of manganese content determination, the working parameters of the atomic absorption spectrophotometer were optimized, and the optimal parameters were set as follows: Lamp current 10mA; Determination wavelength 279.5nm; Monochromator slit width 0.2nm; Fuel gas was high-purity acetylene, oxidant gas was compressed air; Fuel gas gauge pressure 0.09MPa, oxidant gas gauge pressure 0.35MPa; Sample injection method was manual continuous sample injection; The measurement mode was absorbance mode.

2.4. Test Operation Steps

2.4.1. Sample Collection and Pretreatment

According to the "Technical Specification for Monitoring of Drinking Water Quality" (HJ/T 91-2002), water samples were collected at the raw water intake, coagulation and sedimentation tank effluent, filter effluent and final effluent of the waterworks (Phase I and Phase II systems). For the determination of dissolved manganese, the water sample was immediately filtered through a 0.45μm microporous filter membrane after collection, and the filtrate was collected in a clean polyethylene sampling bottle. 1.5mL of concentrated nitric acid was added to each liter of filtrate for acidification (to make the $pH < 2$) for fixation, and the sample was stored in a cool and dark place for testing within 24h.

2.4.2. Sample Determination

Before the test, the exhaust system, gas cylinder and atomic absorption spectrophotometer were turned on in turn, and the manganese hollow cathode lamp was installed for preheating for 30min to ensure the instrument was in a stable working state. The manganese standard solution series with mass concentrations of 0.0mg/L, 0.1mg/L, 0.2mg/L, 0.4mg/L, 0.6mg/L and 0.8mg/L were prepared by gradient dilution, and the standard working curve was drawn by determining the absorbance of the standard series under the optimal instrument parameters. Under the same test conditions, the absorbance of the water sample to be tested was determined, and the blank test was carried out simultaneously to eliminate the system error. The mass concentration of manganese in the water sample was calculated according to the standard working curve and the absorbance value of the sample to be tested.

3. Results and Analysis

3.1. Causes of Excessive Manganese in Reservoir Raw Water

The raw water of the waterworks is taken from Tiechang Reservoir and Yunzhe Reservoir. The geological stratum in the surrounding area of the two reservoirs is rich in manganese-containing minerals, and a large amount of manganese ions are deposited at the bottom of the reservoirs for a long time, mainly in the form of stable manganese-containing complexes, which are not easy to be naturally oxidized and released into the water body under normal conditions. However, affected by the high temperature climate in summer, the surface water temperature of the reservoir rises rapidly, the water density decreases, and the obvious thermal stratification phenomenon occurs in the water body, which hinders the convection and exchange of the upper and lower water bodies. The dissolved oxygen in the upper water body cannot be transferred to the bottom of the reservoir, resulting in a serious anoxic environment at the reservoir bottom. Under the anoxic condition, the insoluble tetravalent manganese in the bottom sediment is reduced to soluble divalent manganese, which is released from the sediment and floats up to the upper water body with the water flow, resulting in a sharp increase of manganese content in the raw water of the reservoir.

The water quality monitoring data showed that the manganese content in the raw water of Tiechang Reservoir increased to a maximum of 0.8mg/L in summer, and the manganese content in the raw water of Yunzhe Reservoir was about 0.6mg/L under normal conditions. Due to the low water intake height of Yunzhe Reservoir, it is easily affected by the disturbance of water discharge from the bottom outlet of the reservoir. In mid-September 2023, the manganese content in the raw water of Yunzhe Reservoir further rose to more than 1.0mg/L due to the bottom discharge disturbance, which far exceeded the limit value of drinking water and brought great pressure to the water treatment of the waterworks.

3.2. Analysis of Conventional Manganese Removal Oxidants for Waterworks

The core of chemical oxidation manganese removal technology for waterworks is to select appropriate oxidants to oxidize soluble divalent manganese in raw water into insoluble tetravalent manganese dioxide precipitate, which is then removed by coagulation, sedimentation and filtration processes. Common oxidants available for waterworks include aeration, chlorine dioxide, sodium hypochlorite, ozone and potassium permanganate. The advantages and disadvantages of various oxidants in manganese removal application are analyzed as follows (Table 1).

