Study on purification method of micro-polluted groundwater

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Abstract: The infiltration of surface water makes the groundwater with only iron, manganese and heavy metal elements exceeding the standard be invaded by ammonia nitrogen, nitrate and organic matter, forming compound pollution groundwater, which has attracted extensive attention of scholars at home and abroad. This paper introduces the source and harm of micro-pollutants in groundwater, and expounds the research progress of biological method, adsorption method and contact oxidation method to treat micro-polluted groundwater, which lays a foundation for the selection of micro-polluted groundwater treatment methods.

1. Introduction

Groundwater is one of the sources of water supply in China. In recent years, however, due to the direct discharge of untreated waste water containing harmful chemicals by some industrial enterprises, as well as the entry of pesticides, fertilizers, dyes, hormones and personal care products into the groundwater system[1], the national water quality test found that the main indicators exceeding the standard of groundwater are iron, manganese and "tri-nitrogen", etc. Some monitoring sites found that the content of organic matter and heavy metals such as arsenic exceeded the standard[2]. The resulting complex groundwater pollution caused by different pollutants not only harms human health, but also increases the difficulty of water purification.

2. Types and sources of groundwater micropollutants

2.1. Iron, manganese and heavy metal arsenic

In the natural environment, a large number of high-valence iron oxides are reduced to form soluble low-valence iron salts, which enter the groundwater through ion exchange; A large amount of manganese ions will be released from bedrock after weathering and microbial action, which will be washed into groundwater by rainfall and surface runoff. The man-made reason for the excessive iron and manganese in groundwater is mainly from the waste water discharged by industrial and mining enterprises and companies without timely treatment into groundwater, and the excessive content affects human health[3-4].

Excessive arsenic and other heavy metals can also cause great harm. Arsenic, with an atomic number of 33, comes from crustal weathering, weather changes and microbial activities in the natural environment. It is often present in the form of arsenate, arsenite, arsenate and methylate. In the southern Yangtze River Delta along the Yangtze River, there are many iron and manganese complexes, in which arsenic is symbiosis with existing iron ore. Lead to the presence of arsenic in groundwater[5].

2.2. Ammonia nitrogen and nitrate

In recent years, the problem of river nitrogen pollution has become increasingly serious, because the excessive use of nitrogen fertilizer is the main cause of exceeding the standard of ammonia nitrogen and nitrate in groundwater in northern China[6]. The water irrigation with high ammonia nitrogen content and the application of nitrogen fertilizer in Jinhe irrigation area in northern China improved the ammonium nitrogen concentration invisibly. In Suihua City, treated sewage with still high ammonia nitrogen content was infiltrated into the water recharge through channels without anti-seepage, resulting in excessive ammonia nitrogen content in the water[7-8].

2.3. Organic matter

The common organic matter that pollutes groundwater is mainly humic acid, antibiotic and so on. The presence of humic acid not only increases the difficulty of removing iron and manganese in groundwater, but also affects the absorption of trace elements by human body. The existence of organic matter not only has an important impact on the migration and change of various pollutants in the water body, but also some toxic organic matter is difficult to be biodecomposed. If it is accumulated in the environment or human body for a long time, it will cause serious impact[9].

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3. Groundwater is a pollutant hazard

3.1. Iron, manganese and heavy metal arsenic

Iron and manganese are essential trace elements in human body. But excess iron and manganese will have a great impact on people's production and life. From the physiological point of view, excessive iron accumulation in the body, damage pancreas liver and other organs, induce diabetes, cirrhosis and other diseases, and increase the infection of infectious diseases. Excessive intake of manganese can lead to changes in human organs, causing manganese rickets. Chronic exposure can induce central nervous disorders. In a certain area of Tokyo, Japan, a large number of rickets patients appeared due to long-term drinking of groundwater with excessive manganese. From the production point of view, if the industrial water iron and manganese content is too high, the product quality will be greatly reduced. Excessive iron and manganese in boiler water will affect the heat transfer efficiency of boiler and affect normal production. In the textile industry, excess iron and manganese will adhere to the textile and cause clothing discoloration. When the dissolved oxygen content in water containing excessive iron and manganese elements is high, it will cause the breeding of iron and manganese bacteria and accelerate pipeline corrosion. In the groundwater with high arsenic, there is a reduction environment accompanied by high iron and manganese, and the reduction environment of iron and manganese bivalent can promote the transfer of arsenic. Drinking water containing arsenic for a long time not only causes skin cancer, lung cancer and kidney cancer, but also causes nervous disorders, muscle weakness and loss of appetite.

