

MnO₂-Loaded Activated Carbon and Its Adsorption of Formaldehyde

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Coconut shell activated carbon (AC) loaded with MnO₂ was tested as an adsorbent for formaldehyde. Preparation conditions of MnO₂-loaded AC (MnO₂-AC) were optimized. The resulting AC and MnO₂-AC were characterized by scanning electron microscopy, Brunauer-Emmet-Teller analysis, X-ray photoelectron spectroscopy, Fourier transform infrared spectrometry, and X-ray diffraction. The results showed that the adsorption efficiency of formaldehyde (3.5 mg/L) by MnO₂-AC (concentration of manganese nitrate/sodium carbonate was 0.3 mol/L, impregnation oscillation time of 4 h, calcination temperature and time of 350 °C and 4 h, respectively) was 93.1%, which increased by 251% compared to that of the AC. The adsorption equilibrium of MnO₂-AC was achieved after 4 h. With increasing dosage of MnO₂-AC, the rate of increasing of the adsorption efficiency became more gradual. The adsorption process of the formaldehyde solution with a low concentration fit the Langmuir adsorption isothermal model, where the adsorption capacity was 9.22 mg/g. The stability and regenerability of MnO₂-AC were good.

Keywords: Activated carbon; MnO₂ loaded activated carbon; Adsorb; Formaldehyde

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INTRODUCTION

Formaldehyde is a dangerous allergen according to the World Health Organization; it has high carcinogenicity and high deformity hazards (Sekine 2002). The pollution of water by formaldehyde is mainly attributable to the discharged waste water from leather, synthetic fiber, paint, dyestuff, wood processing, and other industries. Additionally, the degradation of organic compounds in water produces formaldehyde. Drinking formaldehyde-containing water may result in general sickness, nerve disorders, nasopharyngeal tumors, and even death (Torres *et al.* 2011). Therefore, removing formaldehyde from water is of great significance for environmental health.

Currently, several approaches are widely adopted to remove formaldehyde from water, such as oxidation (Wen *et al.* 2009; Kibanova *et al.* 2012), biological treatment (Kempeneer *et al.* 2004), and adsorption (Rong *et al.* 2002; Srisuda and Virote 2008). Moreover, adsorption is one of the most promising method due to its advantages on low cost, simplicity of operation, and easy industrial production. Activated carbon, which has high specific surface area and abundant pore structure, is a promising adsorbent for formaldehyde adsorption (Rong *et al.* 2003). However, using activated carbon directly for formaldehyde adsorption leads to a small adsorption capacity and a slow adsorption rate. Therefore, it is necessary to develop special methods to improve the adsorption

performance of activated carbon (Wen *et al.* 2011; Rong *et al.* 2017). One method is loading TiO₂ onto activated carbon (Hager *et al.* 2000; Zhang and He 2007). However, the TiO₂-loaded activated carbon can play a successful role only in combination with ultraviolet light. By contrast, a system based on loading MnO₂ to activated carbon does not need an additional light source. MnO₂ not only has the advantages of low cost, abundant availability of raw materials, but also has structural flexibility and novel physical and chemical properties (Wang *et al.* 2015; Wang *et al.* 2018; Zon *et al.* 2018; Miao *et al.* 2019). It has a high reaction potential with formaldehyde at room temperature and in the absence of light, and it is able to completely convert formaldehyde into CO₂ and H₂O (Wang *et al.* 2015; Lin *et al.* 2016; Rong *et al.* 2017; Miao *et al.* 2019).

Most previous studies have focused on preparing electrode materials for supercapacitors and wastewater treatment (Kanungo *et al.* 2004; Lee *et al.* 2010). Recently, numerous studies have reported that activated carbon-based MnO₂ is an efficient adsorbent for adsorption of formaldehyde from aqueous solution (Wang *et al.* 2015; Lin *et al.* 2016; Zon *et al.* 2018). It is reported that the adsorption effect of activated carbon-based MnO₂ on formaldehyde is remarkable in comparison with that of activated carbon (Wang *et al.* 2015; Lin *et al.* 2016; Zon *et al.* 2018). However, most of previous studies have focused on the preparation of activated carbon based MnO₂ using potassium permanganate. There has been a lack of research on the preparation of activated carbon loaded with MnO₂ by coprecipitation of manganese nitrate/sodium carbonate, as well as the influence of its preparation process on the its capacity of formaldehyde adsorption. Therefore, this study aimed to investigate the preparation of activated carbon loaded with MnO₂ by manganese nitrate/sodium carbonate coprecipitation and calcination, which fully utilizes the advantages of MnO₂ and activated carbon to enhance its adsorption capacity for formaldehyde.

In this paper, coconut shell activated carbon, washed to neutral, was used as the raw material. The effect of manganese nitrate/sodium carbonate concentration, impregnation oscillation time, calcination temperature, and calcination time on formaldehyde (3.5 mg/L) adsorption capacity of MnO₂-loaded AC (MnO₂-AC) was investigated through a single factor experiment. The MnO₂-AC (prepared under optimized conditions) was used to adsorb formaldehyde solution with a certain mass concentration. The effects of MnO₂-AC dosage, adsorption time, and initial mass concentration of formaldehyde were determined. The AC and MnO₂-AC were characterized by scanning electron microscopy, Brunauer-Emmet-Teller analysis, Fourier transform infrared spectrometry, X-ray photoelectron spectroscopy, and X-ray diffraction.

EXPERIMENTAL

Materials and Instruments

The coconut shell activated carbon was obtained from Jiangsu Pu Shida Environmental Protection Technology Co., Ltd, Jiangsu, China, with a specific surface area of 928 m²/g and pH of 8.2. Before the experiment, the raw material was crushed and screened to a size of 20 to 40 mesh. The material was placed in a 100 mL beaker. Once in the beaker, ultra-pure water was added, and the material was stirred and boiled for about 30 minutes, and then cooled down to room temperature. The material was repeatedly

washed to neutral and ash from the coconut shell activated carbon surface was removed. After all of this, the material was dried at 105 °C for 8 h, sealed and reserved, and marked as “AC.”

