



Research Article

# Effects of Bentonite Activation Methods on Chitosan Loading Capacity

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## Abstract

The adsorption capacity of bentonite clay for heavy metal removal from wastewater can be significantly enhanced by a high loading of chitosan on the surface. In order to enhance the chitosan loading, we tested activating bentonite clay by three methods prior to chitosan loading: sulfuric acid, calcination, and microwave treatments. Meanwhile, several parameters during chitosan loading, namely the initial chitosan concentration, stirring speed, reaction time, temperature, and pH value were investigated. Our results indicate that chitosan is attached to bentonite clay through intercalation and surface adsorption according to X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Fourier Transform Infrared Spectroscopy (FTIR) analyses. The maximum chitosan loading on 200-mesh raw bentonite clay (126.30 mg/L) was achieved under the following conditions: the initial chitosan concentration of 1000 mg/L, the stirring speed of 200 rpm, pH of 4.9, 60 min of reaction time, and temperature of 30 °C. The chitosan loading was further increased to 256.30, 233.70, and 208.83 mg/g, when using bentonite clay activated through 6 min of microwave irradiation (800 W), 10 % sulfuric acid treatment, and calcinations at 600 °C, respectively. When the chitosan loading was increased from 34.76 to 233.7 mg/g, the removal percentages of Cu(II), Cr(VI), and Pb(II) were improved, respectively from 78.90 to 95.5 %, from 82.22 to 98.74 %, from 60.09 to 86.18 %. Copyright © 2018 BCREC Group. All rights reserved

**Keywords:** Chitosan; Chitosan-loaded bentonite; Bentonite activation; Loading properties

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## 1. Introduction

Heavy metal ions are among the most hazardous compounds to human health and the environment due to their high level of toxicity, ability to enter the food chain, and poor biodegradability. Therefore, there are strict standards for their discharge into the environment.

Conventional methods for removing heavy metals from water include chemical precipitation, coagulation, flocculation, ion exchange, membrane filtration, and activated carbon adsorption [1,2]. However, these treatments tend to have high costs, leave residuals, and do not completely remove the pollutants. Hence, there is an urgent need to develop new low-cost adsorbents to remove heavy metals in water.

Natural bentonite clays are often used to adsorb metallic contaminants, since they are low-

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cost, abundant materials that have excellent cation exchange capacity and relatively large surface areas [3,4]. Chitosan modification of bentonite clay improves its effectiveness in water treatments, by mitigating certain flaws of bentonite clays, including high swelling and suspendability, difficult separation [5,6]. Meanwhile, bentonite clay remediates some disadvantages of chitosan that affect its adsorption efficacy, e.g. low density, the tendency to float, and difficulty in making contact with pollutants [7,8]. On the other hand, various modification techniques, including acid and thermal (by calcination or microwave radiation) treatments, have been reported to affect the adsorption properties of nature clays for metal ions in aqueous solutions [9-11].

Many studies of chitosan-loaded bentonite adsorbents have focused on their performance in pollution removal, such as the adsorption volume, particle size, optimal conditions (pH, agitation rate, and temperature), equilibrium isotherm, related dynamics and thermodynamics, interfering ions, and the renewing of the adsorbents [12-14]. However, few studies have examined the process and mechanism of loading chitosan onto bentonite. Herein, for the first time, we investigated the effects of various parameters on the loading amount of chitosan: the initial amount of chitosan, stirring speed, pH value, reaction time, temperature and bentonites activation/modification methods (e.g. acidification). Another novelty of the present study is that we compared the effects of the chitosan loading amount for removing Cu(II), Cr(VI), and Pb(II) ions from aqueous solutions. These studies indicate the process and mechanism of chitosan loaded onto bentonite and will surely extend the application of composite chitosan-loaded bentonite adsorbents for removing metal ions in wastewater.

## **2. Materials and Methods**

### **2.1 Reagents and equipment**

The following primary chemical reagents were used: bentonite clay (CTS, 300 mesh, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), chitosan (degree of deacetylation  $\geq$  90 %, Shanghai Lanji Biological Technology Co. Ltd), sulfuric acid (analytical grade), lead nitrate ( $\text{Pb}(\text{NO}_3)_2$ , analytical grade), potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$ , analytical grade), and hydrated copper sulfate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , analytical grade).

Equipment used during the preparation of the adsorbents include: high-temperature box-type resistance furnace (SXL-1200, Zhengzhou

Honglang), microwave oven (MG-5021, LG), 6-paddle electrical stirrer with digital display (JJ-4, Changzhou Guowang), electrothermal constant-temperature water bath (DK-98-1, Shanghai Optical Instrument Factory), and high-speed desktop centrifuge (TGL-16G, Shanghai Anting). Instruments used for characterizing the properties and performance of the adsorbents include: UV spectrophotometer (200-1000 nm, UV-2350, Unico), Precision pH meter (0.00~14.00 pH, S20K, Mettler Toledo), Scanning electron microscope (HV mode Resolution: 3.0 nm, 8.0 nm, 15 nm, LV mode Resolution: 4.0 nm; Magnification: X5-X3000 000, JSM-6360LV, JEOL), X-ray powder diffractometer (Angle range: 5-120°, Target: Cu, Mo, Fe, D8 Advance, Germany Bruker), and Infrared spectrometer (Spectrometer range: 7800-350  $\text{cm}^{-1}$  (KBr), PE-680, Perkin-Elmer).

