

Video Article

Preparation of Biomass-based Mesoporous Carbon with Higher Nitrogen-/Oxygen-chelating Adsorption for Cu(II) Through Microwave Pre-Pyrolysis

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URL: <https://www.jove.com/video/58161>

DOI: [doi:10.3791/58161](https://doi.org/10.3791/58161)

Keywords: Mesoporous carbon, biomass, microwave pyrolysis, electric furnace, copper adsorption, Fourier transform infrared (FTIR) spectroscopy, modification, nitrogen, adsorption isotherm, adsorption kinetics, functional group

Date Published: 8/1/2018

Citation: Li, K., Wan, Z. Preparation of Biomass-based Mesoporous Carbon with Higher Nitrogen-/Oxygen-chelating Adsorption for Cu(II) Through Microwave Pre-Pyrolysis. *J. Vis. Exp.* (), e58161, doi:10.3791/58161 (2018).

Abstract

An environment-friendly technique for synthesizing biomass-based mesoporous activated carbon with high nitrogen/oxygen-chelating adsorption for Cu(II) is proposed. Bagasse impregnated with phosphoric acid is utilized as the precursor. To pyrolyze the precursor, two separate heating modes are used: microwave pyrolysis and conventional electric-heating pyrolysis. The resulting bagasse-derived carbon samples are modified with nitrification and reduction modification. Nitrogen (N)/oxygen (O) functional groups are simultaneously introduced to the surface of activated carbon, enhancing its adsorption of Cu(II) by complexing and ion-exchange. Characterization and copper adsorption experiments are performed to investigate the physicochemical properties of four prepared carbon samples and determine which heating method favors the subsequent modification for doping of N/O functional groups. In this technique, based on analyzing data of nitrogen adsorption, Fourier transform infrared spectroscopy, and batch adsorption experiments, it is proven that microwave-pyrolyzed carbon has more defect sites and, therefore, time-saving effective microwave pyrolysis contributes more N/O species to the carbon, although it leads to a lower specific surface area. This technique offers a promising route to synthesis adsorbents with higher nitrogen and oxygen content and a higher adsorption capacity of heavy-metal ions in wastewater remediation applications.

Introduction

Activated carbon has unique adsorption properties, such as a developed porous structure, a high specific surface area, and various surface functional groups; therefore, it is employed as an adsorbent in water treatment or purification^{1,2,3,4}. Besides its physical advantages, activated carbon is cost-effective and harmless to the environment, and its raw material (e.g., biomass) is abundant and easily obtained^{5,6}. The physicochemical properties of activated carbon depend on the precursors that are used in its preparation and on the experimental conditions of the activation process⁷.

Two methods are typically used to prepare activated carbon: a one-step and a two-step approach⁸. The term one-step approach refers to precursors being carbonized and activated simultaneously while the two-step approach refers to that sequentially. In view of energy conservation and environmental protection, the one-step approach is more preferred for its lower temperature and pressure demanding.

Besides, chemical and physical activation are utilized to improve the textural properties of activated carbon. Chemical activation possesses apparent advantages over physical activation because of its lower activation temperature, shorter activation time, higher carbon yield, and more developed and controllable pore structure in a certain degree⁹. It has been tested that chemical activation can be performed by impregnating biomass used as feedstock with H₃PO₄, ZnCl₂, or other specific chemicals, followed by pyrolysis to increase the porosity of the activated carbon, because lignocellulosic components of biomass can be easily removed by a subsequent heating treatment, owing to the dehydrogenation capability of these chemicals^{10,11}. Hence, chemical activation greatly enhances the formation of activated carbon's pores or improves the adsorptive performance to contaminants¹². An acidic activator is preferred to H₃PO₄, due to its relatively lower energy demand, higher yield, and less impact on the environment¹³.

Microwave pyrolysis has the superiority in time savings, uniform interior heating, energy-efficiency, and selective heating, making it an alternative heating method to synthesis-activated carbon^{14,15}. Compared with conventional electric heating, microwave pyrolysis can enhance thermochemical processes and promote certain chemical reactions¹⁶. Recently, extensive studies have focused on preparing activated carbon by chemical activation from biomass using one-step microwave pyrolysis^{9,17,18,19}. So, it is considerably informative and environment-friendly to synthesis biomass-based activated carbon by microwave-assisted H₃PO₄ activation.