Table 1. Comparison of advantages and disadvantages of common oxidants for manganese removal in waterworks

Oxidant	Advantages	Disadvantages
Aeration	Low cost, simple operation	Low oxidation capacity, limited manganese removal effect for high-concentration manganese; easy to cause physical disturbance and affect flocculation and sedimentation
Chlorine dioxide	Fast oxidation speed, good manganese removal effect	On-site preparation is required; special equipment is needed; easy to cause excessive chlorite in effluent
Sodium hypochlorite	Easy to store and transport, simple dosing	Only effective under high pH (pH>9.5); long reaction time; easy to cause excessive disinfection by-products and aluminum
Ozone	Ultra-fast oxidation speed, no residual pollution	High cost, need special generation equipment; easy to oxidize manganese to heptavalent state if the dosage is too high
Potassium permanganate	Good oxidation effect, short reaction time (completed in a few minutes); high removal efficiency	The dosage must be accurately controlled; excessive dosage will cause "red water" phenomenon in effluent

3.3. Targeted Manganese Removal Measures and Effect of the Waterworks

The waterworks has two sets of independent coagulation and sedimentation tank systems (Phase I and Phase II), which are respectively responsible for the treatment of raw water from Tiechang Reservoir and Yunzhe Reservoir. According to the different manganese content in the raw water of the two reservoirs, the waterworks adopted targeted manganese removal measures: strengthening the pre-chlorination process for the raw water with low manganese content (Phase I), and adding potassium permanganate composite salt for the raw water with high manganese content (Phase II). The original coagulation, sedimentation and filtration process of the waterworks was not changed, and the manganese removal transformation was completed on the basis of the original process, which realized the advantages of low transformation cost and quick effect.

3.3.1. Manganese Removal Measures and Effect of Phase I Water System (Tiechang Reservoir Raw Water)

The water quality test showed that the total manganese content in the raw water of Tiechang Reservoir was 0.45mg/L, and the dissolved divalent manganese content after filtration was 0.32mg/L. The divalent manganese content was relatively low, so it was decided to adopt the measure of strengthening the pre-chlorination process in the Phase I coagulation tank to realize manganese removal, with sodium hypochlorite as the oxidant. The oxidation reaction formula of sodium hypochlorite and divalent manganese is as follows: $Mn_2^{+}+ClO^{-}+H_2O=MnO_2\downarrow+Cl^{-}+2H^{+}$

It can be seen from the reaction formula that the reaction produces H+ ions, which will inhibit the progress of the oxidation reaction. Therefore, the reaction can be accelerated in an alkaline environment. Based on the reaction principle and the actual water quality of the waterworks, the key process parameters of strengthened pre-chlorination were optimized as follows:

(1) Determination of pre-chlorination dosage: According to the reaction stoichiometric ratio, 1mol of divalent manganese requires 1mol of sodium hypochlorite for oxidation. Combined with the actual divalent manganese content of 0.32mg/L in the raw water, and considering the consumption of sodium hypochlorite by other reducing substances in the water, the effective chlorine dosage of pre-chlorination was set to 0.5mg/L, that is, the dosage of 10% sodium hypochlorite solution was increased to 5kg per 1000 tons of water.

(2) Adjustment of raw water pH value: Relevant literature shows that the oxidation reaction of sodium hypochlorite and divalent manganese can proceed rapidly when the pH value is above 9.5 (Li et al., 2023). However, considering that the excessive pH value of the effluent will lead to the problem of excessive aluminum, the raw water pH value was adjusted to 8.5 by adding alkali in advance, which provided a weak alkaline environment for the oxidation reaction and avoided the secondary water quality problem caused by excessive pH value.

(3) Strengthening water quality monitoring: The content of disinfection by-products and aluminum in the filter effluent and final effluent was regularly determined to ensure that all water quality indicators meet the standard while removing manganese.

After the implementation of the above measures, the water quality monitoring results showed that the manganese content in the filter effluent of the Phase I water system decreased from 0.45mg/L of raw water to below 0.05mg/L, which was far lower than the limit value of 0.1mg/L specified in GB 5749-2022, and the disinfection by-products and aluminum content in the effluent were all within the standard range. The strengthened pre-chlorination process achieved an ideal manganese removal effect, and the operation was simple and the cost was low, which was suitable for the long-term operation of the Phase I water system.

