Research Article **SRR (2019) 12:108**

Scientific Research and Reviews
(ISSN:2638-3500)

Comparative study on removal of divalent manganese ions by nanometer TiO_2 with different morphology

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ABSTRACT

In order to solve the problem of excessive Mn(II) content in water in some areas of China, TiO_2 nanotubes and TiO_2 powder are used to remove Mn(II). The experimental results show that both TiO_2 nanotubes and TiO_2 powder have certain manganese removal effect, and the effect of powder is better. When the pH was 5.6 and the 20W UV lamp was irradiated for 40 min, the removal rate of the powder was 64.3 %, and the removal rate of the nanotubes anodized for 1h was 35.3 %, and the removal rate of the nanotubes anodized for 30 min was 23.9 %. When the pH is adjusted to 7-8, the removal rate of the nanotubes is significantly improved. When the pH was 8, 20W UV lamp was irradiated for 40 min, the removal rate of nanotubes anodized for 1h was 60.4%.

Keywords: Divalent manganese ion; Photocatalytic; Nano titanium dioxide; Remove

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How to cite this article:
Wenhao Wei, Guangming Liu, Jiakun Wang. Comparative study on removal of divalent manganese ions by nanometer TiO_2 with different morphology. Scientific Research and Reviews, 2019, 12:108.

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1. Introduction

Mn(II) is mainly found in groundwater, and its main source is the dissolution of insoluble manganese compounds in rocks and minerals by carbonic acid in groundwater[1]. In recent years, a large number of unsatisfactory industrial wastewater has been discharged into surface water and acid rain to wash rocks and soil, causing seasonal and sudden over-standard conditions of Mn(II) in surface water[2]. The precipitation of Mn (II) after oxidation will cause the chromaticity of water to increase and cause great harm to human health. Therefore, how to effectively remove Mn(II) has become an urgent problem to be solved.

At present, the main methods to remove Mn(II) are oxidation and adsorption[3-4]. The oxidation method uses an oxidizing agent to oxidize Mn(II) to a high valence, and then reacts with hydroxide in water to form a precipitate and then removes it[5-6]. The adsorption method uses some materials with large specific surface area and strong adsorption performance to remove Mn(II) after adsorption. The adsorption method has the advantages of large capacity, low energy consumption, small pollution, fast removal and recyclability[7-8]. Nano-TiO_2 can not only oxidize Mn(II) to high valence by photocatalytic oxidation, but also adsorb Mn(II). TiO_2 nanotubes prepared by anodization are easy to recycle and reusable[9-10].

In this study, nano- TiO_2 was used to remove Mn (II). The removal efficiency of Mn(II) was compared between titanium dioxide nanotubes and titanium dioxide powder. The effects of photocatalysis time and pH on removal efficiency were studied.

2. Materials and methods

2.1 Materials

$MnSO_4$,CH_3COONa,$K_4P_2O_7$,NaOH,HCl,KIO_4,NH_4F,$(CH_2OH)_2$ and TiO_2 powder were of analytical grade and obtained from Shanghai Chemical Co. (Shanghai, China).

Formulating $MnSO_4$ into 2mg/L experimental water sample. Adjust the pH of the water sample to 7 with NaOH and HCl at a concentration of 0.1 mol/L.

2.2 Method for detecting Mn(II)

Potassium periodate spectrophotometry. The detection principle is that in a neutral potassium pyrophosphate medium, potassium periodate can oxidize Mn(II) to purple Mn(VII), and then measure by spectrophotometry at 525 nm.

2.3 Preparation of TiO_2 nanotubes by anodization

Weigh 4.971 g of ammonium fluoride, add 75mL of distilled water and 1425mL of ethylene glycol, and mix well to obtain an electrolyte. Titanium sheet as anode and stainless steel as cathode, placed in electrolyte. Anodization was carried out using a DC voltage of 30V with magnetic stirring. The oxidation time was 30min and 1h, respectively. Rinse the excess electrolyte on the surface with distilled water, and then dry it for 10minutes at 60% power to remove the surface coating and impurities. Then put it into a muffle furnace and slowly heat it to 450 °C for 3h until it is naturally cooled to room temperature with the furnace temperature. This causes the nanotubes to produce anatase and rutile crystal forms. The anodizing time of class A nanotubes is 1h, and the class B nanotubes is 30min.

