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Original Research Article

Study on Adsorption Properties of Modified MWNTs to Pb^{2+} in Water

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Abstract

In order to remove the residual harmful lead ion(Pb^{2+}) in water, modified multi-walled carbon nanotubes (O-MWNTs), as a adsorbent, was used to enrich and remove Pb^{2+} in water samples. O-MWNTs was obtained by mixed acid oxidation. It was analyzed and confirmed that O-MWNTs had been obtained successfully by FITR and TEM. The adsorption property of O-MWNTs to Pb^{2+} in water was investigated. The adsorption efficiency of adsorbent dosage, adsorption time, adsorption pH and adsorption temperature was investigated, and conclusions are as follows: when pH is 5, the temperature is 20℃, adsorption time is 40 min, and adsorbent dosage is 40 mg/L, the adsorption efficiency was the highest. Adsorption rate of can reach 81.7% under optimal conditions.

Keywords: Multi-walled carbon nanotubes; Chemical modification; Lead ion; Adsorption.

INTRODUCTION

Water environment security is a major issue concerning human health and national economy and people's livelihood. As one of the most widely distributed heavy metals in the earth's crust, Pb^{2+} is highly toxic and harmful, and which is harm to systems and organs of human, especially to the central nervous system and digestive system. Many natural and human behaviors will release Pb^{2+} in water bodies, and the Pb^{2+} content in water bodies will gradually increase, which seriously threatening the growth of animals and plants and the health of human. Therefore, it is of great practical significance to effectively remove and detect heavy metal Pb^{2+} in different water bodies.

Among many methods to control heavy metal pollution, adsorption method has been widely used because of its advantages of convenient operation and low cost. Therefore, it is of great significance to study new and efficient adsorption materials. The high specific surface area and pore structure of modified MWNTs determine its good adsorption capacity and desorption capacity, it is a superior adsorbent, and can be used in recycling desorption, so there is a big potential in heavy metal wastewater treatment. However, the adsorption properties and mechanism of modified MWNTs have to be further studied, and its application potential has not been fully explored.

The surface properties of modified MWNTs will affect their adsorption efficiency. The adsorption effect of MWNTs before and after modification was investigated, the results show that compared with the unmodified MWNTs, the MWNTs modified adsorption quantity were ascending [1]. Yang studied the active sites for adsorption of nickel ions on MWNTs through theoretical calculation, and confirmed that the defects of ston-Wales on the surface of MWNTs enhanced their adsorption to nickel, which also indicated that the enhanced defects of MWNTs after modification was one of the important factors for the improvement of its adsorption rate [2]. CVD-MWNTs, due to its surface has a great deal of defects, which will enhance the adsorption ability to small molecules in water [3]. Temperature and acidity are also important factors affecting the adsorption efficiency of modified MWNTs. The increase of temperature will cause aggregation of MWNTs and affect its adsorption effect, which requires the temperature of the adsorption system [4]. Kandah studied the adsorption of nickel ions by modified MWNTs in water, and found that the modified MWNTs has large adsorption capacity, the electrical force between nickel ions and MWNTs was deemed to the adsorption mechanism [5]. Chen also studied the adsorption of nickel ion by MWNTs which treated by nitric acid, and the adsorbent dosage, time, solution pH, temperature and ionic strength were inspected respectively, the desorption likely to occur when pH is less than 2.00, it shows that the pH of exploration has important significance to improve the adsorption efficiency of adsorbent [6]. In order to further determine the degree of influence of pH to adsorption efficiency, Chen also used MWNTs to adsorb Zn^{2+}, and found that adsorption equilibrium could be achieved within a short period of time, and adsorption was also greatly affected by pH, and the adsorption effect was better than activated carbon [7]. The concentration of the pollutants is also one of the important factors affecting the adsorption efficiency of MWNTs. Zhang studied the adsorption performance of MWNTs to Pb^{2+}, and analyzed the initial concentration of Pb^{2+} to the effect on the equilibrium adsorption [8]. Yin prepared S-FE/MWNTs, which could remove 78.6% Pb^{2+} in water, and analyzed its removal mechanism [9]. Ji prepared MWNTs, which was modified by mercaptosilane, and applied it to the removal of Pb^{2+} in water, and the adsorption mechanism was preliminarily studied [10]. Zhang prepared a series of modified MWNTs composite, which was used to modify electrodes to detect Pb^{2+} in water, and investigated the factors such as the concentration of bottom solution on the detection of Pb^{2+} [11]. Wang used MWNTs to react with CS_2 to improve the adsorption efficiency of Pb^{2+} [12]. Liused NH_2-MWNTs to detect Pb^{2+} in water, the results showed that it can enrich more Pb^{2+} in water [13]. Liinvestigated the thermodynamic and kinetic properties of Pb^{2+} adsorption on MWNTs and its desorption behavior, and found that MWNTs adsorption of Pb^{2+} conforms to the Langmuir equation in a certain concentration range [14].