### **2.2 Optimization of chitosan loading conditions**

The loading of chitosan on bentonite was examined using various reaction times (10-90 min), initial chitosan concentrations (250-2500 mg/L), stirring speeds (50-300 rpm), temperatures (30-50 °C), and pH values (2-12). Specifically, 1 g of raw bentonite clay was dispersed in 150 mL of distilled water. The pH was adjusted with HCl and NaOH solutions. Chitosan solution of given concentration was then added to the bentonite suspension, up to a volume of 200 mL.

### **2.3 Activation and modification of bentonite clays**

The acid activation of bentonite clays has been prepared using 5 g of bentonite was placed in a 500 mL beaker, to which 200 mL of sulfuric acid solution of given concentration (5-30 %) was added. The suspension was kept at 80 °C and stirred at the rate of 500 rpm. After 4 h of reaction, the mixture was centrifuged, and then the precipitate was washed until the filtrate reached a pH value of 7.0-8.0. The clay was then dried, grinded, and sieved (200 meshes, 0.075 mm sieve size) [15]. To activate the clay by calcination, 5 g of bentonite clay was placed by a griddle in a muffle furnace, and calcinated at given temperature between 150-750 °C for 2 h. After the oven cooled, the clay was grinded and sieved (200 meshes, 0.075 mm sieve size) [10]. For microwave activation, a griddle was used to place 5 g of bentonite clay in a microwave oven. The bentonite clay was then treated for 2-10 min at the output power of 300-1000 W [11].

## 2.4 Determination of chitosan loading

The primary amino groups of chitosan react chromogenically with Congo red under certain conditions, causing an absorption at 545 nm that is linearly proportional to the chitosan concentration [16,17]. On this basis, a spectrophotometric method was used to directly determine the content of chitosan. The standard curve in Figure 1 displays the following relationship (Equation (1)) between chitosan concentration ( $y$ , in mg/L) and light absorption (a.u.):

$$y = 2277.2337x + 45.1916 \quad (1)$$

The high linear correlation coefficient ( $R^2 = 0.9973$ ) indicates a good fit.

To load chitosan on bentonite, a chitosan solution of given concentration was slowly added to the bentonite suspension up to a volume of 200 mL, and then the reaction was carried out at specified temperature and stirring speed for a fixed duration. The resulting mixture was centrifugally separated. The precipitate was heat-dried, grinded, and sieved (200 mesh, 0.075 mm sieve size) to obtain chitosan-loaded bentonite clay [5,7]. The amount of chitosan loading ( $M_{ct}$ , in mg/g) was calculated as the difference between the initial amount of chitosan ( $M_q$ ) and that in the supernatant after the separation ( $M_{qe}$ ) (Equation (2)).

$$M_{ct} = M_q - M_{qe} \quad (2)$$

## 2.5 Characterization and analysis

To investigate the interactions between chitosan and bentonite, a Scanning Electron Microscopy (SEM, JSMLV-6360) was performed on raw, activated (by acidification, calcination, or microwave irradiation), and chitosan-loaded bentonite clays to analyze their microscopic

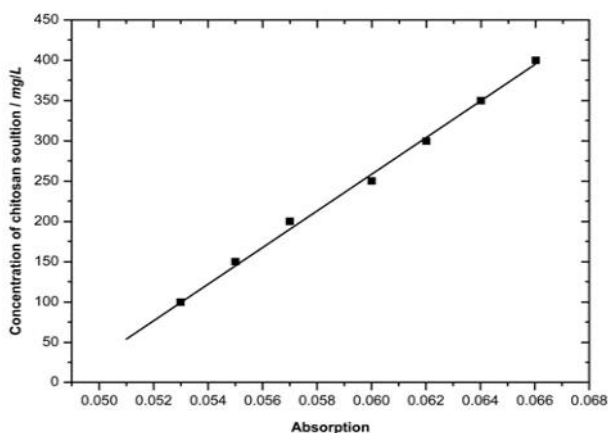


Figure 1. Standard curve for chitosan concentration measurement

morphologies. An X-ray Diffraction (XRD, D8 Advance) was used to analyze the composition of the bentonite materials. The structural analysis was performed using a Fourier Transform Infra Red (FTIR) spectroscopy (PE-680 infrared spectrometer).