In addition, to improve the adsorption affinities of activated carbon toward specific heavy-metal ions, modification by heteroatom [N, O, sulfur (S), etc.] doping into carbon structures has been proposed, and this has proven to be a desirable method^{20,21,22,23,24,25,26}. Defective sites in or at the edges of a graphite layer can be replaced by heteroatoms to generate functional groups²⁷. Hence, nitrification and reduction modification are used to modify resultant carbon samples to dope N/O functional groups which play a crucial role in efficiently coordinating with heavy metal to form complexing and ion-exchange²⁸.

Based on the findings above, we present a protocol to synthesize N/O dual-doped mesoporous carbon from biomass by chemical activation and two different pyrolysis methods followed up by modification. This protocol also determines which heating method favors the ensuing modification for doping of the N/O functional groups and, thus, enhancing the adsorption performance.

Protocol

1. Preparation of Bagasse-based Activated Carbon

1. Preparation of the precursor for bagasse-based activated carbon

1. Rinse the bagasse (obtained from a farm in Jiangsu, China) with deionized water and put the samples in a drying oven at 100 °C for 10 h.
2. Crush the dried bagasse with a grinder and sieve the powder through a 50-mesh sieve.
3. Place 30 g of fine bagasse powder into a 15 wt% phosphoric acid (H_3PO_4) solution in a 1:1 weight ratio for 24 h. Dry the mixture in an oven at 105 °C for 6 h. Collect the resulting product as the precursor for bagasse-based activated carbon (BAC).

2. Conventional electric-heating pyrolysis of the precursor

1. Put 15 g of the precursor into a quartz boat and then insert the quartz boat into a quartz glass tube of an electric furnace.
2. Set the heating rate of the furnace at 5 °C min⁻¹ to carbonize the sample. When the temperature reaches 500 °C, keep the temperature for 90 min and then allow the resulting activated-carbon sample to cool to room temperature in nitrogen. Ensure a nitrogen flow of 80 mL min⁻¹ with a rotor flowmeter during the overall process.
3. Triturate and collect the electrical-furnace-pyrolyzed bagasse-based activated carbon (EBAC) in a beaker and then heat it in a vacuum drying oven at 105 °C for 24 h.

3. Microwave pyrolysis of the precursor

1. Put 15 g of the precursor in a microwave oven (with a 2.45 GHz frequency).
2. Set the power of the microwave oven at 900 W to pyrolyze the sample for 22 min, and ensure the nitrogen flow rate at 20 mL min⁻¹ with a rotor flowmeter. The air inlet of the rotor flowmeter is connected to a nitrogen cylinder using a hose, while the outlet is connected to the air inlet of the microwave oven.
3. Allow the resultant carbon to cool to room temperature in nitrogen. Triturate and collect the carbon sample in a beaker and then add 300 mL of hydrochloric acid (0.1 M). Stir the mixture using a magnetic stirrer (at 200 rpm) for more than 12 h at room temperature.
4. Filter the carbon by filter paper with vacuum filtration and rinse the sample with deionized water until the pH value of the wash water is > 6. Dry the microwave-pyrolyzed bagasse-based activated carbon (MBAC) in a vacuum drying oven at 105 °C for 24 h.

2. Modification of Electrical-furnace-pyrolyzed Bagasse-based Activated Carbon and Microwave-pyrolyzed Bagasse-based Activated Carbon

Note: The modification of the two samples was conducted according to the literature²⁹.

1. Nitrification

1. Mix 50 mL of concentrated sulfuric and 50 mL of concentrated nitric acids in a beaker at 0 °C (in an ice bath).
CAUTION: When the mixture of concentrated sulfuric acid and concentrated nitric acid is mixed, the concentrated sulfuric acid should be slowly added to the concentrated nitric acid and stirred with a glass rod and cooled in time.
2. Add 10 g of EBAC/MBAC to the mixed solution. Use a magnetic stirrer to stir the mixture for 120 min (at 200 rpm).
3. Filter the nitrified EBAC/MBAC by filter paper with vacuum filtration. Wash the carbon with deionized water until the wash water reaches pH 6, and then dry it in a drying oven at 90 °C for 24 h.