The test reagent manganese nitrate ($\text{Mn}(\text{NO}_3)_2$) AR is from Shanghai Jiuyi Chemical Reagent Co., Ltd, Shanghai, China. The sodium carbonate (Na_2CO_3) AR is from Nanjing Chemical Reagent Co., Ltd, Nanjing, China. The formaldehyde (CH_2O) AR is from Shanghai Jiuyi Chemical Reagent Co., Ltd, Shanghai, China. The instruments utilized in this study include a 722N visible spectrophotometer (Shanghai Jingke Co., Ltd, Shanghai, China), a speed regulation multi-purpose oscillator, and a SHA-B type constant temperature oscillator (Guohua Electric Co., Ltd, Changzhou, China). Scanning electron microscopy was carried out on a JSM-7600F field emission scanning electron microscope from Japan Electronics Corporation (Japan Electronics Co., Ltd, Akio, Japan), with a resolution of analytical mode of 3.0 nm (15.0 kV, 5.0 nA, work distance = 8.0 mm). The specific surface area was analyzed by an Autosorb Specific Surface Area Analyser (Quantachrome, Boynton Beach, FL, USA). The test was conducted at 77 K. Before analysis, the sample was degassed at 300 °C for 900 min. The specific surface area was calculated by BET, and aperture distribution was calculated by Barret-Joyner-Halenda Theory. Fourier infrared spectroscopy was tested on a VERTEX 80V Fourier infrared spectrometer manufactured from Bruker, Germany (Bruker, Karlsruhe, Germany), using KBr pellets. XPS was tested on an AXIS Ultra DLD photoelectron spectroscopy made by the Shimadzu Corporation in UK. (Shimadzu Corporation, Manchester, UK). An Ultima IV combined multifunctional horizontal X-ray diffractometer (Rigaku, Tokyo, Japan) was used, with a range of 10° to 90°. The minimum stepper was 0.02 and the maximum output power was 2 KW.

Methods

The preparation of MnO_2 loaded AC

The chemical equation for manganese nitrate/sodium carbonate coprecipitation and calcination can be shown as follows:



In this experiment, the solid-liquid ratio was 8:20 (adding 10 mL of $\text{Mn}(\text{NO}_3)_2$ and 10 mL of Na_2CO_3 to 8 g of AC), and the load conditions were set to a constant oscillation frequency (170 to 190 times/min). The first condition was five concentrations (0.1, 0.3, 0.5, 0.7, 0.9 M) of $\text{Mn}(\text{NO}_3)_2$ and Na_2CO_3 solution (both with the same concentration). The second condition was the impregnation of the oscillation time at 2, 4, 6, 8, and 10 h. The next conditions were the calcination temperature at 260, 290, 320, 350, and 380 °C, and the calcination time at 2, 3, 4, 5, and 6 h. A variable-controlling method was used to conduct the single factor tests. The temperature was raised to the setting temperature to preserve the heat and was not changed until the preservation time was attained. After the muffle furnace was cooled, the samples were taken out, washed, filtered, and dried at 120 °C for 6 h. The products were sealed for prior to experiment.

Determination of formaldehyde concentration

The formaldehyde concentration was determined by a test method based on GB/T1556-1995 (the measure of formaldehyde quality in the air was accomplished through an acetylacetone spectrophotometry analysis).

The characterization of activated carbon

The specific surface area, surface morphology, surface functional groups, surface elements, phase composition, and crystal type of the MnO₂ of AC before and after loading MnO₂ are characterized by Specific Surface Area Meter, SEM, FT-IR, XPS, and an XRD, accordingly.

Adsorption Test

Activated carbon adsorbing a certain mass concentration of formaldehyde solution

A certain mass concentration of formaldehyde solution and a certain weight of activated carbon were put into a conical flask with a cover according to the test requirements and oscillated at 25 °C (constant frequency: 120 to 150 times/min). After a specified period of time, the contents of the flask were filtered with a filter paper. The concentration of formaldehyde in water was analyzed by acetylacetone spectrophotometry method. In brief, approximately 10 mL of filtrate was obtained in a colorimetric tube. Then, 2.0 mL of a 0.25% acetylacetone solution was added to the tube.

The sample was mixed evenly and heated in a boiling water bath for 3 minutes and then cooled to room temperature. The absorbance of the samples were determined by 722N visible spectrophotometer at 413 nm wavelength. The adsorption amount and adsorption capacity of the activated carbon was then calculated according to the following formulas:

$$E = (A_0 - A_t) / A_0 \quad (4)$$

$$Q = (P_0 - P_e) V / m \quad (5)$$

In the above formulas, E represents the adsorption percentage (%), A_0 represents the initial absorbance of the formaldehyde solution (1), A_t represents the absorbance of the formaldehyde solution at time t (1), P_e represents the equilibrium concentration of the formaldehyde solution (mg/L), V represents the volume of the formaldehyde solution (L), m represents the quality of the activated carbon (g), and Q is the adsorption capacity (mg/g).

The effects of adsorption time on adsorption capacity

Eight 250 mL tapered bottles with stoppers were labeled, and the corresponding labels were attached. Then, 0.5 g of AC was placed into the bottles. Following this, 25 mL of a 3.5 mg/L formaldehyde solution, with an absorbance of 0.770, was added to the eight labeled tapered bottles with stoppers. The stoppers were then covered and placed into a constant temperature oscillator, where they were oscillated at an unchanged frequency of 120 to 150 times/min at a temperature of 25 °C. The reaction was tested every 2 hours. The absorbance of the AC was acquired using previous method. The adsorption capacity of the AC is characterized by the formaldehyde adsorption. Similarly, MnO₂-AC was tested.

The effects of adsorbents dosage on adsorption capacity

Six 250 mL plugged conical bottles were labeled. In each of these bottles, AC (0.05,

0.1, 0.2, 0.3, 0.4, and 0.5 g) was added to match the label. Then, 25 mL of the formaldehyde solution (mass concentration of 3.5 mg/L and absorbance of 0.770) was added into each of the tapered bottles and covered with a stopper. The bottles were placed into a constant temperature oscillator and oscillated at an unchanged frequency of 120 to 150 times/min at a temperature of 25 °C for 24 h. The absorbance of the AC was acquired using previous method. The adsorption capacity of the AC is characterized by the formaldehyde adsorption. Similarly, MnO₂-AC was tested.

The effect of initial mass concentration of formaldehyde on adsorption capacity

Formaldehyde solution with a mass concentration of 0.6, 1, 1.4, 1.8, and 2 mg/L was prepared. Then, 25 mL of the formaldehyde solution with different mass concentrations was placed in five plugged conical bottles with labels, after which 0.5 g of the MnO₂-AC solution was added sequentially. The caps of each bottle were double-checked for tightness, and then the bottles were oscillated at an unchanged frequency of 120 to 150 times/min at a temperature of 25 °C for 24 h. The absorbance of the MnO₂-AC was acquired using previous method. The adsorption capacity of the MnO₂-AC was characterized by the formaldehyde adsorption percentage.

