

Research Progress on the treatment of arsenic pollution by manganese oxide

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Abstract. Arsenic is a kind of protoplasmic poison, which exists widely in the natural environment. Consuming too much arsenic can cause a number of health problems. Manganese oxide plays an important role in arsenic pollution removal technology. In this paper, arsenic hazard and its treatment methods and the application of manganese oxides in arsenic pollution treatment are summarized, and the prospect of research on arsenic pollution treatment by manganese oxides is put forward.

1 Introduction

Arsenic is widely found in the natural environment, mainly in the form of arsenite (As(III)) and arsenate (As(V))^[1-3]. Arsenic compounds are protoplasmic poisons with metal-like properties that have a wide range of biological effects and are defined as class I carcinogens by the International Agency for Research on Cancer (IARC). Excessive intake of arsenic will cause a series of health problems such as nervous disorders, deformities, melanosis, keratosis and cancer^[4]. Due to its high toxicity, the concentration of arsenic in drinking water should not exceed 10 µg/L according to China's sanitary standards and the World Health Organization. Arsenic pollution is the world's second largest water health hazard after pathogenic microorganisms^[5].

The arsenic pollution problem is particularly prominent in China. The total area of groundwater arsenic content above 10 µg/L is 5.8×10⁵ km², and the average arsenic content in soil is 11.2 mg/kg, about 1.5 times of the world average (7.2 mg/kg)^[6]. According to the 2014 National Soil Pollution Survey Bulletin, the total soil exceeding standard rate in China is 16.1%, and the point exceeding rates of Cd, Hg, Arsenic, Copper and Lead are 7.0%, 1.6%, 2.7%, 2.1% and 1.5% respectively. Arsenic is the primary contaminant among the heavy metal pollutants in soil in China^[6]. Rice is the main arsenic contaminated food crop in China. The arsenic intake per capita in China is about 42 g/d, much higher than that in western countries, which is 4 to 4.7 times of the total arsenic intake in the United States, Canada, Australia and France. Among them, the arsenic intake through rice accounts for 60% of the total arsenic intake^[7].

Due to the increasing frequency of arsenic contamination and poisoning, researchers are gradually paying attention to and expanding arsenic pollution removal technology. Manganese oxide plays an important role in arsenic pollution treatment because of its strong oxidation. In this paper, arsenic hazard and its treatment

methods and the application of manganese oxides in arsenic pollution treatment are summarized, and the prospect of research on arsenic pollution treatment by manganese oxides is put forward.

2 Overview of sources and treatment technologies of arsenic pollution

2.1 Sources of arsenic pollution

Arsenic pollution is a global problem. The sources of soil arsenic pollution are complex and can be generally divided into two types: natural sources and man-made sources. Natural sources are mainly parent rocks. In addition, crustal changes, volcanic eruptions, rock weathering, and soil erosion can also produce arsenic. Anthropogenic sources are the pollution caused by human production activities, which can be divided into agricultural pollution and industrial pollution. China is a large agricultural country. Arsenic-containing substances, such as pesticides and herbicides, are essential elements in agricultural production activities. Sewage irrigation and sludge reuse are the main sources of agricultural pollution. Arsenic pollution in the environment is mainly caused by industrial wastes. Specifically, there are mainly two aspects: one is the pollution caused by arsenic-containing soot, waste water, waste gas, waste residue discharged in the mining of arsenic-containing metal ore^[8], sintering and smelting process; The second is to use arsenic-containing pesticides to prevent and control the pollution of water, air, soil, fruits and vegetables caused by pests and diseases. It is worth mentioning that metal ores and waste rocks are exposed to the surface in mining for a long time. After long-term rainwater washing and leaching, a large amount of acid wastewater is generated to infiltrate into the soil and cause soil arsenic pollution. At the same time, it will also pollute the water system and farmland, thus endangering human health.

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2.2 Arsenic pollution treatment technology

2.2.1 Precipitation method

Sedimentation method mainly uses additional agents or energy to have chemical or physical effects with arsenic pollutants in the water to separate the precipitate or flocculate formed from the water so as to achieve the purpose of arsenic removal. Chemical precipitation method has the advantages of simple process, less investment and convenient operation, which is suitable for the wastewater with high arsenic content discharged from mines and enterprises. In the area with relatively poor economic conditions, it has high economic benefits and is the first choice for arsenic removal. However, this method requires a large amount of precipitants, which cannot be used to produce a large amount of arsenic-containing waste residue, and the long-term accumulation is easy to cause secondary pollution. Therefore, the application of this method is limited to some extent.