2. Reductive modification

1. In a three-necked flask, add the 5.05 g of resulting product, 50 mL of deionized water, and 20 mL of ammonia solution (15 M). Stir this mixture for 15 min with a magnetic stirrer (at 200 rpm), then add 28 g of $\text{Na}_2\text{S}_2\text{O}_4$, and leave the mixture stirring at room temperature for 20 h.
2. Fit a reflux condenser to the flask and warm the mixture up to 100 °C using an oil bath. Add 120 mL of CH_3COOH (2.9 M) to the flask and allow the mixture to stir for 5 h with a magnetic stirrer (at 200 rpm) under reflux.
3. Remove the oil bath to allow the solution to cool down to room temperature. Filter the carbon sample and wash it with deionized water until the solution pH > 6. Dry the modified EBAC/MBAC at 90 °C and denote it as "EBAC-N/MBAC-N".

3. Adsorbent Characterization

1. Structural characterization—Nitrogen adsorption/desorption isotherms

1. Weigh an empty sample tube. Add a carbon sample (~0.15 g) to the sample tube.
2. Degas the sample at 110 °C for 5 h in a vacuum. Weigh the sample tube containing carbon. Calculate the weight of the carbon sample.
3. Install the sample tube into the test area of the surface-area and porosimetry analyzer using liquid nitrogen to measure it at -196 °C³⁰.

2. Chemical characterization—Fourier transform infrared spectroscopy

1. Check the temperature and hygrometer and observe whether the environment meets the requirements: the temperature should be 16 - 25 °C and the relative humidity 20% - 50%.
2. Remove the desiccant and dust cover in the sample storehouse.

3. Dry the carbon sample and potassium bromide at 110 °C for 4 h to avoid the effect of water on the spectrum. Mix the carbon sample with potassium bromide and then use a press mechanism to prepare the test sample.
4. Put the sample in the test area and set the parameters of the software.
5. Save the spectra and take out the sample. Perform a required data processing for the spectra³¹.

4. Cu(II)-adsorption Experiments

1. Adsorption isotherm

1. Place 0.05 g of adsorbent in each of the conical flasks, which contain 25 mL of a CuSO₄ solution (pH 5) with a selected initial concentration (10, 20, 30, 40, 50, 60, 80, and 100 mg L⁻¹). Use a 0.1 M HNO₃ and 0.1 M NaOH solution to adjust the pH of each copper solution.
Note: A solution with the selected initial concentration is diluted by a 1 g L⁻¹ CuSO₄ solution, which is made up of a dissolved 3.90625 g of blue vitriol solid using the vase with a 1,000 mL volume.
2. Fit lids on the conical flasks and put them in a thermostatic orbital shaker (with a stirring rate of 150 rpm) at 5 °C/25 °C/45 °C for 240 min.
3. Use 0.22 µm membrane filters to separate the adsorbents from the solution.
4. Use a flame atomic absorption spectrophotometry to determine the copper concentration of the filtrate.
Note: All experiments were carried out in triplicate and the data were averaged. The adsorption capacity for Cu(II), q_e , was calculated as follows:

$$q_e = \frac{V(C_0 - C_e)}{m} \quad (1)$$

Here,

C_0 = the initial copper concentration (mg L⁻¹),

C_e = the final concentration (mg L⁻¹),

V = the solution volume, and

m = the weight of each adsorbent (g).

2. Influence of pH

1. Place 0.05 g of adsorbent in each of conical flasks, which contain 25 mL of a CuSO₄ solution (40 mg L⁻¹) with a selected initial pH (2, 3, 4, 5, 6, and 7).
2. Fit lids on the conical flasks and put them in a thermostatic orbital shaker (with a stirring rate of 150 rpm) at 25 °C for 24 h to reach adsorption equilibrium conditions.
3. Repeat step 4.1.3-4.1.4.

3. Adsorption kinetics

1. Place 0.25 g of adsorbent in a beaker which contains 125 mL of a CuSO₄ solution (30 mg L⁻¹ or 100 mg L⁻¹, pH 5) in a 25 °C water bath with magnetic stirring (at 200 rpm).
2. Use pipettes to draw 5 mL of the solution when the contact time reaches 0.5, 1, 2.5, 5, 10, 30, 60, 120, and 180 min.
3. Repeat step 4.1.3-4.1.4.

Representative Results

Nitrogen adsorption/desorption isotherms of four samples are presented in **Figure 1**. All adsorption isotherms show a rapid increase in low P/P_0 region and these isotherms belong to type IV (IUPAC classification) demonstrating their pore structure that consists of micropores and dominant mesopores³².