Regeneration of MnO₂-AC

In this study, a typical sample of MnO₂-AC was selected to study the regeneration capacity. The MnO₂-AC sample adsorbed formaldehyde (3.5 mg/L) was placed in a beaker and dried at 120 °C for 6 h. The regeneration of the sample MnO₂-AC was determined, and the formaldehyde adsorption capacity was calculated repeatedly. Desorption experiments were conducted again using the same adsorption method.

RESULTS AND DISCUSSION

Drawing Standard Curve of Formaldehyde

The standard curve of the formaldehyde concentration as a function of absorbance is shown in Fig. 1.

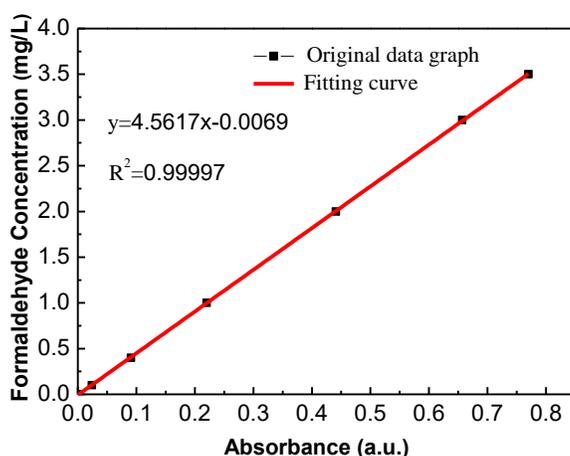


Fig. 1. Stand curve of formaldehyde concentration as a function of absorbance

The line of best fit is

$$y = 4.5617x - 0.0069 \quad (6)$$

and the goodness of fit was $R^2 = 0.99997$.

Determination of the Optimum Load Conditions

Effect of manganese nitrate/sodium carbonate concentration on the formaldehyde adsorption capacity of MnO₂-loaded AC

The effect of manganese nitrate/sodium carbonate concentration on the formaldehyde adsorption capacity of MnO₂-loaded AC (MnO₂-AC) (0.5 g of AC in 25 mL of formaldehyde solution with concentration being 3.5 mg/L, adsorption time is 24 h) is shown in Fig. 2, while the impregnation oscillation time was 4 h and calcination occurred at a temperature of 350 °C for 3 h.

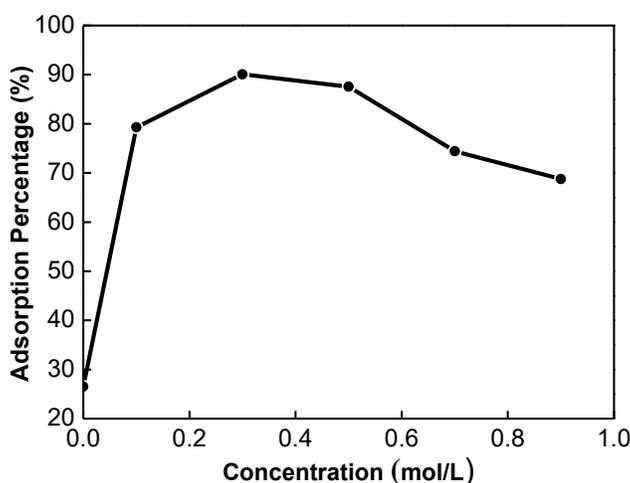


Fig. 2. Effect of concentration on the adsorption of activated carbon

The formaldehyde adsorption of AC under the same conditions is shown in Fig. 2, with the concentration of manganese nitrate/sodium carbonate solution being zero. The adsorption of AC for formaldehyde was 26.5%, as is shown in Fig. 2. The formaldehyde adsorption of MnO₂-AC prepared by the co-precipitation calcination of manganese nitrate and sodium carbonate were much higher than that of the AC. With the increasing concentration of manganese nitrate/sodium carbonate solution, the formaldehyde adsorption increased dramatically at first, and then they slightly decreased. The adsorption of the MnO₂-AC was the highest (90.1%) at a concentration of 0.3 M. When the concentration was higher than 0.3 M, the adsorption began to decrease.

Perhaps when the concentration of MnO₂ was too high, the pores of the MnO₂-AC were blocked and the enrichment function of the MnO₂-AC could not fulfill its full role, resulting in a relative decrease of the adsorption. However, its specific mechanism will be further verified later in this paper. The concentration of manganese nitrate/sodium carbonate of 0.3 M was adopted for all subsequent experiments if not otherwise indicated.

Effects of impregnation oscillation time on the formaldehyde adsorption capacity of MnO₂-AC

The influence of the impregnation oscillation time on the formaldehyde adsorption capacity of MnO₂-AC is shown in Fig. 3. When the concentration of manganese nitrate/sodium carbonate was 0.3 M, the impregnation oscillation time had little effect on the formaldehyde adsorption of the MnO₂-AC. However, with an increasing impregnation time, the adsorption of the MnO₂-AC first increases and then decreased, with the maximum value being 90.1% when the impregnation oscillation time was 4 h. This may due to the fact that a longer impregnation times resulted in more loaded-MnO₂ and more blocked pores. Therefore, in the following experiments, the impregnation oscillation time of 4 h was selected if not mentioned as otherwise.

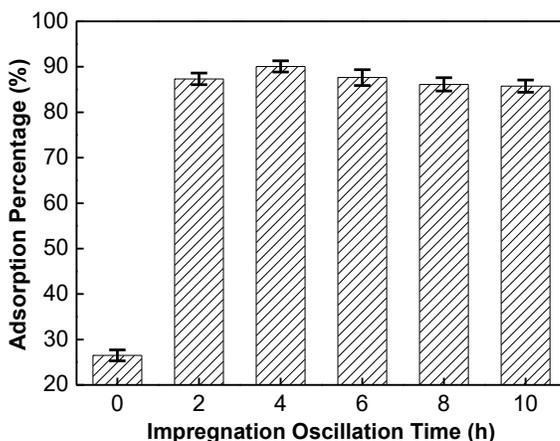


Fig. 3. The effect of the impregnation oscillation time on the adsorption of activated carbon

Effect of calcination temperature on formaldehyde adsorption capacity of MnO₂-loaded AC

The influence of calcination temperature on the formaldehyde adsorption capacity of MnO₂-AC is shown in Fig. 4.