## 2.6 Heavy metal ion adsorption experiments

To test the performance of various clay adsorbents for removing heavy metals, the raw, activated, and chitosan-loaded bentonite clays were tested in aqueous solutions containing Cu(II), Cr(VI), or Pb(II) ions. Bentonite samples loaded with different amounts of chitosan were prepared after acidification for studying the effects of the adsorbent amount and chitosan loading. Single-metal solutions of Cu(II), Pb(II), and Cr(VI)(100 mg/L) were prepared from the respective salts using distilled-deionized water, and their pH adjusted to  $5.0 \pm 0.01$  with 0.1 mol/L HCl or NaOH. The metal ion contents in the solution were measured before and after adsorption, using a flame atomic absorption spectroscopy (Spectra AA 220FS, Varian, USA). The removal rate ( $W_e$ , %) was calculated in Equation (3).

$$W_e = \frac{C_0 - C_e}{C_0} \cdot 100\% \quad (3)$$

where  $C_0$  and  $C_e$  are the initial and equilibrium concentrations of the heavy metal ion (mg/L), respectively.

## 3. Results and Discussion

### 3.1 Chitosan loading parameters

According to Figure 2, the amount of chitosan loading increased with reaction time from

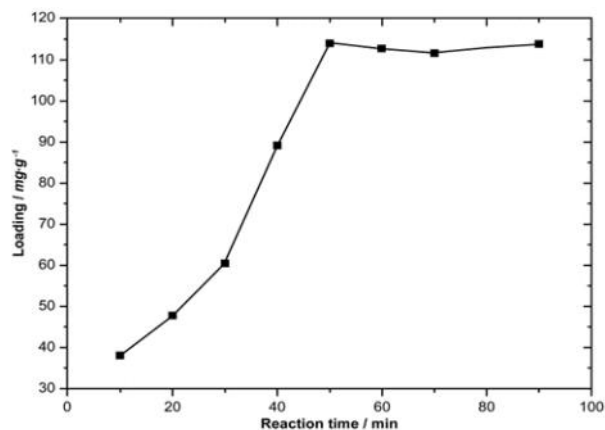


Figure 2. Effects of reaction time on chitosan loading

10 to 50 min, as more and more chitosan occupied the active adsorption sites on the bentonite [18]. The increase of chitosan loading became stagnant from 50 to 90 min, with a maximum value of 112.62 mg/g after 50 min of reaction.

In Figure 3, the chitosan loading continuously increased with the initial chitosan concentration, reaching a plateau value of 108.83 mg/g at 1000 mg/L. At lower initial concentrations, active adsorption sites on the bentonite surface are not fully occupied, resulting in unsaturated loading [19]. The chitosan loading increased with the stirring speed used during the reaction, reaching a plateau value of 118.10 mg/g at 200 rpm (Figure 4). An appropriate stirring speed provides the necessary mass transfer for the loading process, while a lower speed leads to slower chitosan diffusion and consequently insufficient loading [20].

Figure 5 shows the effects of temperature on chitosan loading capacity. When the temperature increased from 30 to 50 °C, the chitosan

loading decreased from 121.48 to 55.98 mg/g. As the temperature increases, the velocity of the chitosan molecules in the solution increases, which promotes chitosan desorption and reduces the loading. This trend also indicates that the loading of chitosan onto the bentonite surface is an exothermic reaction [21].

In Figure 6, as the pH value increased, the loading amount first increased to reach a maximum capacity of 126.30 mg/g at pH = 4.88, and then was lowered upon further pH increase. The main reason for these phenomena is that the  $-NH_2$  groups of chitosan molecules bond with  $H^+$  in the solution to form  $-NH_3^+$ , which electrostatically interacts with the negatively charged surface of bentonite. At lower pH (i.e., higher  $H^+$  concentration), however,  $H^+$  can also compete with chitosan for the negatively charged loading sites. The protonation of the  $-NH_2$  groups and competitive adsorption, taken together, lead to an optimum pH for chitosan loading [22-24].