2.2.2 Adsorption method

Adsorption method is a simple and easy wastewater treatment technology, which is generally suitable for the water treatment system with large amount of treatment and low concentration. In this method, insoluble solid materials with high specific surface area are used as adsorbents to fix arsenic contaminants on the surface of water by physical adsorption, chemical adsorption or ion exchange, so as to achieve the purpose of arsenic removal.

2.2.3 Oxidation method

Trivalent arsenic is 60 times more toxic than pentavalent arsenic. And As(III) is much more difficult to remove than As(V). Many reagents have good removal effect on

pentavalent arsenic, but poor removal effect on trivalent arsenic. Arsenic removal by oxidation is an effective method for arsenic trivalent, but the reaction kinetics is slow and the investment is high, so its application is limited to some extent.

2.2.4 Ion exchange method

Ion exchange is also an effective method for arsenic removal. Suzuki et al. used monoclinic crystal hydrated zirconia to fill the porous resin, which could reduce the concentration of arsenic to 0.1 mg/L, meeting the industrial emission standard^[9]. However, because the ion exchange method can only treat the wastewater with low concentration, large amount of treatment, simple composition and high recovery value, its treatment process is more complex and the cost is high, so it is difficult to be commercialized.

2.2.5 Biological arsenic removal technology

Arsenic is not only enriched by organisms, but also oxidized and methylated by those organisms. Since the toxicity of methylated arsenic is much lower than that of inorganic arsenic, the process of arsenic enrichment by microorganisms in water is also a process of arsenic degradation and detoxification. Using this characteristic, the wastewater containing high concentration arsenic can be treated by biochemical method.

In addition to the main arsenic removal methods introduced above, according to the nature of wastewater and the development of new environmental protection technology, people have also tried some other arsenic removal technologies, such as electrolysis, solvent extraction, membrane separation, etc. The advantages and disadvantages of common processing techniques are shown in Table 1.

Table 1. Processing technology advantages and disadvantages

technology	advantages	disadvantages
Ion exchange method	Arsenic removal efficiency is high, can recover adsorbed arsenic.	High investment, complex process, high operating cost, the need for ion exchange resin regeneration or backwashing.
Membrane separation	No secondary pollution, arsenic can be recycled, energy saving, normal temperature can be operated.	The production operation has high investment, complex management and needs a large amount of backflow water.
Biological methods	No secondary pollution, low cost.	The technology is not yet mature and the capital construction cost is high.
Soil leaching	High efficiency, short cycle, simple process.	High cost, difficult to collect and treat leachate, easy to cause secondary pollution.
Precipitation method	Simple process, low cost, simple operation.	The complex environment is not effective in removing arsenic and produces a large number of other compounds.

3 Application of manganese oxides in arsenic pollution treatment

Manganese oxide is a strong abiotic oxidant, which has been proved to oxidize As(III), Fe(II), Co(II), U(IV), Cr(III) and organic matter^[10]. Manganese rich formations are usually formed in areas with frequent fluctuations of groundwater level, such as shallow sea areas and shallow aquifers^[11]. The deposition process of manganese rich materials in alluvial and flood plains also produces manganese rich environments^[12]. The important natural manganese oxides include sodium water manganese minerals ($[\text{Na}, \text{Ca}, \text{Mn(II)}]\text{Mn}_7\text{O}_{14} \cdot 2.8\text{H}_2\text{O}$), spodumene ($\text{LiAl}_2[\text{Mn(IV)}_2\text{Mn(III)}]\text{O}_6(\text{OH})_6$) (double-layer structure), barium magnesium manganese ore ($((\text{Ca}, \text{Na}, \text{K})_{0.3-0.5}[\text{Mn(IV)}, \text{Mn(III)}], \text{Mg})_6\text{O}_{12} \cdot 3-4.5\text{H}_2\text{O}$) (tunnel structure), and its low zero charge ($\text{pH} 1.7-3.5$) make it an effective adsorbent for various heavy metals (Zn, Ni, Co and Pb)^[13]. The reduction of manganese oxide is thermodynamically more advantageous than Fe(III) and As(V) because of its relatively high REDOX potential (about 400mV)^[14]. Manganese oxides have REDOX chemical properties similar to iron, and can rapidly oxidize As(III) and Fe(II) under oxidizing conditions, and are strongly associated with the fixation/migration of As in the oxygen-containing/hypoxic cycle of soil and sediments^[15].

Manning B A et al.^[16] used both a conventional stirred reaction apparatus and extended X-ray absorption fine structure (EXAFS) spectroscopy to investigate the reactions of As(III) and As(V) with synthetic birnessite (MnO_2). Stirred reactor experiments indicate that As(III) is oxidized by MnO_2 followed by the adsorption of the As(V) reaction product on the MnO_2 solid phase. The As(V)-Mn interatomic distance determined by EXAFS analysis for both As(III)- and As(V)-treated MnO_2 was 3.22 Å, giving evidence for the formation of As(V) adsorption complexes on MnO_2 crystallite surfaces.