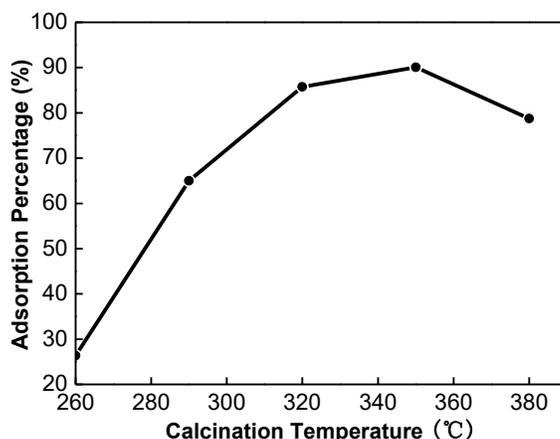


Fig. 4. Effect of calcination temperature on adsorption of activated carbon

It can be seen that when the concentration of manganese nitrate/sodium carbonate was 0.3 M, the impregnation oscillation time and the calcination were 4 h and 3 h. The calcination temperature showed a great influence on its adsorption capacity. The adsorption of the MnO₂-AC (26.4%) was much lower than that of the AC (26.5%) at a calcination temperature of 260 °C. A possible reason is that the decomposition of manganese carbonate was slow at 260 °C, as a large amount of manganese carbonate covered the inner and outer surface of MnO₂-AC. Manganese carbonate was decomposed rapidly and reacted with oxygen to produce MnO₂ when the calcination temperature was higher than 300 °C. When the temperature reached 350 °C, the maximum adsorption (90.1%) was reached. With the further rise of calcination temperature, the adsorption capacity of formaldehyde gradually decreased. This was because MnO₂-AC begins to burn to produce ash at high temperature. Therefore, the calcination temperature of 350 °C was used for all subsequent experiments, except where specified otherwise.

The effect of calcination time on the formaldehyde adsorption capacity of MnO₂-loaded AC

The influence of calcination time on formaldehyde adsorption capacity of MnO₂-AC is presented in Fig. 5. When the concentration of manganese nitrate/sodium carbonate was 0.3 M, the impregnation oscillation time was 4 h, the calcination temperature was 350 °C, and the calcination time was 4 h. Under these conditions, the adsorption by MnO₂-AC was the highest, which was 93.1%. With an increase in the calcination time, the formaldehyde adsorption increased at first and then decreased, which may have resulted from the fuller reaction of manganese carbonate with the increase of calcination time from 4 h. The manganese carbonate reaction is the main factor affecting the reaction. After 4 h, manganese carbonate completely reacted, and the burnout of carbon becomes the main factor affecting the formaldehyde adsorption. Therefore, the calcination time was 4 h. In this experiment, the concentration of manganese nitrate/sodium carbonate was 0.3 M, the soaking oscillation time was 4 h, the calcination temperature was 350 °C, and the calcination time was 4 h.

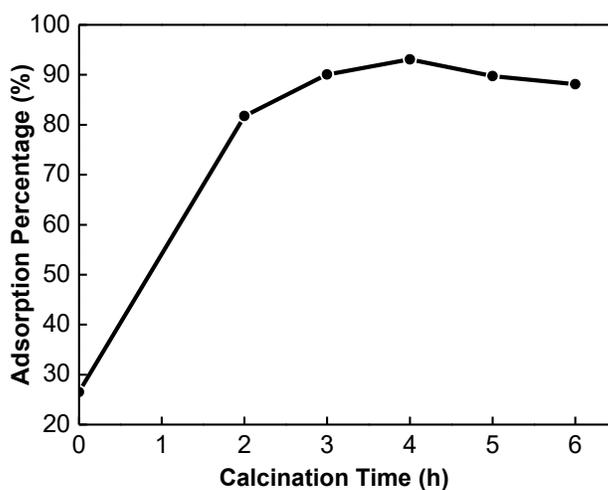


Fig. 5. Effect of calcination time on the adsorption of activated carbon

Characterization of Activated Carbon

Scanning electron microscope analysis

Results of scanning electron microscope analysis of AC and MnO₂-AC are shown in Fig. 6. The technical index was magnified 5000 times.

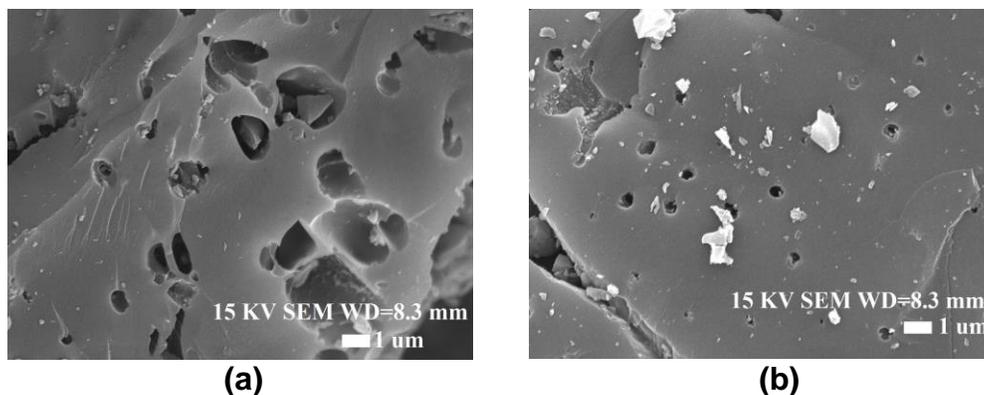


Fig. 6. Scanning electron microscopic images of (a) AC and (b) MnO₂- AC

Activated carbon can be described as an amorphous form of graphite with a random structure of graphite plates having a highly porous structure (Wang and Chen 2014). From Fig. 6(a) and (b), it can be seen that there was a porous structures on the AC and MnO₂-AC surface. Comparing Figs. 6 (a) and 6 (b), there were some granular solids (MnO₂) on the surface of MnO₂-AC, but most of MnO₂ particles were not blocking the pores of the MnO₂-AC.

Specific surface area analysis

The specific surface area and pore size distribution of the activated carbon are the main factors affecting its physical adsorption capacity. The N₂ adsorption and desorption curves of AC as well as MnO₂-AC are shown in Fig. 7. The specific surface area analysis and pore size analysis of AC and MnO₂-AC are shown in Table 1.