The surface physical parameters for all samples obtained from the nitrogen adsorption isotherms are shown in **Table 1**. Microwave pyrolysis and modification both contribute to a smaller Brunauer-Emmett-Teller (BET) surface area and total pore volume, changing the physical morphology of the samples.

Fourier transform infrared (FTIR) spectra of the four samples are given in **Figure 2**. Bands of MBAC at 1167 cm⁻¹ [carbon (C) - O stretching vibration], 1620 cm⁻¹ (C = O stretching vibration), 2852 cm⁻¹ [N - hydrogen (H) stretching vibration], 2922 cm⁻¹ (C - H stretching vibration), and 3442 cm⁻¹ (O - H stretching vibration) are more intense than EBAC. These may be attributed to the microwave pyrolysis contributing more oxygen functional groups to the BAC surface. For EBAC-N and MBAC-N, bands around 1573 cm⁻¹ and 1400 cm⁻¹ likely represent C = N and N - H groups, respectively. It can be found that the modified carbon materials have obtained distinct nitrogen/oxygen functional groups, and the microwave-pyrolyzed carbon gets more, which is in accordance with the elemental analysis as shown in **Table 1**. It can be speculated that microwave pyrolysis is more adequate to activate the precursor and lay root for further modifications than conventional electric-heating pyrolysis. MBAC-N possesses mainly hydroxyl, carboxyl, amino, and imine functional groups.

Figure 3 shows the adsorption capacity of the four samples under different pH conditions. The four adsorbents reach the optimal adsorption capacity at pH 5, so the following adsorption experiments are all carried out at pH 5. The samples prepared by microwave pyrolysis exhibited better Cu(II) adsorption capacity before and after the modification, although they had a lower specific surface area and pore volume. In general, the adsorbability of adsorbents depends on the pore structure and surface functional groups. Therefore, the high adsorption capacity of MBAC-N is attributed to more abundant N/O surface groups. The results confirm that the microwave pyrolysis benefits the follow-up introduction of surface functional groups to improve the adsorption capacity more than electric-heating pyrolysis.

The adsorption isotherms of MBAC-N on Cu(II) at 5 °C, 25 °C, and 45 °C are shown in **Figure 4a**. The adsorption properties of samples for Cu(II) become better when the temperature increases. By comparing the isotherm parameters in **Table 2**, it is clear that the Langmuir isotherm model indicates a higher linear correlation coefficient (R^2) which is over 0.99 (the fitting line in **Figure 4b**), and the measured adsorption capacity (q_{mea}^0) is identical with the calculated one (q_{cal}^0). Therefore, the model is more suitable than the Freundlich and Temkin isotherm models, which indicates that the absorption of Cu(II) is a chemical adsorption process³³.

As shown in **Figure 4c**, MBAC-N can reach about 75% of Cu(II) equilibrium adsorption capacity within 15 min, and it can almost reach the adsorption equilibrium of Cu(II) in about 50 min at different initial concentrations. These prove that MBAC-N has excellent adsorption properties. As can be seen from **Table 3**, the pseudo-second-order model is better than the Lagergren and Elovich models with $R^2 = 0.999$ (the fitting line in **Figure 4d**). The above results confirm that the adsorption of Cu(II) on MBAC-N is chemisorption. Hence, the chemical interaction mechanism of Cu(II) by the modified carbon is proposed in **Figure 5**. **Table 4** compares the adsorption capacity of Cu(II) by biomass-based activated carbon reported in recent references^{34,35,36,37,38}. It is found that MBAC-N has a higher adsorption capacity than other adsorbents reported in the literature, demonstrating it as a promising adsorbent for removing Cu(II).

