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Sources and Treatment Methods of Excessive Manganese Ion in Groundwater in A Certain Area

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ABSTRACT

Trace element manganese is an essential element for human body, but the high concentration of manganese will adversely affect human health and all aspects of daily production and life. Elevated levels of manganese directly affect the color of the water, making it more prone to discoloration when used to wash clothes or dishes. Prolonged exposure to this water may cause organ damage. The groundwater in the study area is sampled and tested, and the test data is analyzed. The main results are as follows: the groundwater manganese ions in the study area exceed the standard, and the concentration of manganese ions in the southwest mountainous area is higher than that in other areas. In southwest China, due to the planting of a large number of tea trees, the main source of manganese in groundwater is manganese-containing fertilizer, and sewage recovery and treatment should be considered in combination with slope rainwater recovery equipment. In other fields, the manganese in groundwater is mainly from domestic sewage. The combined treatment of manganese ions in groundwater by chemical method and contact oxidation method is considered.

KEYWORDS

Rural area, groundwater pollution, manganese removal.

1. INTRODUCTION

At present, groundwater pollution sources are in a multi-faceted state. It is mainly manifested in the following aspects: industrial waste gas, automobile exhaust and other pollutants pollute the atmosphere, fall to the ground with rainfall, and then penetrate into the groundwater system to cause pollution; Urban drainage facilities are old, pipe networks are broken, resulting in sewage into the underground; In rural areas, sewage facilities are backward, and water for production and domestic use is directly discharged into the ground or rivers and permeated into groundwater[1]. Various mining pits, mechanized Wells and seepage Wells also have a great impact on groundwater. Almost all natural rocks contain manganese ions, after differentiation and denudation, manganese is released from the primary minerals, and then combined with oxygen-containing particles to form MnO_2, $MnCO_3$ and other secondary minerals. When the soil pH value is lower than 5.5, the secondary manganese minerals dissolved into soluble manganese into the soil, and then into the groundwater system, resulting in groundwater pollution. In addition to natural factors, human factors lead to a large number of manganese elements into the groundwater system, with the continuous progress of science and technology, human life appears a large number of additives, chemicals, etc., with wastewater or rainwater into the soil, and then into the groundwater[2].

Foreign research on groundwater manganese removal technology began more than 100 years ago, in the 1870s, Germany built the first manganese removal plant, the treatment process is relatively simple, the raw water after aeration to add oxidant. In the following decades of continuous improvement, in the traditional process to add lime to soften manganese, sodium silicate and other separation of manganese. In the 1940s, McCall and Edwards believed that the manganese filter material on the surface of the filter membrane could treat the divalent manganese ions in water, and on this basis, various oxidants were continuously added to carry out research[3]. In the 1960s, Finland began to study the formation manganese removal process, which injected water containing dissolved oxygen into the groundwater system, changed the reducing environment of the underground system into an oxidizing environment, and formed a closed environment, and manganese was oxidized and adsorbed in the formation of the oxidizing environment during pumping. So far, the biological method to remove manganese in foreign countries has been continuously studied and demonstrated, in addition, the biofilm method is also the focus of foreign experts[4].

It is common in China that the concentration of manganese ions in groundwater exceeds the standard, and the concentration of iron and manganese ions in groundwater in North China Plain is generally excessive. The research of manganese removal technology in groundwater in China can be traced back to the 1950s. Just after the founding of New China, the relevant science and technology departments in China have established the topic of "iron and manganese removal from groundwater". The techniques of manganese removal in China include air natural oxidation, contact oxidation, biological oxidation and chemical oxidation.

2. STATUS OF MANGANESE POLLUTION IN REGIONAL GROUNDWATER

2.1. Single factor index evaluation method

Water quality evaluation methods are divided into two categories. One is based on the measured values of physical and chemical parameters of water quality. The other kind of biological evaluation method is based on the relationship between aquatic species and water quality. The evaluation method of physical and chemical parameters is mostly used. At present, the main water quality evaluation methods include single factor index evaluation method, principal component analysis method, comprehensive pollution index method, etc. Different water quality assessment methods have different characteristics and functions in water quality assessment. In this paper, single factor index evaluation method and comprehensive pollution index method are used to evaluate the water quality in the study area.

The single factor index evaluation method is to compare the actual result of each monitored project with the standard value stipulated by the state, and then select the category of the worst single evaluation project in all the monitored pollution projects as the evaluation of water quality. This method is simple and practical, can directly determine the water quality status, is currently the most used water quality evaluation method. The formula of single factor standard pollution index is[5]:

$$P_i = \frac{C_i}{S_i} \tag{1}$$

In the formula: Pi represents the standard index of a single water quality parameter i; Ci represents the measured concentration value of pollution item i, mg/L; Si represents the maximum allowable concentration of water quality parameter i in the water body, mg/L.