3.2. Ammonia nitrogen and nitrate

Due to the oxidation of ammonia nitrogen, the concentration of dissolved oxygen in water is reduced, resulting in smelly water, and the decline of water quality affects the survival of aquatic plants. If the content of nitrite nitrogen and nitrate nitrogen in drinking water exceeds the standard for a long time, it will lead to methemoglobinemia and severe hypoxia. Nitrite nitrogen and nitrate nitrogen in water are important culprits in the production of nitrosamines, the "three" substances.

3.3. Organic matter

Common organic pollutants (pops) such as bisphenol A, antibiotics. Plastic products in the human production and living in A large number of dependent, ringing in the shadow of the external conditions, the plastic is broken into particle size less than 5 mm of plastic debris in the process of bisphenol A and other additives will be released into the environment, ultimately through feeding concentration to the human body, not only affects the human body endocrine system, also cause certain influence to the normal body functions. Bisphenol A (bpa) will inhibit the growth of animals and plants, also affect the soil microbial breeding. Antibiotics are new pollutants in water treatment is a common material, including tetracycline for high quality and low price as the most widely used type of the antibiotics. Tetracycline into the water, however, by inhibiting the embedded objects inside the chloroplast DNA to inhibit plant growth and development, due to the toxicity of raw grain, can cause toxicity to human body damage, etc. Nano zero-valent iron are often used to restore the degradation of organic pollutants.

4. Micro-polluted water treatment methods

4.1. Adsorption

Common adsorption filter materials are activated carbon, volcanic rock, zeolite and so on. The adsorption selectivity of activated carbon is poor; the content of hydroxyl on the surface of unmodified volcanic rock is less, and the removal effect of iron and manganese ions is not good enough. The modified zeolite has a greater adsorption capacity for pollutants.

Ma Wenjie with natural zeolite as the carrier, such as the preparation of the slightly polluted groundwater Fe-Mn can be synchronized to remove ammonia nitrogen of composite materials. For iron, manganese and ammonia nitrogen saturated adsorption capacity of 215.1 mg.g⁻¹, 23.6 mg.g⁻¹ 7.6 mg.g⁻¹. Priority selectivity of zeolite adsorption removal of ammonia nitrogen in water, water Fe Mn ions were attached on the surface of the zeolite, manganese by two oxygen adsorption and catalytic oxidation. Xiao-tian Liu research found that formed by the microorganisms of iron and manganese oxides on the As (III) and As (V) maximum adsorption capacity, respectively is 563.24 mu g/g and 303.47 g, both has good adsorption performance. Does not affect the filter under higher water concentration of iron and manganese removal effect, arsenic concentration of effluent can reach the national standard. Zhang ying to explore the modified live such as carbon removing Fe-Mn best preparation process of groundwater, found that when sodium hydroxide concentration 2 mol/L, the modification time 4 h, modification temperature 60 °C, modification of activated carbon adsorption manganese iron works best. Yao Xuanzhu with hanging film after the success of iron and manganese compound oxide slightly polluted underground water filter material to remove the typical organic matter bisphenol A and tetracycline. One study found that, 601.70 mg, 149.45 mg bisphenol A tetracycline 40 g iron manganese oxides can be effective adsorption removal filter material.

4.2. Biological method

Only the groundwater source with excessive iron and manganese was formed into compound micro-polluted groundwater due to the infiltration of surface water containing ammonia nitrogen and organic matter. The
research on biological contact oxidation process for treating compound groundwater has become a new hot spot.

The new theory of biological removal of iron and manganese was proposed by the project team of Northeast Design and Research Institute of China Municipal Engineering in the early 1990s. Due to the infiltration of surface water containing ammonia nitrogen and organic matter and other phenomena, compound micro-polluted groundwater has been formed. The research on the treatment of compound groundwater by biological contact oxidation process has become a new hotspot.