3.3.2. Manganese Removal Measures and Effect of Phase II Water System (Yunzhe Reservoir Raw Water)

The water quality test showed that the total manganese content in the raw water of Yunzhe Reservoir was as high as 1.10mg/L, and the dissolved divalent manganese content after filtration was 0.81mg/L. The divalent manganese content was much higher than that of the Phase I raw water, and the strengthened pre-chlorination process could not achieve the standard manganese removal effect. Therefore, it was decided to adopt the measure of adding potassium permanganate composite salt for manganese removal. The mass ratio of potassium permanganate in the composite salt was 50%, which had the advantages of high oxidation efficiency and easy dosing. The oxidation reaction formula of potassium permanganate and divalent manganese under neutral conditions is as follows: $2KMnO_4+3Mn_2^{+}+2H_2O=5MnO_2\downarrow+2K^{+}+4H^{+}$

According to the reaction formula, the theoretical dosage of potassium permanganate is 1.91 times the mass concentration of divalent manganese. Considering that the manganese dioxide precipitate generated in the reaction has an adsorption effect on divalent manganese, and the organic matter in the raw water will consume part of potassium permanganate, the actual dosage of potassium permanganate is generally 1.5~2.5 times the mass concentration of divalent manganese (Ma et al., 2023). In order to determine the optimal dosage of potassium permanganate composite salt, the manganese oxidation stirring test was carried out in the laboratory first, and then the industrial application was carried out according to the test results. The specific implementation measures are as follows:

(1) Laboratory stirring test to determine the optimal dosage: Potassium permanganate composite salt solution with a certain concentration was prepared, and 1L of raw water of Yunzhe Reservoir was taken in each beaker. The potassium permanganate composite salt solution was added to each beaker according to 3~5 times the mass concentration of divalent manganese (0.81mg/L), and stirred at a constant speed for 2min to make it fully react. The reaction solution was filtered with a 0.45μm microporous filter membrane, and the manganese content in the filtrate was determined. The test results showed that when the dosage of potassium permanganate composite salt was 3.6 times the mass concentration of divalent manganese (i.e., 2.9mg/L), the manganese content in the filtrate was the lowest and met the standard. Therefore, the optimal dosage of potassium permanganate composite salt was determined to be 2.9kg per 1000 tons of water.

(2) Determination of reasonable dosing point: The dosing point of potassium permanganate composite salt was selected at the front end of the folded plate reaction tank (before adding alum).

When the pH value of the raw water is above 6.5, the oxidation reaction of potassium permanganate and divalent manganese can be completed in a few minutes (Li et al., 2023). The folded plate reaction tank has a good mixing effect, which can make the potassium permanganate composite salt fully contact and react with the raw water, and the manganese dioxide precipitate generated by the reaction can be adsorbed and flocculated with the alum floc, which is convenient for subsequent sedimentation and filtration removal.

(3) Dosing method and operation control: The potassium permanganate composite salt solution with a certain concentration was prepared in the chemical dosing tank of the waterworks, and a digital metering pump was used to add the composite salt into the raw water pipe according to the raw water flow rate and the optimal dosage. The water sample was taken from the second or third row of the folded plate reaction tank for manganese content determination, and the dosing amount was adjusted in real time according to the test results. If the filtrate showed purple-red, it indicated that the dosage of potassium permanganate composite salt was excessive, and the dosage should be reduced immediately to avoid the "red water" phenomenon in the effluent. At the same time, the normal operation of the valveless filter was ensured, and the backwashing frequency of the filter was appropriately increased to prevent the manganese dioxide precipitate from blocking the filter material and affecting the filtration effect.

(4) Key points of process operation: In the process of adding potassium permanganate composite salt for manganese removal, four key operation points should be grasped: ① Control the turbidity of the filter effluent to be not more than 0.5NTU to ensure that the manganese dioxide precipitate is fully intercepted; ② If there are reducing interfering substances such as sulfide and ammonia in the raw water, sodium hypochlorite should be added first to remove them to avoid affecting the manganese removal effect; ③ Strengthen the continuous monitoring of manganese content in the raw water, folded plate reaction tank effluent and filter effluent, and feed back the monitoring results in a timely manner to adjust the dosing amount; ④ Ensure that the pH value of the raw water is maintained at 6.5~7.5 (neutral range), so as to ensure that the oxidation reaction can proceed normally and generate manganese dioxide precipitate.