In this paper, the O-MWNTs was used to adsorb Pb^{2+}, and the dosage of adsorbent, the concentration of Pb^{2+}, pH of solution and adsorption time were invested. The optimum adsorption conditions were obtained, which provides the theory basis in water treatment.

MATERIALS AND METHODS

Materials and Reagents

MWNTs (Suiheng Technology Co., LTD of China Shenzhen, 97%). concentrated sulfuric acid, concentrated nitric acid, Ethanol are analytical pure.

Instruments and equipment

Supercentrifuge (CP100WX, HITACHI of Japan), vacuum drying oven (DGF-6030, the company of Shanghai yiheng scientific instrument), electronic analytical balance (ALC-310.2, LTD. co. Beijing taike instrument), circulating water multi-purpose vacuum pump(SHB-IIIA, LTD. co. zhengzhou Great Wall science and trade), constant temperature magnetic stirring water bath (HJ-A2, LTD. co. changzhou maikonuo instrument), Uv-visible spectrophotometer (Uv-3600, HITACHI, Japan), transmission electron microscope(TEM, JEM2100Plus, Japan electron).

METHODS

The Preparation of O-MWNTs

The MWNTs was acidified by mixed acid. The specific process was as follows: an appropriate amount of MWNTs was weighed into a round-bottom flask, and the prepared sulfuric acid and nitric acid were added into the round-bottom flask according to the volume ratio of 3:1. The reaction conditions were as follows: water bath temperature 50 ℃, time of reaction was 1 hours. O-MWNTs was obtained after acidification.

The Adsorption of Pb^{2+} by O-MWNTs

50 mg O-MWNTs were put in conical flask (150 mL), the solution of Pb^{2+}(40 mg/L, 100 mL) was added, oscillating adsorption was proceed at 25 ℃. The solution was filtered by membrane (0.45 μm), and the absorbance of the filtrate was determined by spectrophotometry. The concentration of Pb^{2+} was compared with the standard working curve, and the adsorption rate of Pb^{2+} was obtained.

The Calculation of adsorption rate

Equation 1 is the adsorption efficiency formula of O-MWNTs to Pb^{2+}, C_0 is the initial concentration of Pb^{2+} (mg/L), C_t is the concentration of Pb^{2+} at time T.

$$\eta = (C_0 - C_t)/C_0 \times 100\% \quad \text{........... (1)}$$

RESULTS AND ANALYSIS

The analysis of O-MWNTs

As shown in Figure-1, curve (a) is FTIR of R-MWNTs (raw-MWNTs) and curve (b) is FTIR of O-MWNTs. The characteristic peak of -OH appears at 3380cm^{-1} in curve b, and a superposition peak of the bending vibration of double bond -OH and C=O appear at 1620cm^{-1}. There is only one peak at 1600cm^{-1} in curve a, which is the bending vibration of C-C single bond. These results indicate that a large number of -OH and C=O are introduced into the surface of MWNTs treated with mixed acid, therefore, mixed acid oxidation treatment is an important step to enable MWNTs to disperse in water.

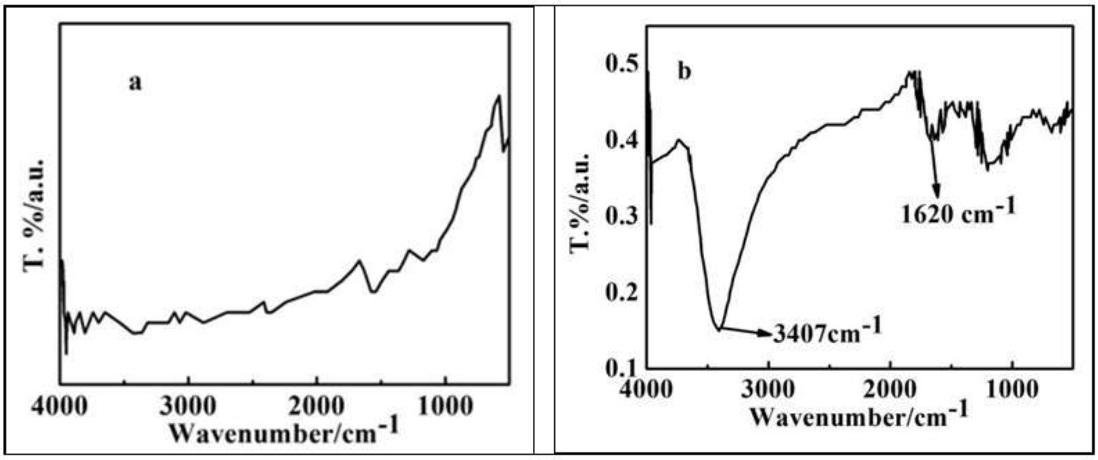

Fig-1: FTIR of (a) R-MWNTs and (b) O-MWNTs

Images of R-MWNTs and O-MWNTs

As is shown in Figure-2, the images of R-MWNTs and O-MWNTs were observed by transmission electron microscopy.

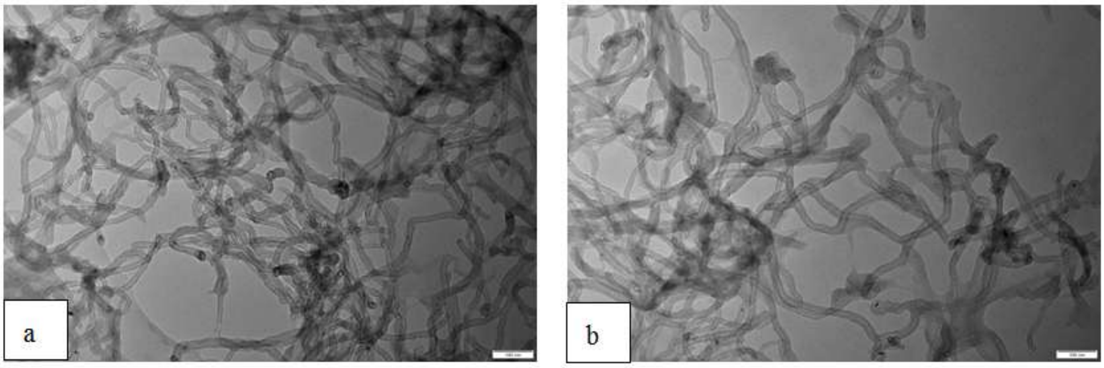

Fig-2: Images of (a) R-MWNTs and (b) O-MWNTs

It can be seen from Figure-2, (a) is the image of R-MWNTs and (b) is the image of O-MWNTs. Obviously. The R-MWNTs in image are thick, the end of the tubes are mostly closed, and the tubes are mixed with black particles. There are flocculent on the wall, that is, impurities such as catalyst particles and amorphous carbon exist. O-MWNTs in image b, which was modified by mixed acid oxidation, were thin, with few impurities, and the end of the tube body has obvious fracture marks, which is due to the non-treatment of mixed acid oxidation. Only impurities were removed from the nanotubes, and the defective parts were eroded away.

The Comparison of adsorption properties of R-MWNTs and O-MWNTs

Table-1 are the adsorption effects of R-MWNTs and O-MWNTs to Pb^{2+}, respectively.