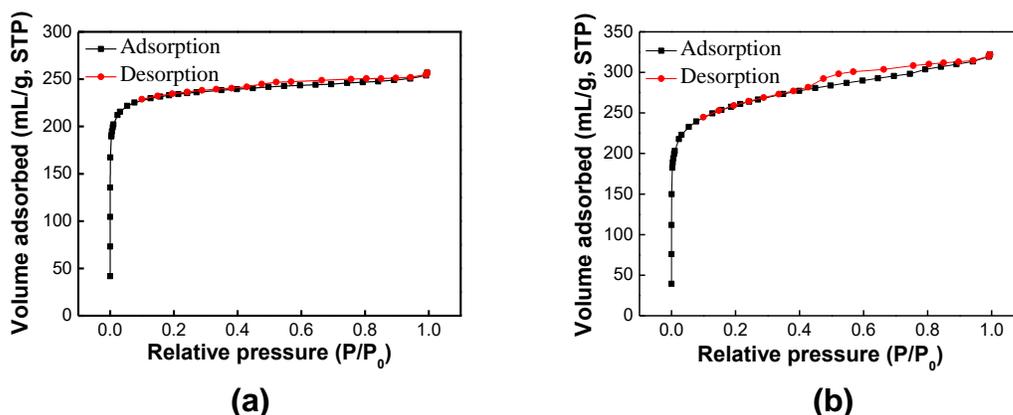


Fig. 7. The N₂ adsorption and desorption curves of (a) AC and (b) MnO₂- AC AC

It can be seen that the desorption of MnO₂-AC did not coincide with the adsorption isotherm, and a closed hysteresis loop was formed, while the coincidence of the adsorption

and desorption curves for MnO₂-AC was not as close as that of AC (Ge *et al.* 2016).

Table 1. Specific Surface Area and Pore Size of Activated Carbon

Test Index Type	Specific Surface Area (m ² /g)	Total Pore Volume (cm ³ /g)	Average Pore Diameter (nm)	Mesoporous Specific Surface Area (m ² /g)
AC	927.736	0.3973	1.7223	20.819
MnO ₂ -AC	974.431	0.4980	2.0443	68.492

Table 1 indicates that the specific surface area of MnO₂-AC was higher than that of AC, which is consistent with the scanning electron microscope results. This can be a reason for the not lower formaldehyde adsorption capacity of the MnO₂-AC.

Fourier infrared spectroscopy (FT-IR)

As the physical and chemical structure of activated carbon are extremely complex, the absorption peaks of functional groups are also different. According to the FT-IR absorption mechanism, the higher the absorption spectra of characteristic peaks, the greater the content of the functional groups in the sample. Figure 8 shows the Fourier infrared spectra of the two kinds of activated carbon. The shape and size of the absorption peaks of AC and MnO₂-AC were similar, indicating that the two kinds of activated carbon contain similar chemical bonds. However, the peak values were quite different, which means that the corresponding chemical bonds were different as well. The difference in the number of absorption peaks indicates the formation of new functional groups.

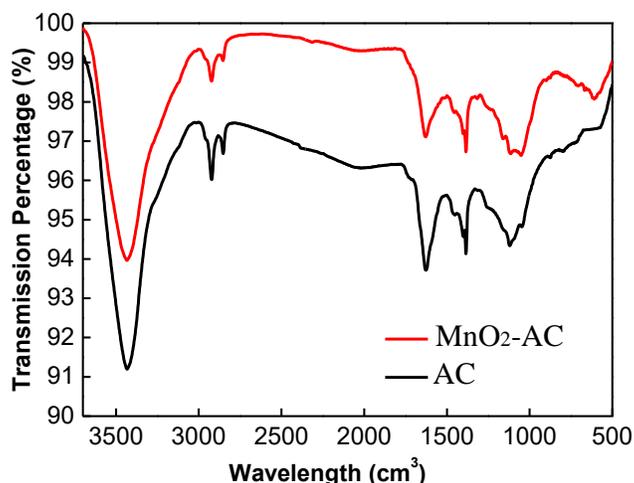


Fig. 8. Fourier-transfer infrared spectroscopy

As is known to all, activated carbon is mainly composed of C, H, and O elements, and so its infrared spectrum vibration is mainly provided by chemical bonds composed of C, H, and O elements. The stretching vibration of -OH is near the wavelength 3500 cm⁻¹ (Du *et al.* 2017; He *et al.* 2018). The stretching vibration of the CH₃ and CH₂ is near the wavelength 3000 cm⁻¹ (Du *et al.* 2017; He *et al.* 2018). As can be seen in Fig. 8, the absorption peaks of both of the two activated carbons were evident, but the peak intensities of MnO₂-AC were significantly lower than those of AC, indicating that the contents of CH₃

and CH₂ in MnO₂-AC were lower than those of AC. The absorption peaks of C=C and C=O double bonds (aldehydes, ketones, carboxylic anhydrides, *etc.*) appeared near the wavelength of 1700 cm⁻¹ (Du *et al.* 2017) for both MnO₂-AC and AC, which suggests the presence of C=C and C=O double bonds before and after the loading of MnO₂. The absorption band around the wavelength of 1400 cm⁻¹ could be attributed to the C=O ether vibration (Ge *et al.* 2016). From Fig. 8, it can be seen that both carbonic samples contain a linkage. The C-H stretching vibration is observed around 1150 cm⁻¹ for AC and MnO₂-AC. The vibration absorption peak of the Mn-O bond is observed around 580 cm⁻¹, suggesting the presence of Mn-O bonds on the surface of the MnO₂-AC. This confirms that the MnO₂ had been successfully loaded onto the AC.

X-Ray electron spectroscopy (XPS)

The chemical properties of the activated carbon surface are determined by the kinds and relative contents of the surface elements and functional groups, which affects the formaldehyde adsorption performance of the activated carbon. The full scan figures of the AC and MnO₂-AC are shown in Fig. 9. It is apparent that the elements on AC and MnO₂-AC were mainly carbon and oxygen, while the manganese was only found in the MnO₂-AC. The contents of elements on the surface of AC and MnO₂-AC are listed in Table 2.