2.4 Experimental method

2.4.1 TiO_2 nanotubes

Put TiO_2 nanotube A and B into multiple 50mL water samples. Photocatalytic oxidation of 0, 10, 20, 30, 40, 50, 60min using a 20W UV lamp. Detect the water sample after the reaction is filtered through a microporous membrane. Determine the best photocatalytic time by experimental data. Under the optimal photocatalytic time condition and keeping other conditions unchanged, adjust the pH of the water sample to 3, 5, 7, and 8 to explore the effect of pH on the photocatalytic.

2.4.2 TiO_2 powder

Add 0.05, 0.10, 0.15, 0.20, 0.25g/L of TiO_2 powder to multiple 50mL water samples. Catalytic oxidation with 20W UV light for 30min. Determine the optimal dosage of TiO_2 powder through experimental data. Under the optimal dosage and keeping other conditions consistent, the photocatalytic time was set to 0, 10, 20, 30, 40 min, and the effect of time on the removal effect was studied. Then adjust the pH of the water sample to 3, 5, 7, and 8 to study the effect of pH on the removal rate.

3. Results and discussion

3.1 Effect of dosage on Mn(II) removal of TiO_2 powder

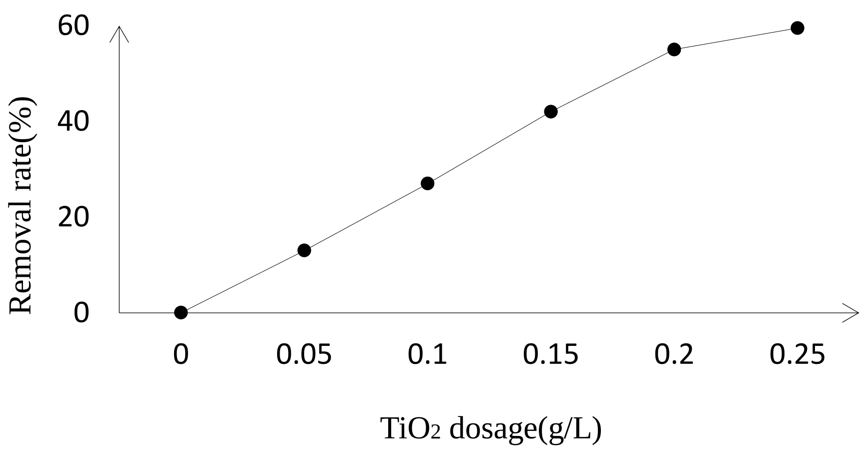

Fig.1 Effect of dosage on Mn(II) removal of TiO_2 powder

As can be seen from Fig.1, the amount of powder added increases, the removal rate also shows an upward trend. When the dosage is 0-0.20 g/L, the removal rate increases rapidly. When the dosage is 0.20-0.25 g/L, the removal rate increases slowly. Taking into account economic factors, the dosage of 0.20 g/L was set as the optimum dosage.