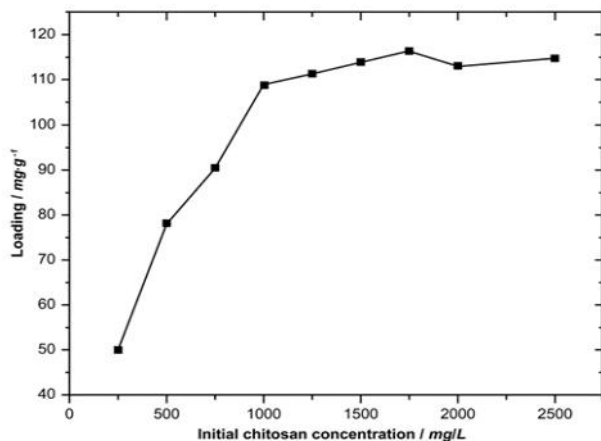


Figure 3. Effects of initial concentration on chitosan loading

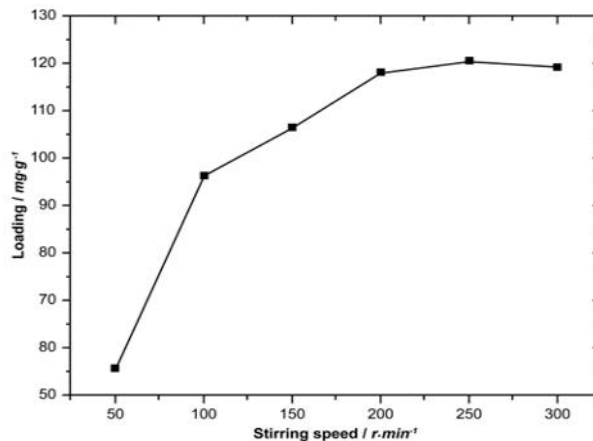


Figure 4. Effects of stirring speed on chitosan loading

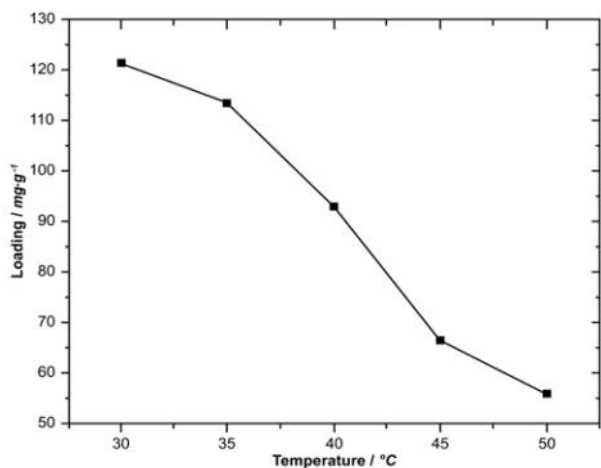


Figure 5. Effects of temperature on chitosan loading

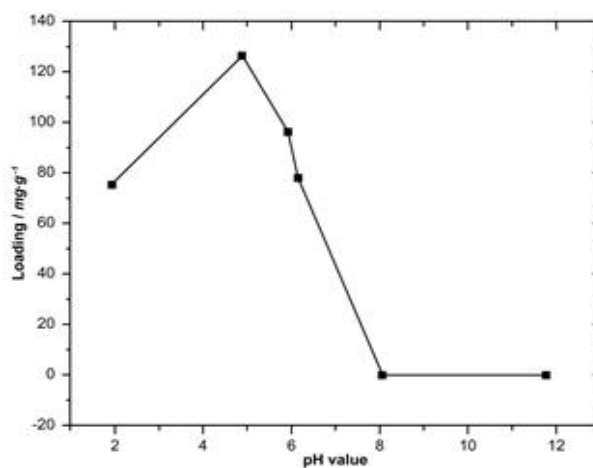


Figure 6. Effects of pH on chitosan loading

### 3.2 Effects of activation treatments on the chitosan loading amount

Bentonite clay was activated by three different methods (acidification, calcination, and microwave irradiation), and then loaded with chitosan under the optimal conditions identified above (initial chitosan concentration: 1000 mg/L, stirring speed: 200 rpm, reaction time: 60 min, 30 °C, and pH = 4.9).

Sulfuric acid has the ability to remove the soluble salts and impurities from the surface and interlayers of bentonite, and thus it increases the surface area, porosity, and the number of chitosan loading sites in bentonite [9,15,22]. Figure 7 shows that the chitosan loading onto bentonite first increased and then decreased with the concentration of sulfuric acid (within 3-20 %) used. The maximum loading amount (233.70 mg/g) was found when using 10 % sulfuric acid. In highly concentrated sulfuric acid, the layer of oxo ions within the bentonite structure could become dehydrated and fractured. As a result, the number of active loading sites for chitosan is reduced drastically.

The calcination process causes sequential loss of surface and then bonded water from bentonite, thus releasing more loading sites [10]. From Figure 8, the calcination activation of bentonite can enhance the loading capacity of chitosan. When the calcination temperature is increased from 150 to 750 °C, the loading amount of chitosan first increases and then decreases, reaching a maximum (208.83 mg/g) at 600 °C. A sufficiently high calcination temperature causes water loss and carbonates loss that improves adsorption ability of bentonite clay and increases the chitosan loading [23]. At excessively high temperatures, however, warping

and shrinkage occur in bentonite, which damage its structural frame and reduce the number of available sites, thus causing the loading amount of chitosan to decrease.

Similar to the calcination method, microwave heating causes the superficially adsorbed and interlayer water to vaporize and escape, which in turn causes more pores and channels to form in bentonite. The result is an increased number of chitosan loading sites [11,24]. Based on Figures 9 and 10, the chitosan loading increases with the microwave radiation output power up to 800 W to reach a maximum of 193.01 mg/g. At this output power, the loading amount first increased with the irradiation time and then decreased, with a maximum at 6 min to produce a chitosan loading of 256.30 mg/g. Upon prolonged irradiation, the channels and pores will “soften” and damage the original layered structure of bentonite, thus reducing the loading capacity.