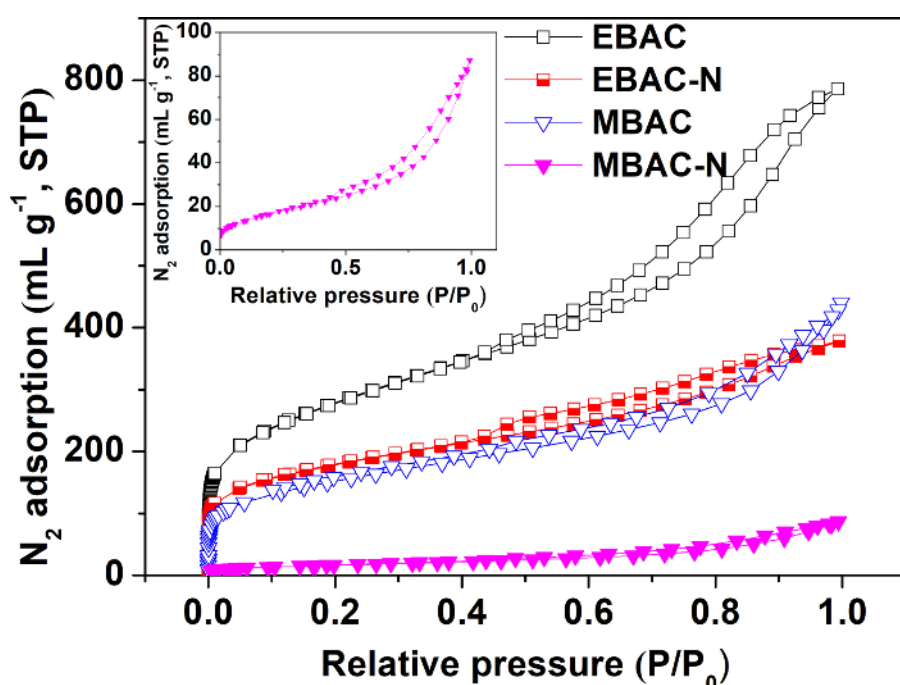


Figure 1: Nitrogen adsorption/desorption isotherms of carbons. The inset graph in **Figure 1** shows the nitrogen adsorption/desorption isotherm of MBAC-N in a smaller ordinate range. The data were obtained from the supporting software of the surface-area and porosimetry analyzer. This figure has been modified from Wan and Li²⁷. [Please click here to view a larger version of this figure.](#)

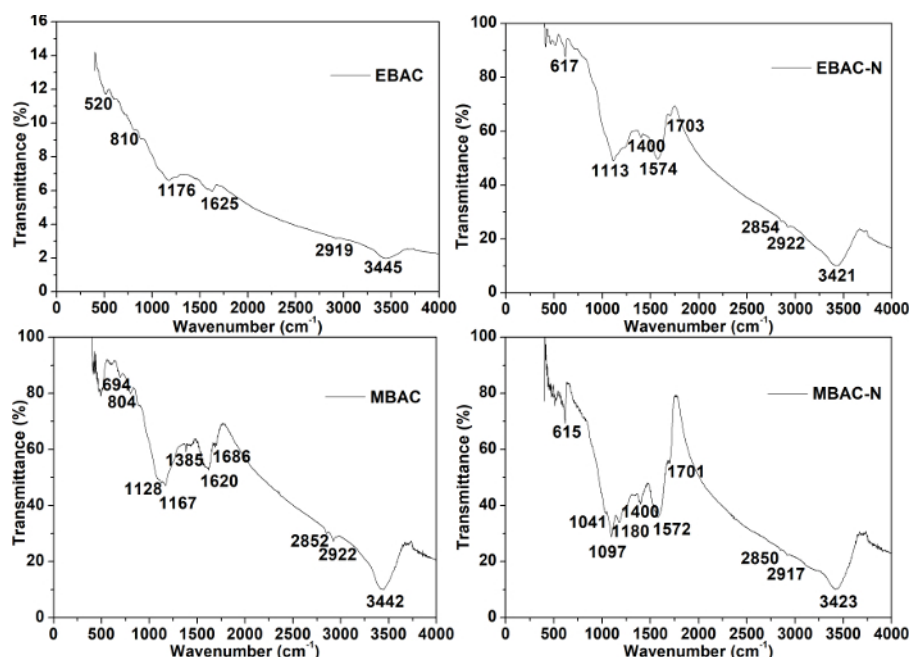


Figure 2: FTIR spectra of EBAC, EBAC-N, MBAC, and MBAC-N. The spectra can confirm the chemical compositions and surface functional groups of the samples. This figure has been modified from Wan and Li²⁷. [Please click here to view a larger version of this figure.](#)