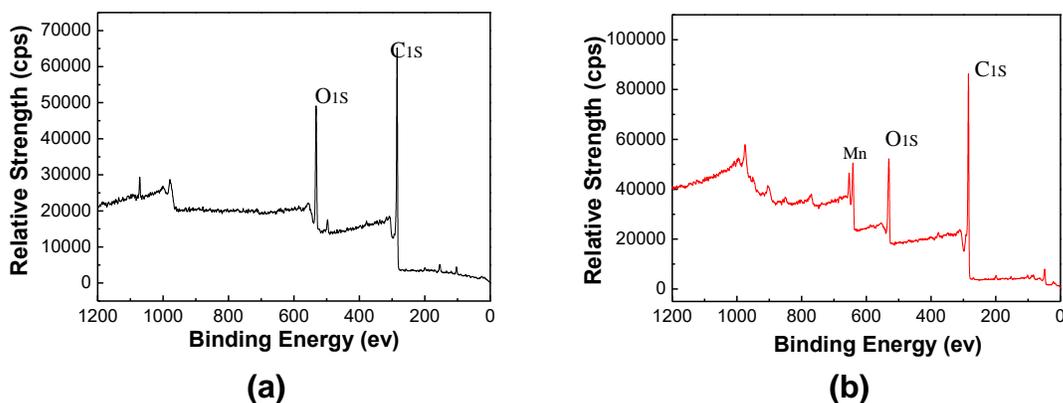


Fig. 9. The typical XPS survey spectra for (a) AC and (b) MnO₂-AC

Table 2. Surface Element Content and the Result of the C1s Peak by Curve Fitting Method

Sample	C (%)	N (%)	O (%)	Mn (%)	C-C (%)	C-O (%)	C=O (%)	O-C=O (%)
AC	82.04	0.67	17.31	—	58.46	22.81	11.81	2.88
MnO ₂ -AC	84.08	0.23	14.10	2.03	65.12	21.33	5.77	1.86

Table 2 shows that the contents of the surface elements and functional groups of the AC become different after loading MnO₂. Carbon and manganese atoms on the surface of the activated carbon can adsorb formaldehyde by chemisorption (Jiang *et al.* 2008). In this study, the sum of the C and Mn content on the surface of MnO₂-AC was higher than

that of AC, and the adsorption capacity of MnO₂-AC was also higher than the AC. This fulfills the research goals of this study. The content of the O-C=O (carboxyl, anhydride) in AC was less, since the coconut shell activated carbon was weakly alkaline with a pH value of 8.2 before washing. The O-C=O content in MnO₂-AC was less than that in AC, which is because the sodium carbonate solution, which is used at the preparation process of MnO₂, neutralized with O=C-O in the AC. The decrease of the acidic functional group contents in the surface of activated carbon leads to the increasing electron density of the carbon skeleton. Therefore, the interaction between AC and the organic matter increases, then enhancing the chemical adsorption of the formaldehyde (Zhang *et al.* 2015). The adsorption of the formaldehyde by MnO₂-AC was much stronger than that by AC, which is consistent with the conclusion. The C content on the surface of MnO₂-AC was higher than that of AC; this may due to the trace amount of manganese carbonate solid in MnO₂-AC formed by the reaction. The O content on the surface of MnO₂-AC was lower compared to that of AC, which may due to the reaction of sodium carbonate with acidic oxygen-containing functional groups in AC. However, the mechanism of MnO₂-AC with more element C and the less O on the surface compared to AC needs further research. The high-resolution XPS spectra were carried out for carbon, and the results are shown in Fig. 10. The binding energy of the graphite carbon is 284.6 eV, the C-O functional groups (such as carbonyl, benzoquinone, *etc.*) are at 286 eV, the C=O functional groups are at 287.0 eV, and the O-C=O functional groups (such as carboxyl, lactone, *etc.*) are at 288.5 eV, respectively.

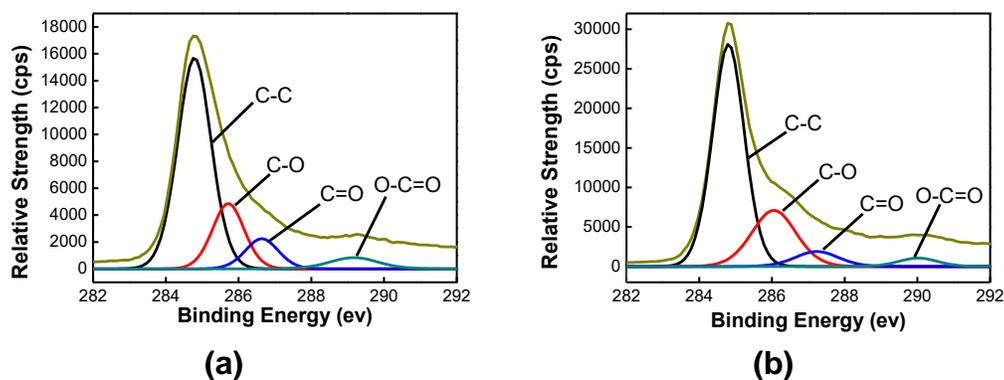


Fig. 10. Spectral peaks of (a) AC and (b) MnO₂- AC for C1s by XPS

X-ray diffraction analysis

To further quantify the MnO₂ on the MnO₂-AC, the AC before and after the loading was characterized by XRD. The results are shown in Fig. 11.

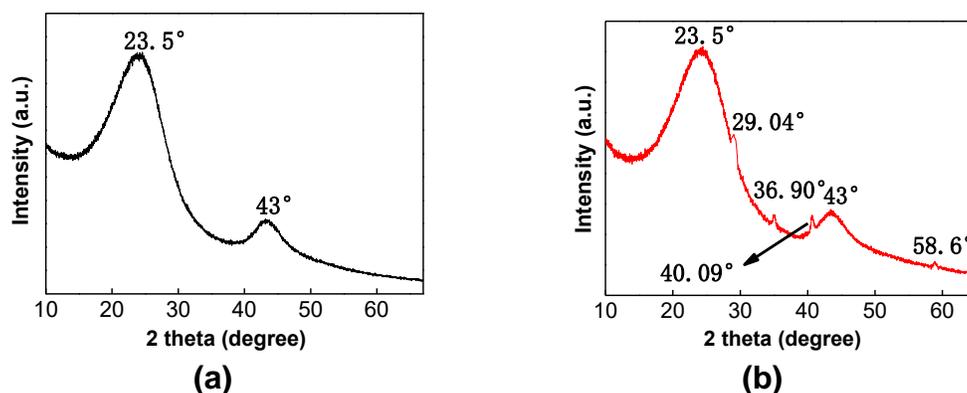


Fig. 11. XRD spectra of (a) AC and (b) MnO_2 -AC

The carbon characteristic diffraction peaks of AC before and after loading MnO_2 were relatively wide near the positions of $2\theta = 23.5^\circ$ and 43° . The characteristic diffraction peaks of MnO_2 -AC appeared near $2\theta = 29.04^\circ$, 36.90° , 40.09° , and 58.6° , which coincides with the γ - MnO_2 diffraction peaks in the standard spectrum (Joint Committee on Powder Diffraction Standards 24-0725), and had a sharp main peak. This result indicates that the crystallinity of the prepared MnO_2 -AC was more favorable.

