

Adsorption Characteristics of Protonated Chitosan for Hexavalent Chromium in Simulated Wastewater

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Abstract

Chitosan was protonated by sulfuric acid solution. The adsorption characteristics of protonated chitosan for hexavalent chromium Cr (VI) in the simulated wastewater containing Cr (VI) were studied. The effects of chitosan protonation degree and pH value of raw water on Cr (VI) adsorption characteristics were investigated. The research results showed that the greater the protonation degree, the higher the removal rate of Cr (VI), and the chitosan protonated in pH 1.5 diluted sulfuric acid had the best adsorption effect of 96%. In addition, the Cr (VI) removal efficiency reached the highest when the pH value of the raw water was three. The adsorption process of the protonated chitosan could well meet the Lagergren pseudo-second order equation and was dominated by chemical adsorption.

Keywords

protonation, chitosan, adsorption, wastewater, hexavalent chromium

I. INTRODUCTION

Human health and ecological environment is under serious threat due to the discharge of chromium-contained wastewater from electroplating, printing and dyeing, metallurgy, leather and other industries. There are two kinds of valence of chromium in aqueous solution, Cr (III) and Cr (VI). Specially, the toxicity of Cr (VI) is 100 times of Cr (III), which is released as the typical environment persistent pollutant by the United Nations

Environment Program (U.S.E PA) [1]. Therefore, it becomes a very important problem that how to remove Cr (VI) in chromium-containing wastewater efficiently in current environmental governance.

At present, the main methods of treating chromium-containing wastewater include reverse osmosis, electro dialysis method, reductive deposition method and adsorption, etc. Among them, the adsorption method is widely applied for its simple technology [2]. There are many kinds of adsorbents for adsorption such as activated carbon, resin and chitosan, etc. Chitosan has been used to treat peat water or wastewater containing heavy metals ([3], [4]). It is the product of chitin taking off the acetylation, which contains large amount of active groups in molecular chain such as $-NH_2$ and $-OH$, which can be used for heavy metal ion chelating agent and adsorbent, producing no secondary pollution [4]. However, the efficiency of water purification is always poor by using chitosan simply. In practical application, the adsorption efficiency of chitosan should be improved through material modification technique. The first method is protonating-modification by changing chitosan's some group $-NH_2$ into $-NH_3^+$, which is beneficial to the adsorption of SO_4^{2-} , $H_2PO_4^-$, $HCrO_4^-$ and any other negative ions([5], [6]). The second method is grafting-modification, which can improve the adsorption capacity of metal cation by raising the chitosan's content of $-NH_2$ [7]. The third method is compositing-modification. The chitosan is combined with another kind of material to make a new

type of composite material such as the magnetic chitosan composite material, which is widely concerned in recent years ([8]-[10]).

In this paper, protonating-modification was carried out by sulfuric acid solution, and the simulated wastewater containing Cr(VI) was configured to study the adsorption characteristics of Cr(VI) by protonated chitosan. The effects of chitosan protonation degree and solution pH value on the adsorption characteristics were investigated. The kinetic simulation of the adsorption process was furthermore carried out. The results will provide a valuable reference for the further research about treating chromium-containing wastewater.

II. MATERIALS AND METHODS

A. Materials

Main reagents: Chitosan and concentrated sulfuric acid were bought from Sinopharm Chemical Reagent Co.,Ltd, China. Hexavalent chromium standard solution with a concentration of 1000mg/L was provided by National Nonferrous Metals and Electronic Materials Analysis and Testing Center, China. Cr(VI) existed in the form of HCrO_4^- .

Main analytical instrument: Inductively Coupled Plasma Atomic Emission Spectrometer(ICP) was used to test the content of Cr(VI) in the solution. X-ray diffractometer(XRD) and Fourier transform infrared Spectrum(FT-IR) were used to test the structural characteristics of protonated chitosan.