Ji Xuemei et al. conducted 42d membrane hanging on the biological filter and found that the effect of iron and manganese removal by biological method was stable under the conditions of $5 \text{mg/L}$ dissolved oxygen in water and 13m/h filtration rate, which solved the problem of groundwater exceeding standard in Jiutang Rural Water Supply Project of Shapotou District, Zhongwei City, Ningxia Hui Autonomous Region. Zhang Jie et al. carried out field tests on filter column of water plant and determined that mature filter material was inoculated. When the filter rate was 4-7m/h, the backwashing intensity was 10-12L $(\text{s.m}^2)$, the backwashing time was 4-5min, and the backwashing cycle was 24-36h, the process of low-temperature biological iron and manganese removal was quickly started. It is concluded that biological purification can treat high iron manganese groundwater at low temperature. Huang Jialu designed a zeolite filter material aerated biofilter. After 60 days of membrane culture, in the condition of sufficient dissolved oxygen, ammonia nitrogen and manganese were removed in the first half of the filter. Simultaneous removal can be performed faster and simultaneously. Li Dong et al. used the biological process of "two-stage aeration + two-stage filtration" which was successfully cultured for 75 days to purify the groundwater with high iron, manganese and ammonia nitrogen, and found that the removal of high iron, manganese and ammonia nitrogen in the groundwater could be realized after the cultivation of 58d filtration rate. According to the analysis mechanism, the conversion removal of ammonia nitrogen and biological nitrification in this process are related to autotrophic nitrogen removal, which provides experimental data for resolving nitrogen loss and abnormal DO consumption caused by ammonia removal mainly through nitrification.

4.3. Contact oxidation process

Such as iron and manganese removal is contact oxidation. Li Guibai in 1958 found a manganese on the surface of the filter material is qualitative membrane catalytic oxidation of Fe-Mn removal of water and an autocatalytic process. Contain iron, manganese ion of groundwater by aeration form the high price of iron manganese oxide can be formed on the surface of filter material membrane and manganese ion quality, and the membrane filter. Catalytic effects of the membrane filter, water can be iron manganese ion oxidation and formed a new can continue to participate in the contact oxidation membrane filter.

Mature after filter material adsorption and oxidation of heavy metal elements in slightly polluted groundwater is also has a good removal efficiency. Huang Kaijie configuration from the rinse water of 4 g/L manganese oxide, the study found that the bivalent manganese removal rate reached 92.4%. Zhang Fan to explore the contact oxidation filter to remove arsenic, iron, manganese and ammonia nitrogen in the groundwater effect. Study table, the presence of bivalent iron and manganese in water adsorption of arsenic on iron manganese oxide film has its effect on promoting into, contact oxidation filter with high efficiency synchronous arsenic removing Fe-Mn, ammonia nitrogen and water. However, the filter material with a long cycle mature has always been the research of the technology, GUO found that the filter material such as mature early add potassium permanganate in water, using its oxidizing water iron oxide manganese ion can shorten week of liao mature period. After the study found that control water surplus manganese ion concentration can quick start contact oxidation filter, in order to achieve synchronization of the purpose of removing Fe-Mn ion ammonia water. Using manganese containing iron oxide film of pilot plant and removal of bisphenol A, manganese and ammonia nitrogen, the study found that the bivalent manganese ion deposit on removal of bisphenol A with synergy, and ammonium ions due to the consumption for the DO hinder the bisphenol A removal.

5. Conclusions and Prospect

Determine the different pollution of groundwater and select the more suitable method to remove the substances in groundwater. In the adsorption method, the adsorbability of the adsorbent to the pollutants is increased by a modification method; in that biological method, the biological filter is started quickly, and different strain are cultured to realize synchronous removal of iron, manganese, ammonia nitrogen and the like in the groundwater; In the contact oxidation process, it is found that the iron and manganese oxide film formed on the surface of mature filter media can effectively remove iron, manganese and ammonia nitrogen from water by catalytic oxidation, and the formed iron and manganese composite oxide has adsorbability, which can effectively adsorb organic matter in water, but the removal effect of organic matter needs to be improved.

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