MnO_2 -AC Adsorbs a Certain Concentration of Formaldehyde Solution

The effects of adsorption time on adsorption capacity

The effects of adsorption time on the formaldehyde adsorption of activated carbon are shown in Fig. 12. The adsorption of the two activated carbon increased, as expected, at the initial stage of adsorption. Then it slowed down with the passage of time. In the initial stage, formaldehyde diffuses from the main solution to the adsorbent surface with a larger concentration gradient and a larger adsorption impetus, resulting in a faster adsorption rate. With the prolongation of the adsorption time, the concentration gradient difference becomes smaller, resulting in a slower adsorption rate until the adsorption equilibrium is reached. For example, the adsorption time of AC and MnO_2 -AC to reach equilibrium was near 4 h, but it is still evident that the AC achieved adsorption equilibrium at longer times than the MnO_2 -AC. The mesoporous specific surface area was larger, and the adsorption equilibrium time of activated carbon was shorter (Jin *et al.* 2007). In addition, the mesoporous specific surface area of MnO_2 -AC was larger than AC, which is consistent with the conclusion.

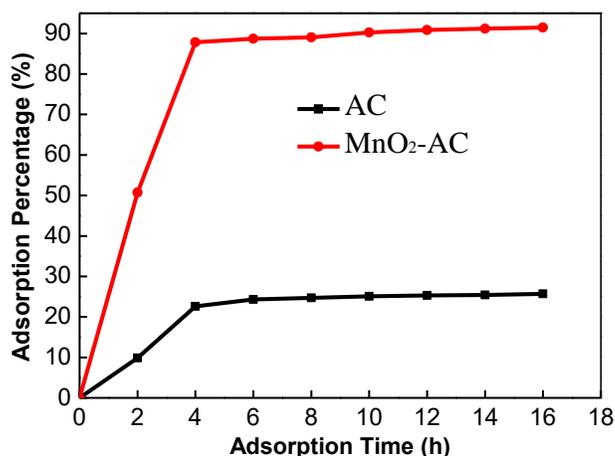


Fig. 12. Effect of adsorption time on the formaldehyde adsorption of activated carbon

The effects of dosage on adsorption capacity

The relationship between the adsorption of the formaldehyde and the dosage of the activated carbon is shown in Fig. 13. As the dosage of the activated carbon increased, the adsorption of the formaldehyde in solution gradually increased. The reason may be that when the amount of activated carbon increases, it can provide enough effective contact surface to make the formaldehyde molecule in the formaldehyde solution have full contact with the activated carbon, resulting in a better effect and a higher formaldehyde adsorption (Wang *et al.* 2015; Ge *et al.* 2016). However, when the dosage of the activated carbon is too much, the increase in the formaldehyde adsorption is not as obvious. The economical dosage of adsorbents is a key parameter to evaluate the adsorption efficiency (Ge *et al.* 2016). In order for better formaldehyde adsorption to take place, so that the water quality will meet the national safety discharge standard in practical life applications, more activated carbon should be added. However, an excessive dosage will result in a waste of resources. In the actual application process, it is necessary to consider both the utilization amount of activated carbon and its adsorption capacity for formaldehyde such that the adsorption process of formaldehyde is optimally economical and feasible.

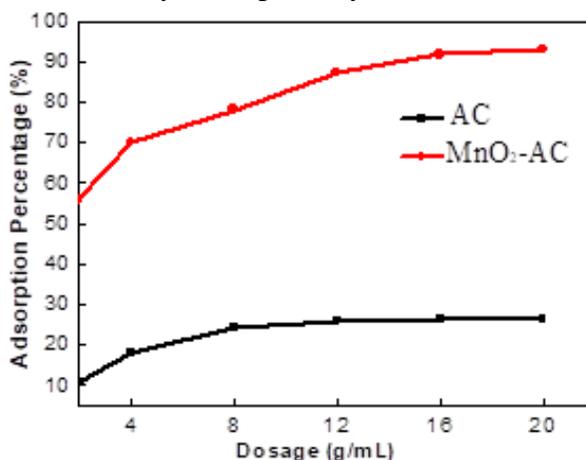


Fig. 13. Effect of dosage of the activated carbon on formaldehyde adsorption

The effect of initial mass concentration of formaldehyde on adsorption capacity

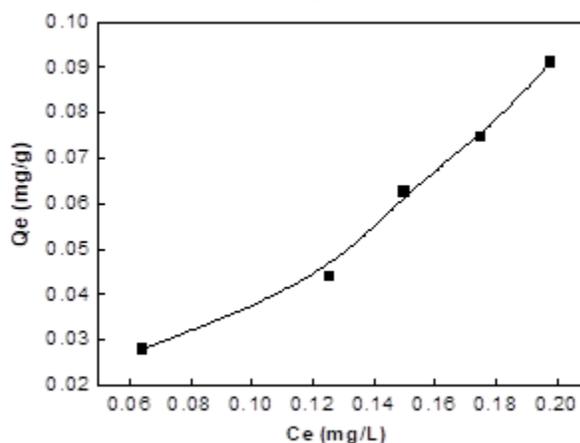
Table 3 shows that the unit adsorption capacity of MnO₂-AC was related to the initial concentration of formaldehyde.

Table 3. Effect of Formaldehyde Concentration on Adsorption of MnO₂-AC

Initial concentration of formaldehyde C ₀ /mg/L	Residual formaldehyde concentration C _e /mg/L	Unit adsorption amount Q _e /mg/g	1/C _e	1/Q _e	lg C _e	lg Q _e
0.6	0.06435	0.026783	15.54000	37.33781	-1.191451	-1.57215
1	0.12540	0.043727	7.971113	22.86898	-0.901519	-1.35924
1.4	0.15010	0.062495	6.662225	16.00128	-0.823619	-1.20415
1.8	0.17500	0.074520	5.714285	13.41921	-0.75696	-1.12772
2	0.19800	0.091000	5.050505	11.09877	-0.70333	-1.04527

When the initial concentration was relatively low, the unit adsorption capacity increased with an increase in the initial concentration, as shown in Table 3. The reason may be that within a certain formaldehyde concentration range, the higher the formaldehyde concentration, the greater the driving force of the formaldehyde solute to the surface of the MnO₂-AC.

The relationship between C_e and Q_e is shown in Fig. 14. The initial isotherms rose rapidly during the initial stage of adsorption when C_e and Q_e values were both lower and there were many readily accessible sites available on the surface of carbons (Ge *et al.* 2016). As shown in Fig. 14, the C_e and Q_e values were both lower, and the initial isotherms rose rapidly during the initial stage of adsorption, which is consistent with the conclusion.