B. Preparation of Protonated Chitosan

The 98% concentrated sulfuric acid was diluted with deionized water according to a certain volume ratio. Five kinds of sulfuric acid solution with different pH values of 1.5, 2.5, 3.5, 4.5, and 5.5 were configured. 180ml of the above-mentioned sulfuric acid solution with different pH values was put into the beakers, respectively. 3.0g chitosan powder was added into each beaker. By stirring them evenly, five beaks of stable suspension solution were formed. The solution was kept for 8 hours and then it was filtered and washed with deionized water to neutral. After that, the filtered

samples were put into the blast oven at a temperature of 80°C for drying. The drying time was about 10 hours. Then the dried samples were taken out from the oven and ground to powder. Finally, the protonated chitosan powder samples were obtained. The samples were stored in the bags for further experiments and marked as CS1.5/CS2.5/CS3.5/ CS4.5/CS5.5 according to the pH value of sulfuric acid solution during the protonation process. The protonation degree of the samples was judged according to the pH value of sulfuric acid solution. The lower pH value, the greater degree of protonation of the sample. In particular, initial chitosan without any protonation was marked as CS.

C. Batch Adsorption Experiment

The Cr (VI) standard solution was beforehand diluted to lower concentration such as 1ppm, 5ppm, 10ppm, 20ppm, respectively, which was treated as simulated wastewater containing Cr (VI) for adsorption experiments.

Firstly, the influence of the protonation degree of the samples on Cr (VI) adsorption in simulated wastewater was mainly examined. 0.4g protonated chitosan CS1.5/CS2.5/CS3.5/CS4.5/CS5.5 and the untreated chitosan adsorbent CS were respectively placed into 100ml solution whose initial concentration of Cr(VI) was 5ppm and PH value was 3. The change of Cr (VI) concentration with adsorption time at room temperature was measured. The selected adsorption time points were: 30min/60min/90min/120min/240min/360min/480min.

Secondly, the influence of the raw water (Cr (VI)-containing solution) pH value on the absorption properties of the samples was examined. Respectively, 0.2g adsorbent CS1.5/CS2.5/CS3.5/CS were put into 50ml Cr(VI)-containing solution whose initial concentration was 5ppm with different pH values 2, 3, 4.5, 6. The selected adsorption time was 90 min.

III. RESULTS AND DISCUSSION

A. Characteristics of Protonated Chitosan to Cr (VI) Adsorption

1) Effect of Chitosan Protonation Degree

Fig.1 indicates the influence of the protonation degree of the samples on Cr (VI) adsorption in simulated wastewater with PH value 3. The Cr (VI) removal percentage (R %) is defined as the following equation:

$$R \% = \frac{C_0 - C_e}{C_0} \times 100\% \quad (1)$$

Where C_0 (mg /L, ppm) is the initial Cr (VI) concentration, and C_e (mg/L, ppm) is the final Cr (VI) concentration in the solution after adsorption treatment. As shown in Fig.1, CS1.5 presents the best removal effect. Its removal rate reaches 96%. CS2.5 presents lower removal rate with 70%. However, for other samples, CS3.5/CS4.5/CS5.5/CS, they exhibit much lower removal rate no more than 20%.

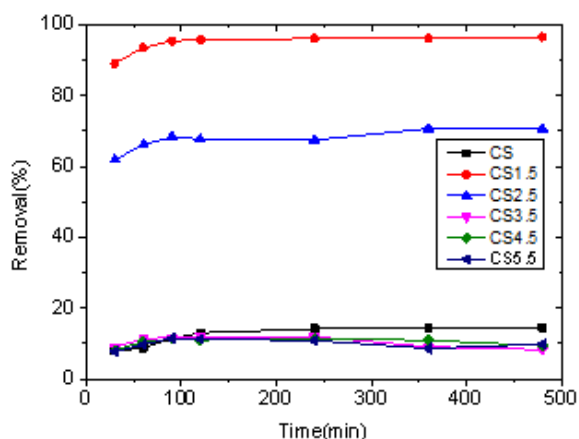


Fig.1: Effect of protonation degree of chitosan on Cr(VI) removal efficiency

The process of protonated chitosan on Cr (VI) adsorption has the effect of inter-molecular force, electrostatic attraction and chemical bond force. Chitosan is a linear polymer with a lot of $-NH_2$ structures, which can be changed into $-NH_3^+$ structure by protonation. According to the principle of electrostatic adsorption, protonated chitosan with positive charge could adsorb chromate. So the adsorption mechanism of protonated chitosan includes electrostatic adsorption. For chitosan with greater protonation degree, it contains more $-NH_3^+$ functional groups, so its adsorption rate should be higher than that of chitosan with lower protonation degree.