Bai Dekui et al.^[17] synthesized three minerals, manganese oxide, iron oxide and alumina, and used iron oxide and manganese oxide As adsorbents to study the influence of pH value, ionic strength and time on the adsorption of As(III), and discussed the saturated adsorption capacity and isothermal adsorption experiments of As(III) by manganese oxide, iron oxide and alumina. The conclusions are as follows: 1) Under the optimized conditions, the order of saturated adsorption capacity of manganese oxide, iron oxide and alumina for As(III) is: manganese oxide > iron oxide > alumina. 2) pH had little effect on the adsorption of As(III) by manganese oxide, and the effect of pH 3.5 ~ 8.5 on the adsorption of As(III) by iron oxide fluctuated little in a wide range. When $\text{pH} < 3.5$ or $\text{pH} > 8.5$, the adsorption rate of As(III) by iron oxide decreased. The ionic strength has little effect on the adsorption of As(III) by the oxide. The adsorption reaction between the two is a rapid reaction, and the adsorption equilibrium is reached about 30 min.

Tournassat, C et al.^[18] studied the oxidation products of As(III) into As(V) in 0.011 M arsenite suspension of a well-crystallized hexagonal sodium hydro-manganese ore (H-hydro-sodium hydro-manganese ore, $2.7 \text{ g} \cdot \text{l}^{-1}$) with pH

5 by solution chemistry technique. The reactions were investigated by scanning electron microscopy, energy dispersion spectroscopy (SEM-EDS), atomic force microscopy (AFM) and X-ray absorption near edge structure spectroscopy (XANES). The conclusions are as follows: 1) manganese arsenate precipitates and forms long fibers, which gather on the surface of H- water sodium manganese ore. 2) Oxidation reaction transforms toxic substance As(III) into less toxic water-based substance. 3) The high crystallinity of sodium hydrochloride samples results in a lower depletion rate of As(III) than that measured in previous studies. 4) The surface reaction site may be located at the edge of the water-sodium-manganese ore layer, rather than at the base surface.

Liu Xiuying et al.^[19] modified natural manganese ore with TiCl_4 and optimized the modification conditions. The experimental results show that the best modification conditions are as follows: TiCl_4 concentration is 10 mg/L, soaking time is 18 h, $\text{pH} = 3.05$, and oscillating adsorption time is 1 h. Compared with the removal efficiency of natural manganese ore (82.95% and 77.93%), the removal rates of As (iii) and As (v) by modified manganese ore can reach 94.87% and 99.31% respectively, and the corresponding saturated adsorption amounts are 3.48 mg/g and 31.25 mg/g respectively, which are higher than those of natural manganese ore. The adsorption of modified manganese ore for As (iii) accords with Freundlich isothermal adsorption model, and the adsorption of As (v) accords with Langmuir isothermal adsorption model.

Zhang Fan et al.^[20] studied the surface characteristics and arsenic removal performance of active iron and manganese oxide filter membrane prepared by chemical membrane hanging method. The results show that the pseudo-second-order reaction kinetic equation ($R_2 = 0.922$) can be used to characterize the adsorption process of As(V) by the active Fe-Mn composite oxide. The adsorption isotherm conforms to Langmuir equation ($R_2 = 0.971$), and the saturated adsorption capacity is 11.94 mg/g. The PHZPC of active iron and manganese oxide filter membrane is about 2.5. Carbonate in natural underground water has a strong inhibition effect on the adsorption and removal of arsenic, while other co-existing anions and cations have little effect on the removal of arsenic in neutral water environment. In the process of column test, the concentration of arsenic in the final effluent is reduced to zero after the groundwater with As(V) concentration of 200 and 280 $\mu\text{g/L}$ is treated by the filter column, and the arsenic removal effect is good.

4 Conclusions and perspectives

(1) Different areas have different levels of pollution, sources of pollution and pollution objects. When using manganese oxides to treat pollution, a treatment plan suitable for different objects should be developed according to the local actual situation.

(2) The treatment of arsenic pollution by manganese oxide alone is not complete. When using manganese oxide to treat arsenic pollution, it should be combined with other

treatment methods, such as Fe-Mn oxide activated carbon, which combines physical method and chemical method.

(3) The oxidation method has slow reaction kinetics and high investment, so the process of treating arsenic pollution by manganese oxide should be optimized to reduce the cost.

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