According to the results above, all three activation methods can enhance the chitosan loading capacity on the bentonite surface. Both microwave irradiation and calcination can activate the bentonite clay by increasing the number of active sites for chitosan loading. Compared to these two methods, acidification is a high-efficiency, low-cost, and simple activation method for improving the chitosan loading capacity. Therefore, this method was used for the metal ion adsorption tests discussed in Section 3.4.

### 3.3 Material characterization

To obtain a better understanding of the microscopic morphology, composition, and structure of the various bentonite samples, SEM,

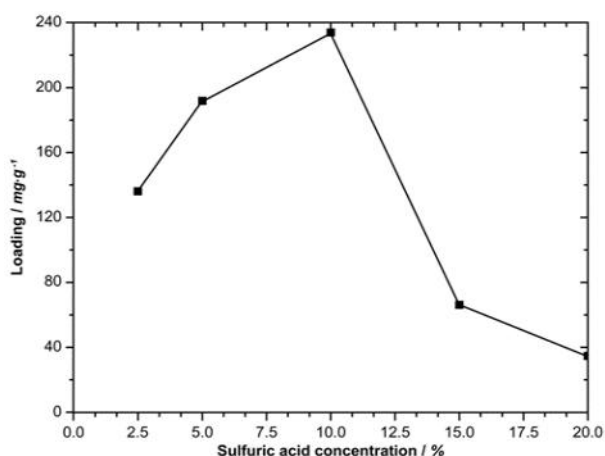


Figure 7. Effects of different concentrations of sulfuric acid used for activation on the loading of chitosan

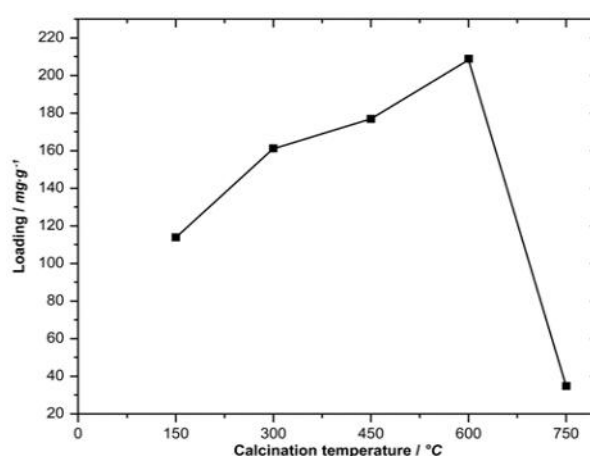


Figure 8. Effects of bentonite calcination temperatures on the loading of chitosan

XRD, and FTIR analyses were performed on raw bentonite clay, bentonite activated by acidification, calcination, or microwave-irradiation (using the respective optimal treatment conditions), as well as chitosan-loaded bentonite.

As shown in Figure 11, the activated/modified bentonite clays, with and without chitosan, have smoother surfaces and more distinct spatial structures compared to the raw bentonite, and the particles were dispersed into smaller wafers. The white chitosan particles adsorbed onto the surface of chitosan-loaded bentonite (Figures 11(E) and 11(F)) and into the spaces between the clumps of clay cause the surface to become relatively coarser and looser, and the interlayer distances become significantly larger. These morphological changes

indicate that: (1) all three activation methods improve the spatial structure of bentonite; (2) chitosan is loaded via surface adsorption and intercalation; and (3) the loading process does not change the basic structure of bentonite [9-12].

In the XRD patterns of Figure 12, all activated bentonite samples have similar shapes in their diffraction patterns, although differences were observed in the position, sharpness, and symmetry of the  $d(001)$  plane diffraction peak. The primary peak in the activated and chitosan-loaded activated clays shifted to smaller  $2\theta$  angles compared to the raw bentonite, especially in the chitosan-loaded activated clay. According to the Bragg equation, this change corresponds to an increase in the interlayer distances. Therefore, all three activation methods

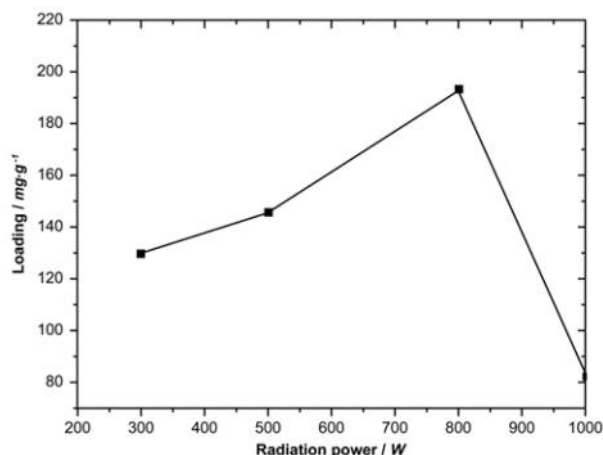


Figure 9. Effects of microwave radiation output powers used for activation on the loading of chitosan