In addition, as shown in Fig.1, the reaction reaches

equilibrium state at 90min and the removal rate of Cr(VI) has no obvious change with increasing adsorption time, which implies that the phenomenon of desorption does not appear during the adsorption process.

2) Effect of Raw Water pH Value

Fig.2 indicates the effect of raw water pH value on Cr (VI) adsorption. As shown in Fig.2, the lower pH value of solution is helpful to improve the adsorption effect of protonated chitosan. When the pH value is increased to 4.5~ 6, the removal rate for CS3.5 and CS decreased significantly, while the removal rate of CS1.5 and CS2.5 decreased little, and CS1.5 has the best adsorption effect. All the samples present high adsorption rate when the raw water PH value is 3.

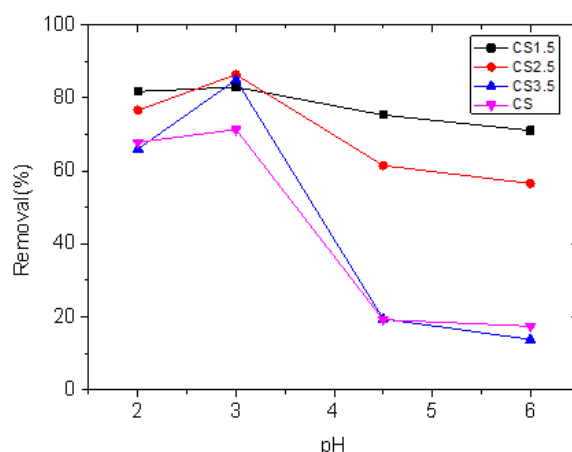


Fig.2: Effect of raw water pH on Cr(VI) removal efficiency

It could be deduced that, when the raw water pH value is low, CS2.5/CS3.5/CS were subject to different degrees of re-protonation, which results in the increasing of the number of $-NH_3^+$ in chitosan and then the comparatively good adsorption effect. Gradually, with the increasing of the raw water pH value, the re-protonation effect of CS3.5/CS is weakened, resulting in the significant decrease of the adsorption rate of CS3.5/CS. When the raw water pH value is 6, closer to the pH value of natural water, the adsorption rate of CS1.5 reaches 71%, which is still higher than that of other adsorbents.

B. Adsorption Kinetics

0.4g protonated chitosan CS1.5/CS2.5/CS3.5/ CS4.5/CS5.5 and non-protonated chitosan CS were put into 100ml Cr (VI)-containing solution with the initial concentration of 5ppm, respectively. Five adsorption time points, 30min, 60min, 90min, 120min and 240min, are selected to study the adsorption kinetics process on Cr (VI) adsorption. Lagergren pseudo-second order kinetic equation is one of the equations commonly used to predict the change of adsorption over time [11], which is based on the assumption that the adsorption rate is determined by the square of the number of adsorbed vacancies that are not occupied by the surface of the adsorbent. Correspondingly, the adsorption kinetic equation is:

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \quad (2)$$

Where Q_t (mg/g) is the amount of adsorbed chromium per specific amount of adsorbent at any time t ; Q_e (mg/g) is the amount of adsorbed chromium per unit mass of adsorbent at equilibrium; k_2 (g/(mg·min)) is the equilibrium rate constant for pseudo-second order kinetic equation.