**Fig. 14.** The relationship between C_e and Q_e

The adsorption isotherm curve can be obtained by plotting the adsorption capacity per unit of the residual formaldehyde concentration. The theoretical Langmuir isotherm as one of the traditional models has maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface. It is calculated from a well-known procedure, whereas the Freundlich model is an empirical equation assuming heterogeneous adsorbent surface (Wang *et al.* 2015; Ge *et al.* 2016). Langmuir and Freundlich equations were used to fit the isothermal adsorption data, respectively (Ge *et al.* 2016). The Langmuir and Freundlich equations are as follows,

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad (7)$$

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e \quad (8)$$

where q_m is the saturated adsorption capacity of the adsorbent at a certain temperature (mg/g), C_e is the concentration at equilibrium, q_e is the equilibrium adsorption amount (mg/g), K_L is the adsorption equilibrium constant, b is the Langmuir constant, and k_F and n are empirical constants. The fitting curve are shown in Figs. 15 and 16.

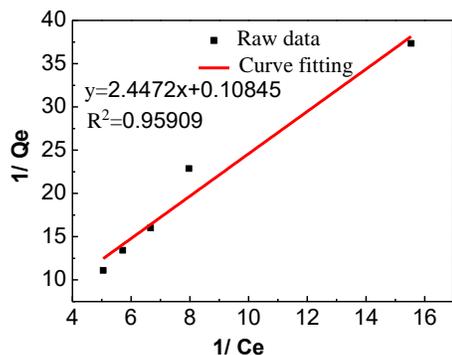


Fig. 15. Langmuir isotherm model

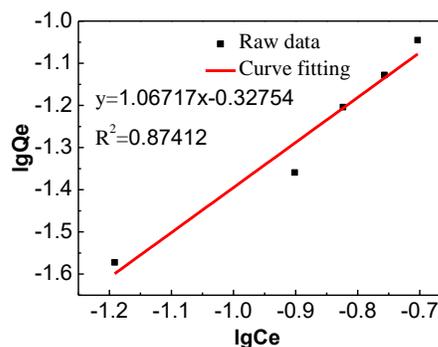


Fig. 16. Freundlich isotherm model

The curve fitting formula of the Langmuir adsorption isotherm model can be concluded from Fig. 15:

$$\frac{1}{Q_e} = 2.4472 \times \frac{1}{C_e} + 0.10845 \quad (9)$$

Additionally, the goodness-of-fit is $R^2 = 0.95909$, and $Q_\infty = 9.22$ mg/g.

The curve fitting formula of the Freundlich adsorption isotherm model can be obtained from Fig. 16:

$$\lg Q_e = 1.06717 \lg C_e - 0.32754 \quad (10)$$

Similarly, the goodness-of-fit was $R^2 = 0.87412$. From the isothermal coefficients, the coefficients of determination were quite different, so Langmuir adsorption isotherm model was judged to be the most suitable one to describe isothermal adsorption of MnO_2 -AC. Not only because its R^2 is a little larger, but also because the Freundlich adsorption isotherm model can better meet the test results when the solute concentration is moderate. Since the formaldehyde concentration in this experiment is relatively low, the Freundlich adsorption isotherm will produce a certain deviation, while the Langmuir adsorption isotherm model can better explain the adsorption mechanism (Wang *et al.* 2015; Ge *et al.* 2016). According to $Q_\infty = 9.22$ mg/g, $K_L = 0.0443$ is obtained. The K_L was relatively small, showing that the affinity of the activated carbon to formaldehyde was small and a higher equilibrium concentration is needed to achieve a larger adsorption capacity (Fu *et al.* 2011).

Regeneration of MnO₂-AC

Adsorption of formaldehyde onto MnO₂-AC for four cycles is shown in Fig. 17.

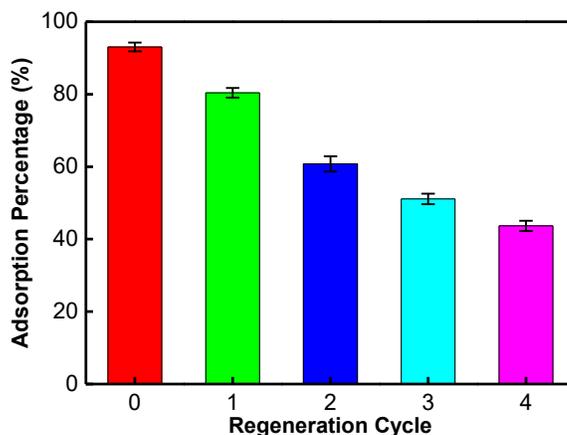


Fig. 17. Adsorption of formaldehyde onto MnO₂-AC for four cycles

From Fig. 17, it can be seen that the MnO₂-AC sample still had a high adsorption capacity for formaldehyde, which adsorption of formaldehyde (43.7%) was higher than AC (26.5%) after four cycles. This indicated that the MnO₂-AC samples had good stability, reusability, and effective adsorption for formaldehyde from aqueous solutions.

CONCLUSIONS

1. Through the experiment of loading MnO₂, the concentration of manganese nitrate/sodium carbonate, the impregnation and oscillation time, the calcination temperature, and the calcination time all had an influence on the formaldehyde adsorption capacity of MnO₂ loaded AC (MnO₂-AC). Among these characteristics, the most important one was the calcination temperature. With an increase in the calcination temperature, the formaldehyde adsorption capacity of MnO₂ loaded AC first increased and then decreased.
2. Under the conditions of a manganese nitrate/sodium carbonate concentration of 0.3 M, impregnation oscillation time of 4 h, calcination temperature of 350 °C, and calcination time of 4 h, the prepared MnO₂-AC had the most significant effect. The formaldehyde adsorption of 3.5 mg/L formaldehyde liquid was 93.1%, which was 251% higher than the AC.
3. Characterization of the activated carbon showed that the specific surface area of MnO₂-AC was larger than that of the AC. There were Mn-O bonds on the surface of the MnO₂-AC at a wavelength of 580 cm⁻¹. In addition, the MnO₂ (crystal pattern was γ -MnO₂ with a good crystallinity) was uniformly loaded on the surface of activated carbon without blocking the pore.
4. The improvement in the formaldehyde adsorption capacity of MnO₂-AC was due to the interaction of the specific surface area, surface functional groups, and MnO₂. The

Langmuir adsorption isotherm model showed that the Q_{∞} of MnO₂-AC was 9.22 mg/g, and a higher equilibrium concentration was needed to achieve a larger adsorption capacity of MnO₂-AC.

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