2.2. Data processing and analysis

The 26 groundwater sources in the study area will be numbered 1-26, and the water samples of the water sources will be submitted for inspection. Since the southern part of the study area is mountainous and hilly, and the northern part is plain, the study area is divided into two regions: the northern plain area from 1 to 12, the southern mountain area from 13 to 25, and the industrial agglomeration area from 26. The test results are shown in Table 1.

Table 1. Measured data of iron and manganese ions in groundwater

Numbered	Manganese(mg/L)	Numbered	Manganese(mg/L)
1	0.67	14	0.93
2	0.53	15	0.78
3	0.30	16	2.77
4	0.82	17	3.21
5	0.23	18	1.98
6	0.48	19	2.42
7	0.47	20	1.56
8	0.51	21	1.06
9	0.65	22	1.62
10	0.77	23	1.30
11	0.29	24	1.31
12	0.67	25	1.33
13	0.93	26	1.68

The data presented in Table 1 indicates an overall excess of manganese ions within the groundwater system in the study area, with a noticeable higher concentration observed in the southern region compared to the northern region. Iron ion levels remain predominantly within normal ranges, although there are isolated instances of excessive iron ions.

The single factor index method was used to calculate the manganese ion content, and the results were shown in Table 2.

Table 2. Results of Single Factor Evaluation of Iron and Manganese

Numbered	P	Numbered	P
1	6.70	14	9.30
2	5.3	15	7.80
3	3.00	16	27.70
4	8.20	17	32.1
5	2.30	18	19.80
6	4.80	19	24.2
7	4.70	20	15.6
8	5.10	21	10.60
9	6.50	22	16.20
10	7.70	23	13.00
11	2.90	24	13.10
12	6.70	25	13.30
13	9.30	26	16.80

Combined with Table 1 and Table 2, the water quality categories of each monitoring point in the study area were obtained in the table 3.

Table 3. Study on regional groundwater quality classification

Numbered	Grade level	Numbered	P Grade level
1	IV	14	IV
2	IV	15	IV
3	IV	16	V
4	IV	17	V
5	IV	18	V
6	IV	19	V
7	IV	20	V
8	IV	21	V
9	IV	22	V
10	IV	23	V
11	IV	24	V
12	IV	25	V
13	IV	26	V

According to the results of single factor index evaluation, the groundwater in the study area is up to the drinking water standard. As a rural water supply source, the groundwater status in this area is not optimistic. The water quality in the southern mountainous area is worse than that in the plain area. Comparing the single factor index of different water quality indexes, it can be found that the single factor index of manganese at all monitoring points is significantly higher than that of iron, indicating that manganese is the main pollutant of groundwater in the study area.

The survey area has a dense rural population and backward sewage facilities, and even some remote mountainous and hilly areas have no sewage facilities. Sewage produced by human production and life is discharged into the soil surface or rivers, and even directly into groundwater, resulting in excessive manganese ion concentration. In addition, 50,000 mu of tea trees are planted in this survey area, and the growth of tea trees requires the application of manganese-containing fertilizer and the spraying of manganese sulfate, so a large amount of manganese ions remain on the surface and inside of the soil. The study area is located in the south-north climate transition zone. The climate is humid and the rainfall is abundant. Manganese ions that remain on the surface and inside of the soil seep into the groundwater with rain.

3. DEVELOPMENT OF MANGANESE REMOVAL PROGRAM

3.1. Manganese removal mechanism

Manganese ions in groundwater mainly exist in the form of Mn^{2+}. The current mechanism of manganese removal is to oxidize Mn^{2+} to MnO_2, which is difficult to dissolve, and to treat it by adsorption or filtration. Through extensive access to data, several current manganese removal schemes were compared, and combined with the different levels and sources of groundwater manganese ion pollution in the study area, the appropriate treatment measures were formulated. The processing method is shown in Table 4.

Table 3. Comparison of Groundwater Manganese Removal Programmes

Method	Equipment	Governance effect	Scheme defect
Contact oxidation method	Filter material, filter material tank	The process of manganese removal is long, the removal of manganese is unstable before the formation of filter membrane, and the effect is good after formation.	The treatment time is long and unstable, and the manganese concentration is too large and requires secondary treatment.
Biological oxidation process	Microbial filter	The structure is simple and easy to construct, the processing time is short, and the water output is large	Studies have shown that if the concentration of iron in raw water is low, it may destroy the activity of the filter membrane and affect the process of manganese removal.
Chemical oxidation process	Oxidizer, reaction tank, oxidizer dosing device	Manganese removal is fast and thorough	Oxidants are generally expensive, the dosage is not easy to determine, and there are by-products.