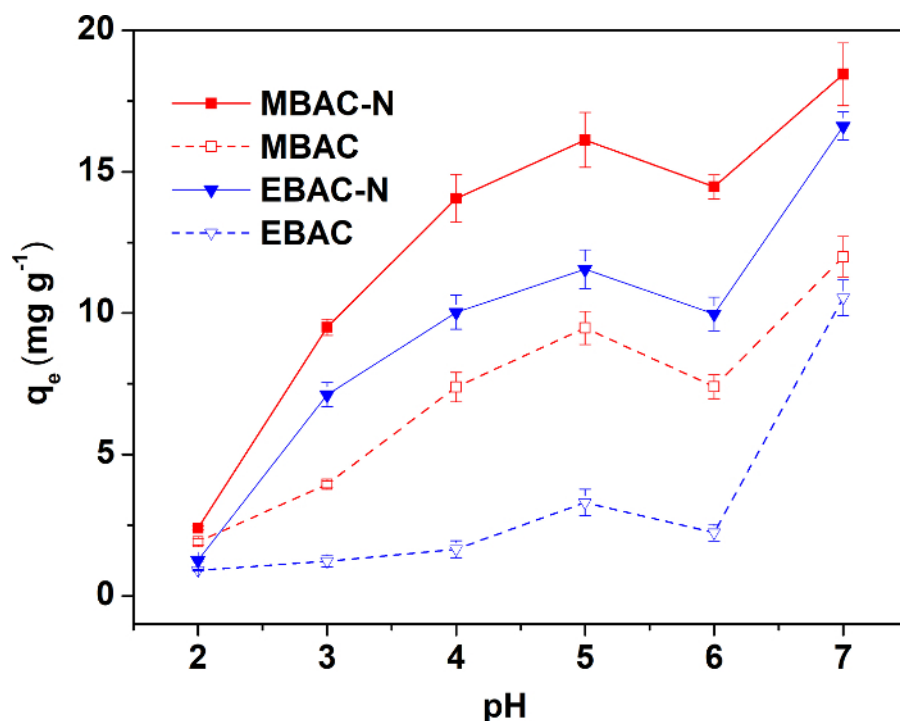


Figure 3: Effect of solution pH on Cu(II) adsorption. The concentration of copper in the solutions is 40 mg L⁻¹. The test is conducted at 25 °C and at 150 rpm for 24 h, to reach adsorption equilibrium. This figure has been modified from Wan and Li²⁷. [Please click here to view a larger version of this figure.](#)

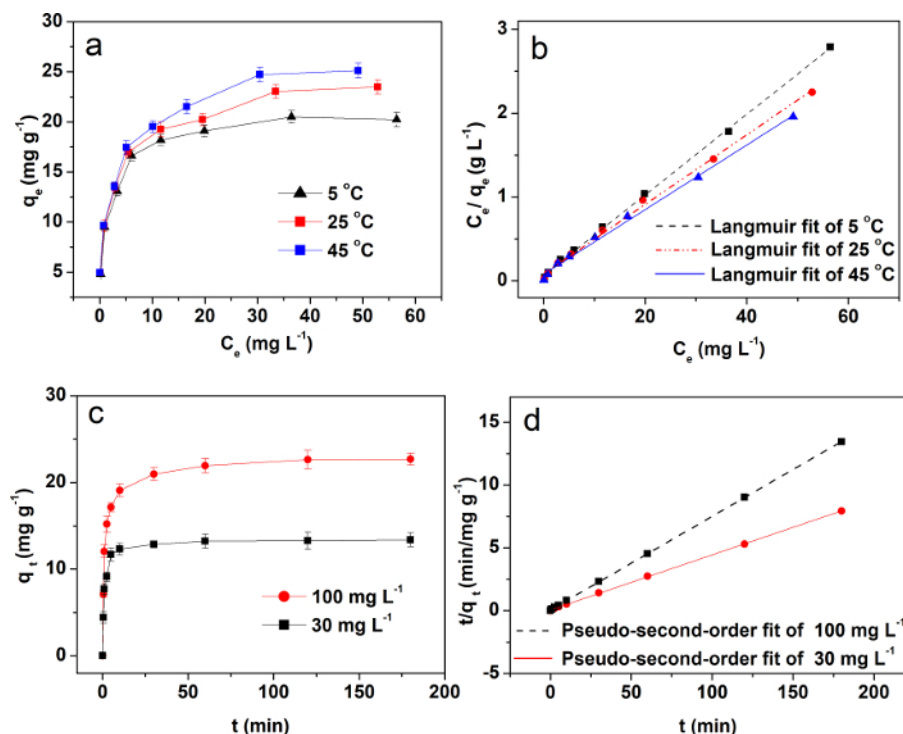


Figure 4: Representative adsorption property analysis of MBAC-N. (a) This panel shows the adsorption isotherms of Cu(II) on MBAC-N at 5 °C, 25 °C, and 45 °C. (b) This panel shows the fitting result for copper adsorption by using the Langmuir isotherm. (c) This panel shows the kinetics of Cu(II) on MBAC-N at the initial concentrations of 30 mg L⁻¹ and 100 mg L⁻¹. (d) This panel shows the fitting result for copper adsorption at 25 °C by using the Pseudo-second-order model. This figure has been modified from Wan and Li²⁷. [Please click here to view a larger version of this figure.](#)

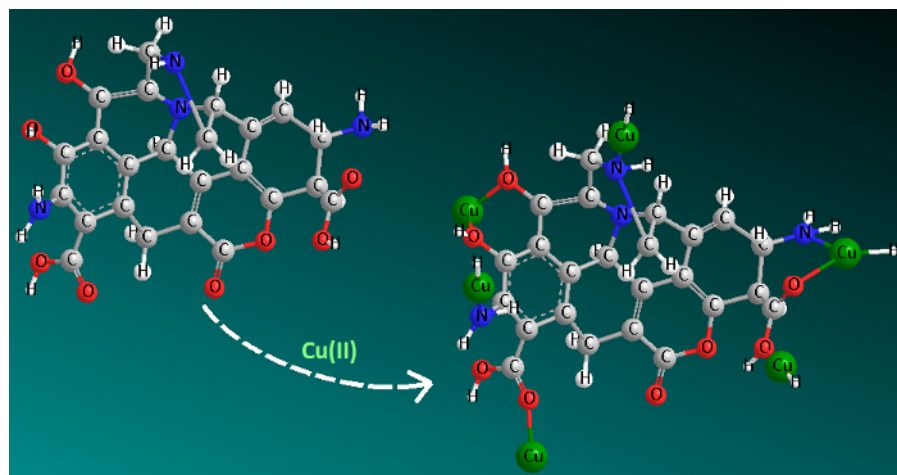


Figure 5: Proposed mechanism for Cu(II) adsorption by modified carbon. In this reaction process, the chemical adsorption mainly involves ion exchange and complexing. [Please click here to view a larger version of this figure.](#)

Adsorbents	EBAC	EBAC-N	MBAC	MBAC-N
Pore structure parameters				
BET surface area ($\text{m}^2 \text{g}^{-1}$)	978	609	543	61
Total pore volume ($\text{cm}^3 \text{g}^{-1}$)	1.22	0.59	0.68	0.13
Mesoporous volume ($\text{cm}^3 \text{g}^{-1}$)	1.09	0.47	0.58	0.11
Mean pore size D_p (nm)	4.97	3.84	5.01	8.89
Mesoporous rate (%)	89.52	80.24	85.32	84.61
Elemental content (wt%)				
C	92.23	79.31	87.28	72.44
H	1.76	1.26	1.65	1.12
N	0.08	4.01	0.58	5.52
O	5.82	15.15	10.33	20.54
S	0.11	0.27	0.16	0.38
Yield (%)	53.35	/	57.23	/

Table 1: Structural characteristics and elemental compositions of EBAC, EBAC-N, MBAC, and MBAC-N. The textural data are analyzed using the BET method. The relative weight percentage of the elements is calculated based on the dry ash-free basis. This table has been modified from Wan and Li²⁷.

		MBAC-N		
Isotherm models	Parameters	5 °C	25 °C	45 °C
Langmuir	q_{cal}^0 (mg g^{-1})	20.82	24.09	25.97
	q_{mea}^0 (mg g^{-1})	20.23	23.47	25.12
	b (L mg^{-1})	0.73	0.51	0.49
	R^2	0.999	0.996	0.995
Freundlich	K_F (L mg^{-1})	8.802	9.65	10.56
	n	3.937	3.902	4.032
	R^2	0.907	0.967	0.987
Temkin	A_T (L mg^{-1})	29.57	32.3	49.8
	B (L mg^{-1})	2.94	3.19	3.16
	R^2	0.969	0.985	0.955

Table 2: Isotherm parameters of Cu(II) on MBAC-N at different temperatures. The fitted parameters are from linearized Langmuir, Freundlich, and Temkin adsorption models. This table has been modified from Wan and Li²⁷.

		MBAC-N	
Kinetic models	Parameters	30 mg L ⁻¹	100 mg L ