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Effective Adsorption of Pb(II) in Water by Using WSCC/MWCNTs-COOH Composite

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Abstract **Original Research Article**

An environment friendly water-soluble carboxymethyl chitosan/carboxyl group of multi-walled carbon nanotubes (WSCC/MWCNTs-COOH) composite was prepared by using carboxyl group of multi-walled carbon nanotubes (MWCNTs-COOH) and aqueous carboxymethyl chitosan (WSCC) solution. The WSCC/MWNTs-COOH composite was used as an adsorbent to adsorb Pb(II) in water via non-covalent adsorption interaction. In the batch adsorption experiments, the optimal adsorption conditions and maximum adsorption efficiency were determined by investigating the influence of adsorbent concentration, contact time and Pb(II) initial concentration, respectively. This study will provide a novel adsorbent for detection and removal of harmful Pb(II) residues in water.

Keywords: WSCC/MWCNTs-COOH, Adsorption；Non-Covalent, Pb(II).

INTRODUCTION

Water pollution is a global problem, affecting the lives of millions of people around the world and posing a serious threat to human health [1]. The discharge of toxic metals in the environment will cause water pollution. Pb(II), one of the most carcinogenic heavy metals, enters the food chain through polluted water and threatens the safety of the whole biosphere [2]. Therefore, scholars have been committed to the removal of Pb(II) in water for a long period of time. Methods for removing heavy metal ions in water include coprecipitation, membrane filtration, reverse osmosis and adsorption [3]. Among these methods, adsorption method is a relatively mature and simple wastewater treatment technology, especially suitable for large volume and low concentration of water treatment system. It has the advantages of simple operation, low cost and good effect [4]. The commonly used adsorbents are activated carbon, biological materials, hydrogel, silica gel and nano composite materials. However, these adsorbents have disadvantages such as small specific surface area and poor adsorbability [5].

Multi-walled carbon nanotubes (MWCNTs) are hollow tubes formed by crimping multilayer graphite sheets, which have a large specific surface area and strong adsorption effect [6]. At present, MWCNTs are commonly used to treat various industrial polluted wastewaters. However, there is a strong van der Waals force between MWCNTs bundles, which makes MWCNTs easily agglomerate. The poor dispersability in water reduces the effective specific surface area, which reduces the adsorption efficiency of heavy metal ions in water. The preparation of water-dispersible MWCNTs composite is an effective way to improve the adsorption efficiency of MWCNTs [7]. Studies showed that MWCNTs treated with acid can effectively remove metal chromium ions from water. The adsorption capacity and efficiency were investigated via pH, the initial concentration of heavy metal ions, and the adsorption equilibrium time. Studies showed that the adsorption capacity of MWCNTs was slightly enhanced after acidification, but the experimental recovery rate of this method was lower than that of others [8, 9]. Podkościelny P *et al.*, discussed the adsorption performance of Oxidized MWCNTs on Cu(II) in water from the theoretical aspects of adsorption equilibrium, adsorption heat effect and adsorption kinetics, also finding that the adsorption efficiency of oxidized MWCNTs was slightly improved compared with that before acidification. Furthermore, it is worth noting that the adsorption mechanism was discussed theoretically in this study [10]. Shah F *et al.*, studied the adsorption capacity of MWCNTs modified with glycerol for Pb(II) in water, finging the adsorbent showed good stability with a high recovery rate of 97%, but a slightly lower adsorption efficiency [11]. The modified Si-MWCNTs were used as adsorbents to study the adsorption of Pb(II) and Co(II) in water, with the detection limits of

Pb(II) and Co(II) being 1.76μg·L^{-1} and 0.55μg·L^{-1}, respectively, So the adsorbent had a higher adsorption performance for Co(II) than Pb(II) [12].

Chitosan is a low-cost environmental protection biopolymer, characterized by a large number of amino and hydroxyl groups, which is particularly important in the removal of pollutants in aqueous solution [13]. The lone pair electron of chitosan nitrogen atom provides the possibility of its application in heavy metal adsorption. Study showed that when chitosan was loaded onto MWCNTs, the composite showed high adsorption capacity and good reusability for the removal of heavy metal Cd (II) [14]. In this study, MWCNTs-COOH were modified by WSCC to improve the dispersability of MWCNTs-COOH in water. The adsorption behavior and effect of WSCC/MWCNTs-COOH composite material on Pb(II) in water were further investigated. The adsorption provided a feasible path for the detection and removal of harmful residues in environmental water.

2. MATERIALS AND METHODS

2.1 Materials

MWCNTs and chitosan were purchased from Suiheng Technology and Aladdin, respectively. Other reagents are analytical pure.

2.2 Instruments and equipment

Supercentrifuge(GL-20G-II, Beijing of China), vacuum drying oven(OHG-9140A, Shanghai of China), electronic analytical balance(AL104, Shanghai of China), circulating water multi-purpose vacuum pump(SHB-IIIA, LTD. co. zhengzhou Great Wall science and trade), constant temperature magnetic stirring water bath(THZ-82, LTD. co. changzhou maikonuo instrument).

2.3 The confirmation of Pb(II) concentration

The equilibrium concentration of Pb(II) was ascertained according to the equation of 1.

$\eta=(C_0-C_t)/C_0\times100\%$......................... (1)

Where, η represents adsorption rate; C_0 and C_t (mg L^{-1}) represent the concentrations of Pb (II) at time of initial and t, respectively.

2.4 Adsorption experiment of WSCC/MWCNTs-COOH on Pb(II)

The aqueous solution of Pb(II) (100 mg/L) was prepared, with 60 mg MWCNTs-COOH added at the assistant of ultrasonic for 30 min at a constant temperature of 30℃. After filtration, the filtrate was detected to obtain the concentration of Pb(II), after which the concentration of Pb(II) was obtained, and the adsorption capacity of WSCC/MWCNTs-COOH was calculated according to Equation 1.

2.5 Orthogonal experiment

After the single factor test results were obtained, $L_9(3^4)$ orthogonal experimental design table was selected on the basis of which, the dosage of WSCC/MWCNT-COOH adsorbent (A), the initial concentration of Pb(II) (B) and the adsorption time (C) were taken as the influencing factors, and the adsorption capacity of Pb(II) was taken as the index to optimize the parameters of the adsorption process, and the optimal adsorption conditions were selected. The orthogonal experimental design of $L_9(3^4)$ Was shown in Table 1.

Table 1: $L_9(3^4)$ Orthogonal test protocol for WSCC/MWCNTs-COOH adsorption of Pb(II)

Number	Dosage of adsorbent (mg/mL)	Pb(II) initial concentration (mg/mL)	adsorption time (min)
1	A1	B1	C1
2	A1	B2	C2
3	A1	B3	C3
4	A2	B1	C2
5	A2	B2	C3
6	A2	B3	C1
7	A3	B1	C3
8	A3	B2	C1
9	A3	B3	C2

3. RESULTS AND DISCUSSION

3.1 Effect of dosage of adsorbent on adsorption rate of Pb(II)

The aqueous solution of Pb(II) (100 mg/L) was prepared, after which 20 mg of WSCC/MWCNTs-COOH were added and shocked at the assistant of ultrasonic for 30 min at room temperature. After filtration, the filtrate was obtained for detecting the concentration of Pb(II). Then the concentration of Pb(II) solution was kept invariability, but the mass of adsorbent was improved to 40 mg, 60 mg and 80 mg, respectively, after which the filtrate concentration of Pb(II) was obtained, and the adsorption rate of Pb(II) was calculated according to equation (1).

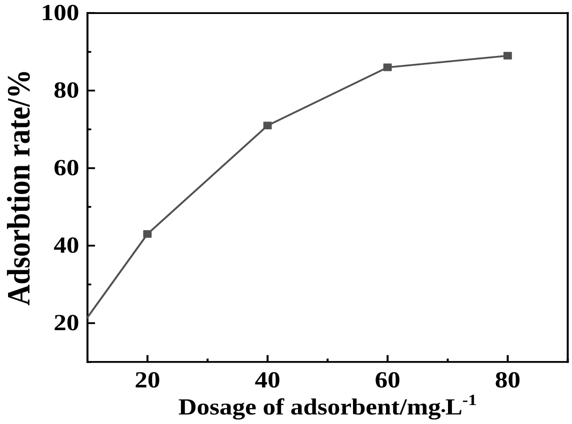

Fig 1: Effect of adsorbent dosage on adsorption rate of Pb(II)

It can be seen from Fig 1 that the adsorption rate of Pb(II) increased gradually with the increase of WSCC/MWCNTs-COOH, but when the dosage of WSCC/MWCNTs-COOH reached 80 mg/L, the adsorption effect of Pb(II) did not improve significantly with the increase of the dosage. Therefore, the optimal dosage of WSCC/MWCNTs-COOH was 60 mg/L, and the adsorption rate of Pb(II) was 84.7%.

3.2 Effect of initial concentration of Pb(II) on adsorption rate

The aqueous solution of WSCC/MWCNTs-COOH (60 mg/L) was prepared, and subsequently 100 mg of Pb(II) was added and shocked at the assistant of ultrasonic for 30 min at room temperature. After filtration, the filtrate was obtained to detect the concentration of Pb(II). Then kept the amount of WSCC/MWCNTs-COOH solution unchanged, but the amount of Pb(II) was changed to 40 mg/L, 60 mg/L, and 80 mg/L, respectively, after which the concentration of Pb(II) filtrate was obtained, and the adsorption rate of Pb(II) was calculated according to equation (1).

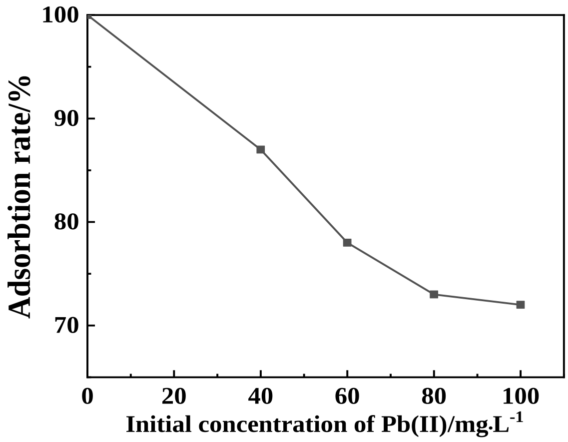

Fig 2: Effect of initial concentration of Pb(II) on adsorption rate

It can be seen from Fig 2 that with the gradual increase of the initial concentration of Pb(II), the remaining Pb(II) content in the solution after adsorption also gradually increases. It can be seen that the adsorption capacity of Pb(II) by WSCC/MWCNTs-COOH was greatly affected by its initial concentration. Considering the impact on the environment, the maximum dosage of Pb(II) in this experiment was 40 mg/L, and the adsorption rate was 87.1%.

3.3 Effect of adsorption time on adsorption rate of Pb(II)

The aqueous solution of Pb(II) (40 mg/L) was prepared. Besides, 60 mg of WSCC/MWCNTs-COOH was added and shocked at the assistant of ultrasonic for 30 min at room temperature. After filtration, the filtrate was obtained to detect the concentration of Pb(II). Then the adsorption time was increased to 60 min, 90min and 120 min, respectively, after which the concentration of Pb(II) was obtained, and the adsorption rate of Pb(II) was calculated according to equation (1), respectively.

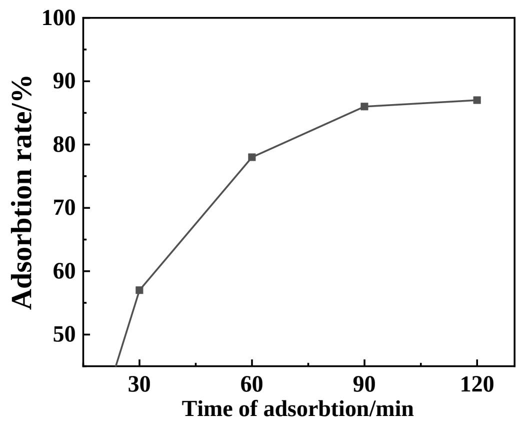

Fig 3: Effect of adsorption time on the adsorption of Pb(II)

As can be seen from Fig 3, the adsorption rate increases gradually with the adsorption time increasing gradually. However, when the adsorption time reached 90 min, the change of adsorption rate was not obvious with the adsorption time being extended. Considering the time cost, the adsorption time was kept 90 min, and the adsorption rate was 86.2%. So the optimal experimental conditions were as follows: the dosage of adsorbent was 60 mg/L, the initial concentration of Pb(II) was 40 mg/L, and the adsorption time was 90 min. Under the optimal conditions, and the adsorption rate of Pb(II) was 89.1% after test.

3.4 Orthogonal test results and analysis

On the basis of single factor experiment, the orthogonal test of three factors and the interaction terms of adsorbent dosage, initial concentration of Pb(II) and adsorption time were carried out. The rate of Pb(II) in the adsorbed solution was taken as the index, and the experiment was carried out according to the orthogonal test table. The specific scheme and results of the orthogonal test were shown in Table 2, and the optimal scheme of influencing factors was finally obtained.

Table 2: $L_9(3^4)$Orthogonal test protocol and results of adsorption of Pb(II)

Number	Dosage of adsorbent (mg/L)	Initial concentration of Pb(II)（mg/L）	Adsorption time (min)	Adsorption rate（%）
1	20	20	30	73.2
2	20	60	60	71.9
3	20	100	90	68.1
4	60	20	60	82.1
5	60	60	90	75.3
6	60	100	30	72.1
7	100	20	90	85.2
8	100	60	30	93.7
9	100	100	60	83.4

Table 3: Analysis of orthogonal test results of Pb(II) adsorption

Index		A/Dosage of adsorbent（mg/L）	B/Initial concentration of Pb(II)（mg/L）	C/Adsorption time (min)
Adsorption rate（%）	K1	213.2	240.5	239
	K2	229.5	240.9	237.4
	K3	262.3	223.6	228.6
	Average of K1	71.1	80.1	79.7
	Average of K2	76.5	80.3	79.1
	Average of K3	87.4	74.5	76.2
	Range (R)	16.3	5.8	3.5
	Factor	A>B>C		
	Optimal decision	$A_3B_2C_1$ (93.7%)		

Based on the adsorption rate of Pb(II) in table 3, the best experimental conditions and the optimal scheme was $A_3B_2C_1$. Furthermore, it can be seen from Ki that the factor of A was $A_3>A_1$. Here, it illustrated that the adsorption rate of Pb(II) varied greatly with the dosage of adsorbent. In addition, and the rate of Pb(II) was fewer different because of the factor of B. In order to avoid new environmental pollution, we choose the initial concentration of Pb(II) for 60 mg/L. Also, because of the adsorption rate of Pb(II) did not obviously vary. Therefore, considering the improvement of efficiency by time cost, the adsorption time was selected at 30 min, and the adsorption rate of Pb(II) was 93.7% at the scheme $A_3B_2C_1$.

4. CONCLUSION

The best single factor experimental conditions were as follows: the amount of adsorbent was 60 mg/L, the initial concentration of Pb(II) was 40 mg/L, and the adsorption time was 90 min, and the adsorption rate of Pb(II) was 89.1%. According to the orthogonal test, based on the adsorption rate of Pb(II) as a index, the relation of the factor was A>B>C, The optimal adsorption scheme was $A_3B_2C_1$. That was to say, the concentration of adsorbent was 100 mg/L, the initial concentration of Pb(II) was 60 mg/L, and the adsorption time was 30 min. The adsorption rate of Pb(II) was 93.7%. Comparing the results of single factor experimental and the orthogonal test, We found the result of orthogonal test was better than that of the single factor experimental, So the orthogonal test provided an effective scheme to improve the adsorption rate of Pb(II) via WSCC/MWCNTs-COOH as an adsorbent.

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