The advantages and disadvantages of these three treatment schemes can be seen directly through comparison. Combined with the actual characteristics of groundwater quality in the study area, if the biological oxidation method is used alone, although the input is less, the technology is complex. In addition, the influence of other components in the groundwater on the biofiltration membrane is unknown, so this method can be abandoned. Manganese removal by contact oxidation alone shows that the maximum treated manganese concentration is 2mg/L. According to Table 3, the manganese ion concentration in some groundwater in the study area exceeds the maximum treated concentration and requires secondary treatment. The combination of chemical oxidation method and contact oxidation method is considered.

3.2. Choice of chemical oxidants

Manganese removal commonly used oxidants are potassium permanganate, chlorine dioxide, sodium suboxide.

3.2.1. Potassium permanganate

Potassium permanganate has strong oxidation, which oxidizes Mn^{2+} in groundwater to MnO_2 brown-black precipitate. The chemical equation is as follows:

$$2KMnO_4+3Mn^{2+}+2H_2O=5MnO_2+2K^++4H^+$$

It can be seen from the chemical reaction formula that 1.92mg potassium permanganate is required for 1mg of manganese in theory, but potassium permanganate, as a strong oxidizing agent, will react with other components in raw water, which may inhibit the chemical reaction and reduce the removal rate of manganese ions. Therefore, manganese dioxide should be removed in time to make the reaction proceed in the forward direction. Manganese dioxide can be removed by adding flocculant to water. The reaction produces hydrogen ions, so the pH of the raw water also affects the removal rate of manganese. The study found that when pH=7.5, the removal rate of manganese was nearly 97%, and when pH=8.5, the removal rate of manganese reached 99%. The pH value in the study area is always between 6.9 and 8.1, and the maximum manganese concentration in groundwater is

2.42mg/L. In this case, the remaining manganese ions after the removal of manganese by potassium permanganate can reach the standard.

3.2.2. Sodium hypochlorite

Sodium hypochlorite has strong oxidation, which also oxidizes Mn2+ to MnO2. The chemical equation is as follows:

$$ClO^{-}+Mn^{2+}+2OH^{-}=MnO_2+Cl^{-}+H_2O$$

According to the chemical equation, 1.24mg sodium hypochlorite is theoretically required for 1mg of manganese. The same as potassium permanganate, flocculant needs to be added to remove manganese dioxide in time to accelerate the reaction. In the case of not adjusting the pH, in the pH range of raw water, the manganese removal rate of sodium hypochlorite is only 60% to 70%, which can not meet the requirements of manganese removal. Therefore, it is necessary to add alkali agents to the raw water to adjust the raw water to an alkaline environment.

3.2.3. Chlorine dioxide

Chlorine dioxide is a yellow-green to orange-yellow gas that is oxidizing and is a safe, non-toxic green disinfectant. The chemical equation for the reaction with manganese ion is as follows:

$$2ClO_2+Mn^{2+}+4OH^{-}=MnO_2+2ClO^{-}_2+2H_2O,$$

$$ClO^{-}_2+2Mn^{2+}+2H_2O=2MnO_2+4H^{+}+Cl^{-}$$

$$2ClO_2+5Mn^{2+}+6H_2O=5MnO_2+12H^{+}+2Cl^{-}$$

It is known that the first step responds faster, and in general engineering, only the first step can be considered in order to pursue efficiency. Therefore, 1mg of manganese requires 2.43mg of chlorine dioxide. In alkaline environment, the removal rate of manganese is 69%~81%.

3.3. Filter material selection

The main components of manganese sand are manganese dioxide, manganese, iron, etc., in a multi-angular shape. Good wear resistance and corrosion resistance. In the early stage of treatment, due to the presence of manganese dioxide, the bivalent manganese in raw water can be adsorbed well, and the adsorption rate is fast. At the same time, manganese dioxide is reduced to manganese trioxide, and there is both chemical adsorption and physical adsorption. In the process of treatment, the adsorption rate is always high. Studies have shown that the adsorption capacity of manganese sand is obviously greater than that of quartz sand and ceramic particles, and manganese sand is stable and efficient as a filter material. Therefore, choose manganese sand as filter material.

When contacted by oxidation alone, the treatment time is long and unstable in areas where the concentration of manganese ions is too high, and the secondary treatment will also cost unnecessary funds. In terms of oxidizing agent, potassium permanganate has the advantage in the treatment of water with high concentration of manganese ions. Therefore, potassium permanganate + manganese sand filtration scheme is used for treatment. In addition, a large amount of potassium permanganate will affect the chroma of the water body, so it is necessary to add powdered activated carbon for treatment.

4. CONCLUSION

(1) On the basis of consulting the water quality reports of previous years, it was found that there was a general excess of manganese ions in the water in the region. On this basis, water is collected for inspection, data is obtained, water quality evaluation is carried out, regional groundwater quality categories are obtained, and sources of manganese ions are analyzed.

(2) After analyzing the feasibility of several manganese removal schemes, a combination of chemical method and contact oxidation method was determined according to the local actual situation, and potassium permanganate was selected as the oxidant and manganese sand as the filter material.

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