3.2 Comparison of effects of photocatalytic time on Mn(II) removal of TiO_2 nanotubes and TiO_2 powders

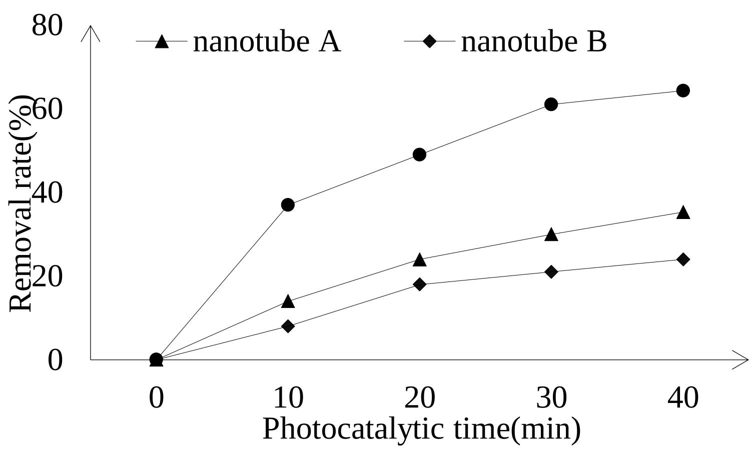

Fig.2 Comparison of the effects of photocatalysis time

As can be seen from Fig.2, with the increase of photocatalytic time, the removal rates of TiO_2 nanotubes A, B and powder increased rapidly. Among them, the powder removal effect is the best, followed by nanotube A, and finally nanotube B. This is because the anatase type nano TiO_2 has the highest catalytic activity. The nanotubes are anatase type by high temperature annealing. The powders are all anatase and can be thoroughly mixed with the water sample. Under the same photocatalytic time, the removal rate of nanotube A with longer anodization time is higher than B. This is because the diffraction peak of anatase TiO_2 gradually increases as the oxidation time increases. The larger the peak area, the more the anatase crystal phase is.

3.3 Comparison of effects of pH on Mn(II) removal of TiO_2 nanotubes and TiO_2 powders

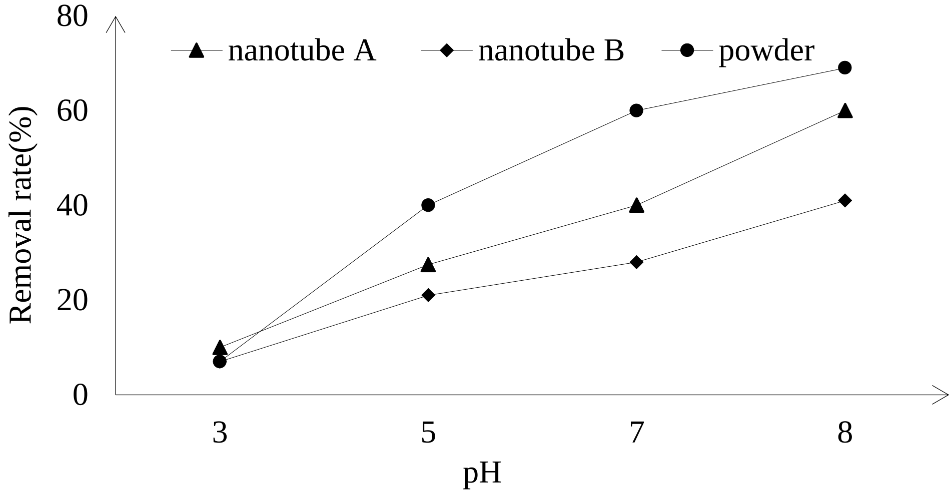

Fig.3 Comparison of effects of pH

As can be seen from Fig.3,with the increase of pH value, the removal rate of Mn(II) by nanotubes A, B and powder increased linearly. Among them, the powder removal effect is the best, followed by nanotube A, and finally nanotube B. At a low pH, the positive charge on the surface of TiO_2 repels Mn(II), so the reaction efficiency is low. When the pH value is high, the surface of TiO_2 is negatively charged to attract Mn(II), which is beneficial to photocatalytic reaction. Considering the practical application and economic factors, the optimum pH of the nanotubes is 7-8, and the optimum pH of the powder is 6-8.

4. Conclusions

1.Based on the actual situation and economic factors, the photocatalytic time is 40min, the ultraviolet light intensity is stronger, and the pH value is 7-8, the TiO_2 nanotubes has a good Mn (II) removal effect..

2.The photocatalytic time is 30min, the dosage is 0.2g/L, and the pH value is 6-8, the TiO_2 powder has a good Mn(II) removal effect.

3.When the other experimental conditions are the same, the Mn(II) removal effect of the nanotubes with longer anodization time is better. This is because the longer the oxidation time in a certain range, the more the anatase crystal phase of the obtained TiO_2 nanotube array, the better the crystallinity.

4.The removal rate of the powder is higher than that of the nanotubes because the anatase crystal form of the powder is much larger than that of the nanotubes. However, nanotubes are easy to recycle and can be reused after ultrasonic cleaning.

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