After the implementation of the above measures, the water quality monitoring results showed that the manganese content in the filter effluent of the Phase II water system decreased from 1.10mg/L of raw water to below 0.05mg/L, which met the limit requirement of GB 5749-2022 for manganese content in drinking water. The manganese removal effect was stable and ideal, and no "red water" phenomenon and other secondary water quality problems occurred in the effluent, which realized the safe and stable water supply of the Phase II water system.

4. Conclusions and Recommendations

4.1. Conclusions

(1) The main reason for the excessive manganese in the raw water of Tiechang Reservoir and Yunzhe Reservoir in Cangnan County is the combined effect of local geological conditions and seasonal environmental changes. The reservoir bottom is rich in manganese-containing sediments,

and the high temperature in summer leads to thermal stratification of the reservoir water body and anoxic environment at the bottom, which makes the insoluble tetravalent manganese be reduced to soluble divalent manganese and released into the water body, resulting in a sharp increase of manganese content in the raw water.

(2) Aiming at the different manganese content in the raw water of the two reservoirs, the waterworks adopted targeted manganese removal measures on the basis of the original conventional water treatment process, and achieved ideal manganese removal effects. For the raw water with low divalent manganese content (≤0.32mg/L), the strengthened pre-chlorination process (effective chlorine dosage 0.5mg/L, raw water pH adjusted to 8.5) can effectively oxidize divalent manganese, and the manganese content in the effluent is stably controlled below 0.05mg/L; for the raw water with high divalent manganese content (>0.8mg/L), the method of adding potassium permanganate composite salt (optimal dosage 2.9mg/L) can achieve efficient manganese removal, and the manganese content in the effluent is also reduced to below 0.05mg/L.

(3) The core of chemical oxidation manganese removal technology for waterworks is to oxidize soluble divalent manganese into insoluble tetravalent manganese dioxide precipitate, which is then removed by the conventional coagulation, sedimentation and filtration processes. The key to the selection of oxidant is to adapt to the actual water quality of the waterworks and the existing process conditions. Potassium permanganate and sodium hypochlorite are suitable for the manganese removal transformation of small and medium-sized waterworks with the advantages of simple operation, low cost and quick effect.

(4) Flame atomic absorption spectrophotometry has the advantages of high determination accuracy, good precision and simple operation, which can accurately determine the manganese content in water samples at each treatment stage of the waterworks, and provide reliable data support for the optimization of manganese removal process parameters and the evaluation of manganese removal effect.

4.2. Recommendations

(1) Strengthen the early warning monitoring of raw water quality: The waterworks should establish a long-term monitoring mechanism for the manganese content in the reservoir raw water, especially strengthen the water quality monitoring in summer and autumn when the manganese content is easy to exceed the standard, and master the change law of manganese content in the raw water in time. At the same time, the water intake height of the reservoir should be optimized to avoid taking water from the bottom water body with high manganese content as far as possible.

(2) Optimize the manganese removal process parameters dynamically: The dosage of oxidants (sodium hypochlorite, potassium permanganate composite salt) should be adjusted dynamically according to the real-time change of manganese content in the raw water and the water quality indicators such as pH value and organic matter content, so as to ensure the manganese removal effect and avoid the secondary water quality problems caused by excessive dosage.

(3) Strengthen the daily operation management of the water treatment process: For the filter, the backwashing frequency and backwashing time should be adjusted according to the actual filtration effect to ensure that the filter material is clean and the manganese dioxide precipitate is

fully intercepted; for the chemical dosing system, the accuracy of the metering pump should be checked regularly to ensure the accurate control of the oxidant dosage.

(4) Carry out the research and development of combined manganese removal technology: On the basis of the existing chemical oxidation manganese removal technology, the waterworks can carry out the research and application of combined manganese removal technology such as "oxidation + adsorption" and "biological manganese removal", further improve the manganese removal efficiency and stability, and provide a more diversified technical scheme for the treatment of excessive manganese in raw water.

(5) Strengthen the protection of reservoir water sources: Combined with the local environmental governance, the pollution control of the surrounding areas of the reservoir should be strengthened, the input of manganese-containing pollutants into the reservoir should be reduced, and the ecological environment of the reservoir water source should be improved from the source, so as to reduce the occurrence probability of excessive manganese in the raw water.

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