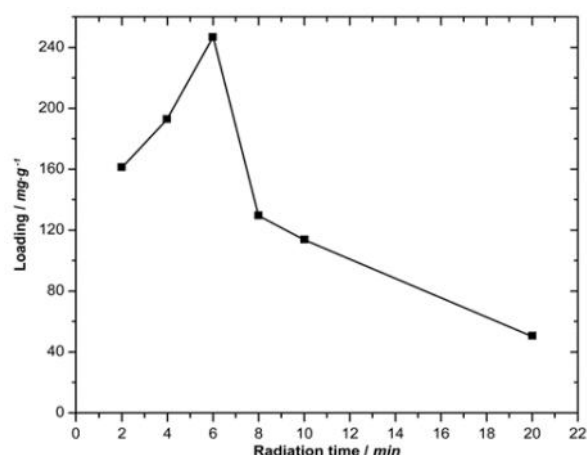


Figure 10. Effects of microwave radiation times used for activation on the loading of chitosan (Radiation power: 800 W)

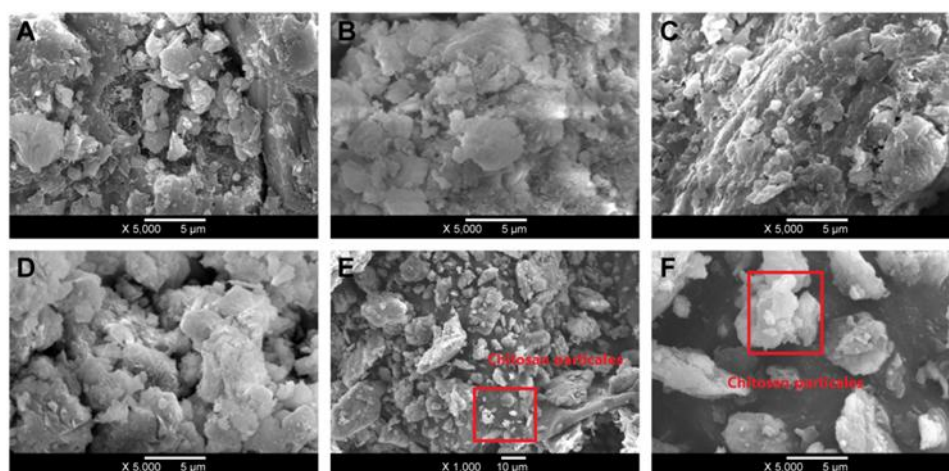


Figure 11. SEM images of different bentonite samples. (A) Raw bentonite clay, (B) acidified bentonite, (C) calcination-activated bentonite, (D) microwave-activated bentonite, (E) chitosan-loaded bentonite (x1000), (F) and chitosan-loaded bentonite (5000x)



enhanced the interlayer structure of bentonite. The largest interlayer distance was observed in the chitosan-loaded activated bentonite, indicating that chitosan molecules could become intercalated between the bentonite layers [13,19,25].

In the FTIR spectra (Figure 13), both calcination and microwave activation caused the 3446 and 3589  $\text{cm}^{-1}$  absorption peaks (O-H stretching vibrations of water between the bentonite layers) to disappear. For the chitosan-loaded bentonite, the new overlapping absorption peaks at around 3500  $\text{cm}^{-1}$  is caused by the O-H and N-H stretching vibrations at similar frequencies. Another peak at 1518  $\text{cm}^{-1}$  corresponds to O-H bending vibrations, while those at 525 and 808  $\text{cm}^{-1}$  correspond to the vibrations of octahedral Al-O. After chitosan loading, the area under the spectral peak at 540  $\text{cm}^{-1}$  is reduced, while the peak at 1077  $\text{cm}^{-1}$  becomes broader. These changes are due to the chemical adsorption of chitosan molecules on the octahedral  $\text{AlO}_6$ , which weakens the Al-O bond. According to these results, chitosan was successfully loaded (either on the surface or intercalated between the layers) onto bentonite clay without changing the basic structure of the latter [5,13,26].