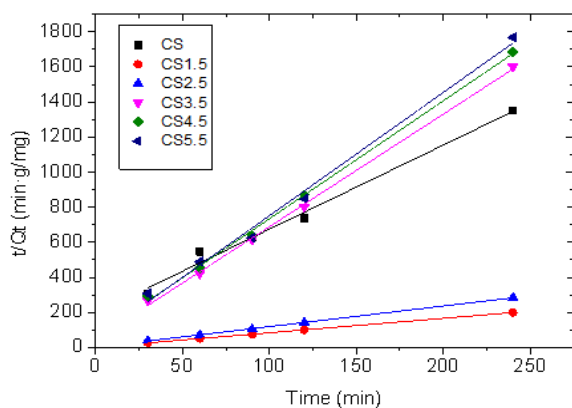


Fig.3: Fitted adsorption kinetics curves of protonated chitosan on Cr (VI) adsorption in 5 ppm containing Cr (VI) solution

The adsorption data-fitting process was conducted according to the above Lagergren pseudo-second order kinetic equation. The calculated results are simultaneously displayed in Fig.3 and Table 1. According to Table 1, the related coefficient (R^2)

corresponding to each sample is greater than 0.99, indicating a good linear relationship, which is also demonstrated by the fitted linear curves shown in Fig.1. The results indicate that the above pseudo-second order kinetic model could well describe the adsorption process of protonated chitosan on Cr (VI) adsorption. Furthermore, the main influencing factors of pseudo-second order kinetic adsorption model are related to the formation of chemical bonds [12]. Thus it can be inferred that the adsorption process is mainly chemical adsorption.

TABLE I Parameters of Pseudo-Second Order Lagergren

Protonated chitosan	K_2 (g/(mg·min))	Q_e (mg/g)	R^2
CS	0.102	0.214	0.9921
CS1.5	0.317	1.220	0.9999
CS2.5	0.433	0.855	0.9994
CS3.5	1.058	0.143	0.9965
CS4.5	7.676	0.127	0.9953
CS5.5	1.229	0.131	0.9920

C.H. Zhang et al. [13] used protonated chitosan for adsorbing phosphate ions, and their research result showed that its adsorption process belonged to mono-molecular layer chemical adsorption. Y.H. Xie et al. [14] used protonated chitosan for adsorbing perchlorate and their result showed that chemical adsorption was considered to play main role in adsorption rate control. For the Cr(VI) adsorption by protonated chitosan in our experiment, as mentioned above, in the initial stage of adsorption, due to the existence of positive charge of $-NH^{3+}$ and the negative charge of $HCrO_4^-$, there would produce a mutual attraction called electrostatic adsorption, which belongs to the physical adsorption category. However, with the further development of the adsorption process, when $-NH^{3+}$ and $HCrO_4^-$ encountered with each other, they would share electron pair. Then the covalent bond is formed, which belongs to the chemical adsorption category. This adsorption mechanism has been confirmed by the former pseudo-second order kinetic model. In general, chemical adsorption plays main role in the adsorption

mechanism.

C. Characterization of XRD and FT-IR

According to the above researches on the adsorption performance of protonated chitosan to Cr (VI), it can be referred that CS1.5 has the best adsorption performance among all the protonated chitosan samples. Specifically, XRD and FT-IR are used to characterize the structure characteristics of CS1.5 and the XRD pattern and FT-IR spectrum of CS are also measured as comparison.

The XRD patterns of CS1.5 and CS are shown in Fig.4. Two diffraction peaks at $2\theta = 10^\circ$, 20° are clearly identified in both adsorbents. As Samules reported [15], chitosan has two different crystal forms, which are called the Form I (2θ around 10°) and Form II (2θ around 20°), both belonging to mono-clinic system. By comparing the XRD spectra of CS and CS1.5, it could be noticed that the strength of the diffraction peak of CS1.5 is a bit weaker than that of CS, but the position of the two diffraction peaks of the two samples are almost unchanged, indicating that the chitosan maintains its crystal form after protonation.