Table-1: Comparison of adsorption effects of R-MWNTs and O-MWNTs to Pb^{2+}

Adsorbent	Initial concentration(mg/L)	Concentration after adsorption(mg/L)	ŋ/Adsorption rate(%)
R-MWNTs	40	23.2	42.0
O-MWNTs	40	9.7	75.8

As can be seen from Table-1, the adsorption rate of Pb^{2+} increased by 180% after MWNTs were oxidized with mixed acid. It was also observed that the filtrate was colorless and transparent when O-MWNTs were used as adsorbents, while R-MWNTs were used as adsorbents, the resulting filtrate was slightly brown.

The adsorption of Pb^{2+} by O-MWNTs
Effect of dosage on adsorption efficiency

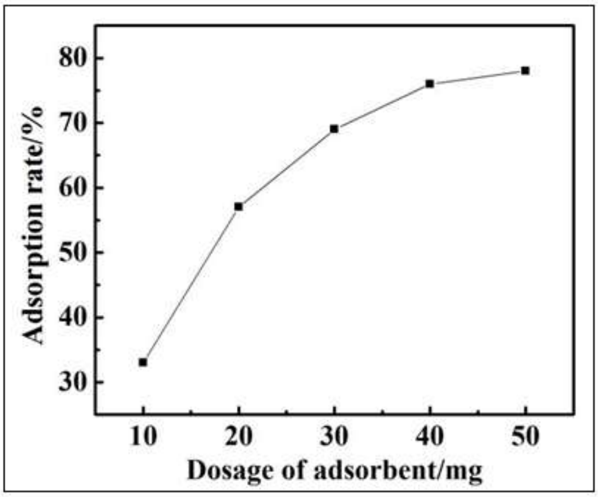

Fig-3: Effect of adsorbent dosage on adsorption efficiency

As is shown in Figure-3, with the increase of adsorbent dosage, the adsorption rate of O-MWNTs to $Pb^{2+}$is increased. As the amount of adsorbent increases, the equilibrium concentration of Pb^{2+} in the solution decreases, leading to a decrease in the adsorption impetus. Although the adsorption rate is still increasing, the unit adsorption capacity of O-MWNTs is decreasing. Considering the economic convenience and the difficulty of solid-liquid separation caused by the increase in the dosage of adsorbent, the dosage of O-MWNTs was selected to be 40 mg/L.

Effect of temperature on adsorption efficiency

In the process of wastewater treatment, temperature is also one of the main conditions in practice. The effect of temperature on the adsorption performance of O-MWNTs is shown in Figure-4.

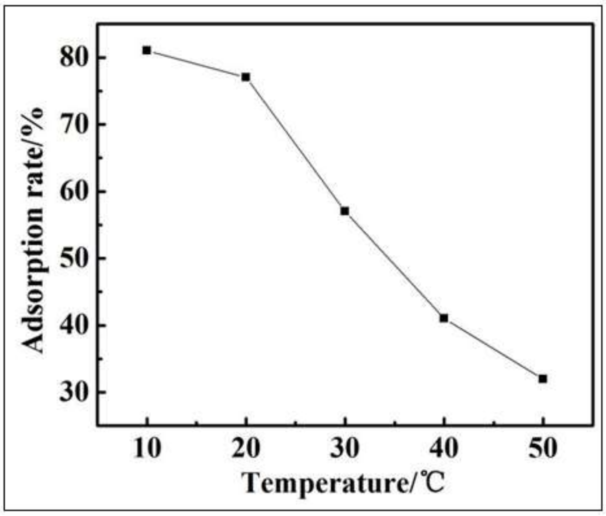

Fig-4: Effect of temperature on adsorption efficiency

It can be seen from Figure-4 that the adsorption capacity of O-MWNTs to Pb^{2+} in water decreases with the increase of temperature. The results show that the adsorption process is exothermic, and lower temperature is favorable for adsorption. Therefore, in practical application, the appropriate adsorption temperature should be around 20 ℃.