### 3.4 Adsorption performance of chitosan-loaded bentonite clay

To test the capacity of the chitosan-loaded bentonite clays for adsorbing heavy metals, we tested various clay samples in Cu(II), Cr(VI), and Pb(II) solutions. For the chitosan-loaded bentonite, we also studied the effects of the adsorbent amount and the chitosan loading. Figure 14 shows the performance of the six clay samples for removing Cu(II), Cr(VI), and Pb(II) ions at 30 °C, with a stirring speed of 200 rpm, pH = 5.0 for 60 min. The amount of adsorbent used was 1 g/L, and the initial ion concentrations were 100 mg/L each. All activation methods improved the performance of bentonite clay in adsorbing Cu(II), Cr(VI), and Pb(II), with the chitosan-modified clay showing a significant increase. Acidification, microwave irradiation, and calcination all increase the number of adsorption sites on bentonite and the cation exchange capacity, thus increasing the heavy metal adsorption capacity. Furthermore, the surface of the chitosan-modified clay features many amino and hydroxyl groups, which can form covalent bonds with the heavy metal ions and further improve the adsorption performance [9,27].

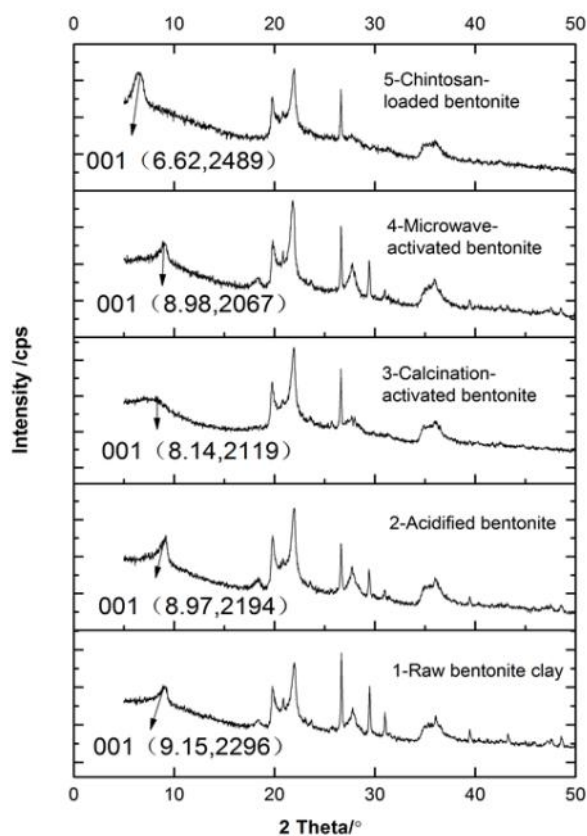


Figure 12. X-ray diffraction patterns of clay samples

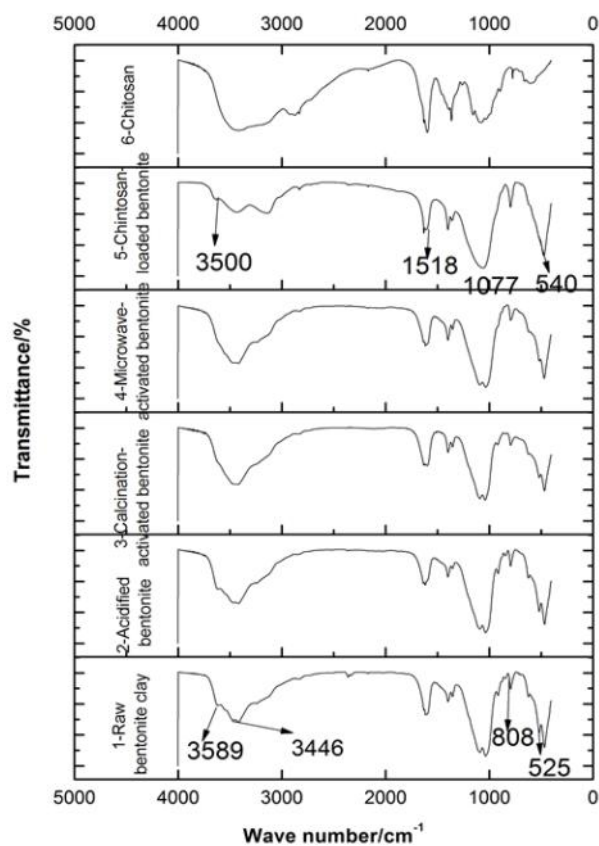


Figure 13. Infrared absorption spectra of clay samples

Figure 15 shows the removal of Cu(II), Cr(VI), and Pb(II) heavy metal ions (100 mg/L) using chitosan-loaded bentonite at the adsorbent amounts of 0.5, 1.0, 1.5, 2.0, and 2.5 g/L. The adsorption was carried out at 30 °C, with a stirring speed of 200 rpm, pH = 5.0 for 60 min. The adsorption percentage of all three heavy metal ions increased with the adsorbent concentration, gradually reaching a plateau value. A higher amount of chitosan-loaded bentonite adsorbent means more adsorption sites available for the heavy metal ions, therefore the heavy metal ion removal is improved [28].