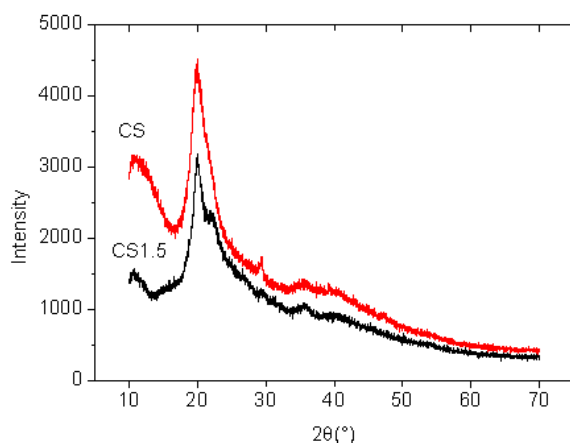


Fig.4: XRD patterns of CS and CS1.5

Fig.5 displays the FT-IR spectra of CS1.5. As shown in Fig.5, the broad peak of CS near 3450cm^{-1} is formed by the overlapping of the stretching vibration absorption peaks of O-H bond from -OH functional group and N-H bond from $-\text{NH}_2$. The peak near 2873cm^{-1} is the stretching vibration absorption peak of C-H bond from $-\text{CH}_3$ functional group. The peak near 1600cm^{-1} is the characteristic absorption peak of $-\text{NH}_2$. In addition, there are three characteristic absorption

peaks of the amide, located in the positions of 1659cm^{-1} , 1550cm^{-1} , 1424cm^{-1} [16]. For CS1.5, the protonated chitosan, the vibration absorption peak of O-H and N-H at 3450cm^{-1} is greatly weakened and the bending vibration peak at 1600cm^{-1} has disappeared. Furthermore, the new peak at 1540cm^{-1} is $-\text{NH}_3^+$, indicating that chitosan has been protonated [17].

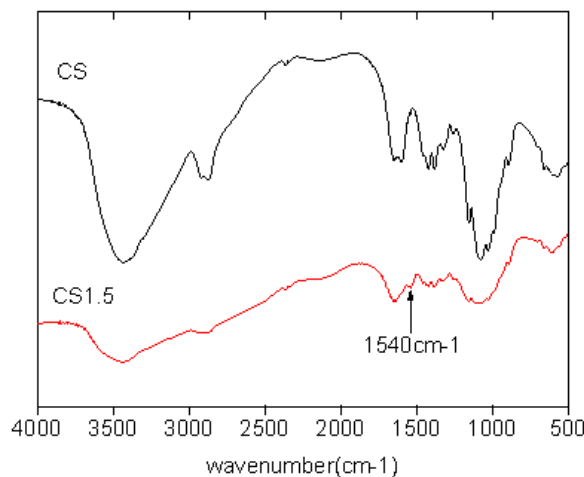


Fig.5: FT-IR spectra of CS and CS1.5

IV. CONCLUSIONS

Five kinds of protonated chitosan were prepared through the treatment by sulfuric acid solution with five different pH values. The results of the adsorption characteristics of protonated chitosan to Cr (VI) in simulated waste-water could be summarized as following:

1) The adsorption performance of protonated chitosan was obviously enhanced with the increase of protonation degree. The chitosan protonated by diluted sulfuric acid with pH value 1.5 had the best characteristics of chromium adsorption. However, the removal rate of chitosan protonated by diluted sulfuric acid with pH value equal to or more than 3.5, together with chitosan without any treatment, was less than 20%. The adsorption achieved equilibrium after around 90min.

2) Raw water pH had a strong impact on Cr (VI) adsorption, and the adsorption efficiency was the highest when the pH value of the raw water was three. Over the PH values ranging from 3 to 6, CS1.5 exhibited a more stable and higher adsorption effect. Whereas, the adsorption performance of chitosan with lower degree of protonation decreased greatly with the

increase of raw water pH.

3) The adsorption kinetic analysis results showed that the Lagergren pseudo-second order kinetic model could well describe the process of protonated chitosan to Cr(VI) adsorption and the adsorption process was dominated by chemical adsorption.

4) The XRD patterns showed that the structural characteristics of chitosan remained unchanged after protonation treatment and the FT-IR spectra demonstrated the protonation characteristics of the sample.

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