Effect of pH on adsorption efficiency

As an important medium factor, pH not only affects the dissociation of adsorption, but also affects the chemical state of heavy metal ions in solution, such as hydrolysis and precipitation. Therefore, pH has a great influence on the adsorption of heavy metal ions by the adsorbent [15]. The effect of initial pH of solution on the adsorption effect of Pb^{2+} was studied, and the results were shown in Figure 5.

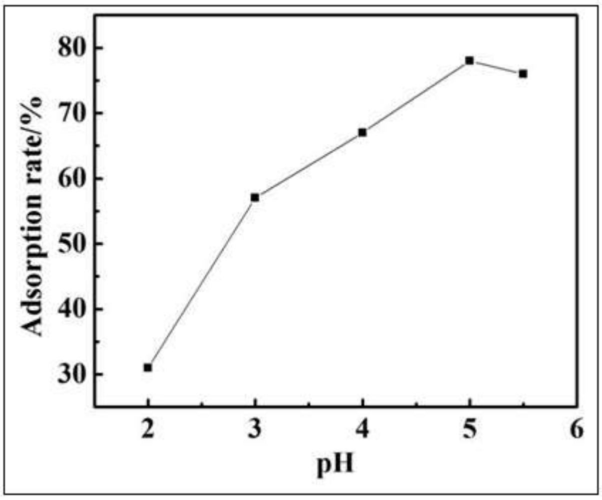

Fig-5: Effect of pH on adsorption efficiency

As can be seen from Figure 5, with the increase of pH in solution, the removal rate of Pb^{2+} by O-MWNTs presents an increasing trend. When the pH of the solution increased, the surface of solution was negatively charged, and the electrostatic repulsion on the surface of the metal cation and O-MWNTs decreased, so the adsorption rate increased. At the same time, as the functional groups on the surface of O-MWNTs are weakly acidic, when the pH of the solution increases, the acidic functional groups are deprotonated, thus increasing the adsorption rate. However, high pH will lead to the formation of metal hydroxide precipitation. Therefore, PH should be strictly controlled during the adsorption process. In this experiment, the adjustment of PH was 5.0.

Effect of time on adsorption efficiency

The initial concentration of Pb^{2+} solution was 40 mg/L, and the adsorption was oscillated at room temperature. The effect of adsorption time on the adsorption rate was investigated, and the results were shown in Figure-5.

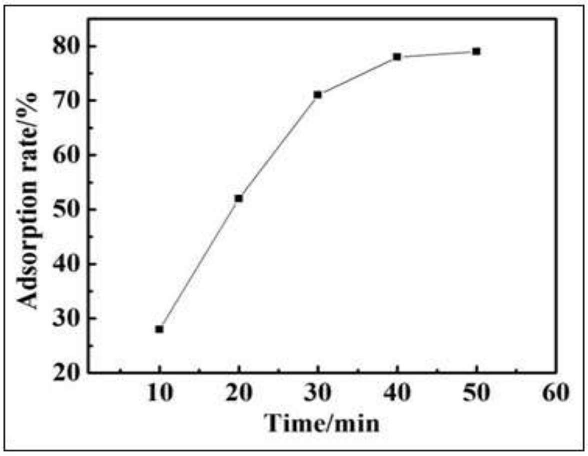

Fig-6: Effect of time on adsorption efficiency

As can be seen from Figure 6, the adsorption rate of O-MWNTs to Pb^{2+} is very high. Within the 50 min, the adsorption and removal rate increases rapidly, reaching 80%. But after 40 min, the adsorption rate changed smaller, so it can be considered to have reached equilibrium.

CONCLUSION

With the development of the society, water safety has attracted wide attention of the whole society. In order to remove the residual harmful Pb^{2+} in water accurately, rapidly and efficiently. In this paper, O-MWNTs was used to enrich and remove Pb^{2+} in water samples. The π-π interaction, electrostatic interaction and hydrogen bonding between O-MWNTs and Pb^{2+} is the essence. The content of Pb^{2+} in water samples treated with adsorbent was obtained by spectrophotometry, and a kind of efficient adsorbent was selected to be applied to the removal of Pb^{2+} in environmental water. This will provide a new idea for the removal and detection of harmful residues in environmental water.

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