Finally, 1 g/L bentonite clay samples loaded with different amounts of chitosan (34.76, 66.41, 136.22, 191.91, and 233.7 mg/g) were tested with 100 mg/L Cu(II), Pb(II), or Cr(VI) solutions at 30 °C, with a stirring speed of 200

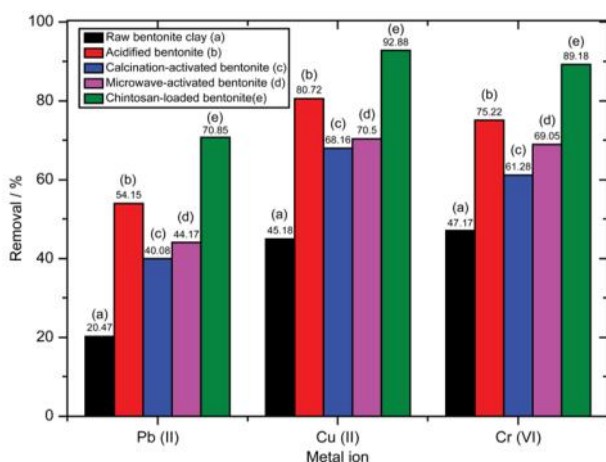


Figure 14. Comparison of Cu(II), Pb(II), and Cr(VI) removal percentages by different bentonite adsorbents

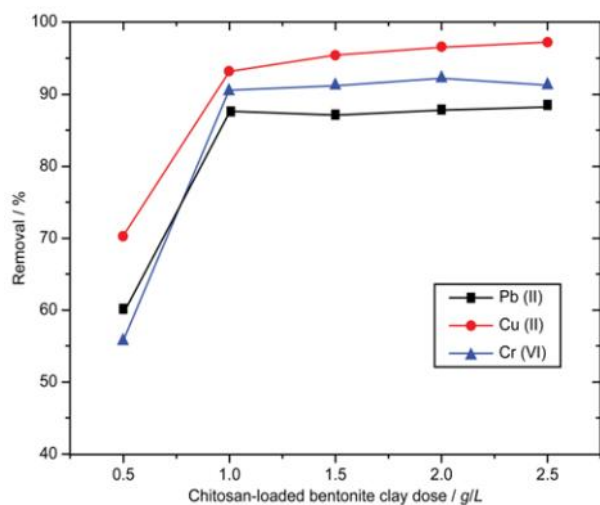


Figure 15. Effect of the amount of chitosan-loaded bentonite on the heavy metal removal percentage

rpm, pH = 5.0 for 60 min (Figure 16). The percentages of Cu(II), Cr(VI), and Pb(II) adsorption increased with the chitosan loading. An optimal chitosan loading should enhance the adsorption capacity of the clay, without clogging its adsorption channels (which is detrimental for the adsorption of heavy metal ions) [6,28].

#### 4. Conclusions

In this study, the loading capacity of chitosan increases and reaches a maximum value after 50 min of reaction with increasing reaction time. The chitosan loading increases with the initial chitosan concentration, and reaches a plateau value at 1000 mg/L. At higher stirring speeds, the loading amount of chitosan increases to reach a plateau value at 200 rpm. When the temperature is increased from 30 to 50 °C, the amount of chitosan loading is reduced. When the pH value is increased from 2 to 12, the loading amount first increases, and then decreases, reaching a maximum loading capacity at pH = 4.88. For sulfuric acid from 3 to 20 %, the chitosan loading first increases and then decreases, with a maximum loading for 10 % sulfuric acid. when the calcination temperature is increased from 150 to 750 °C, with a maximum chitosan loading at 600 °C. The chitosan loading following microwave radiation increases with the microwave output power, with a maximum loading at 800 W. At this output power, the loading amount reaches a maximum loading at 6 min. The removal percentages of Cu(II), Cr(VI), and Pb(II) all increase with the concentration of the adsorbent,

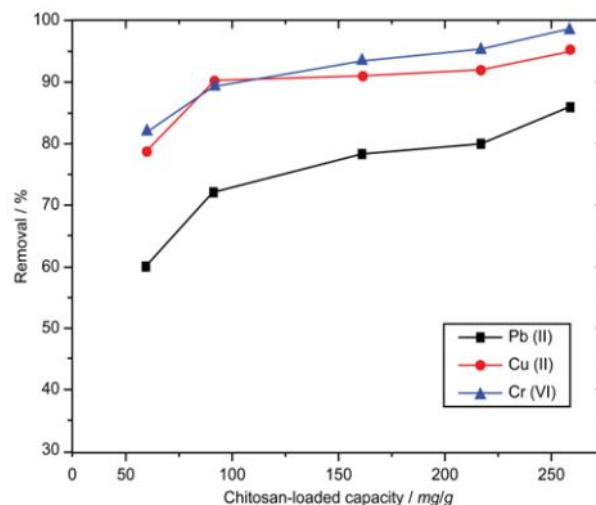


Figure 16. Effect of chitosan-loading on the heavy metal removal percentages by bentonite clay



reaching a plateau value beyond 1 g/L with 66.41 mg/g of chitosan loading.

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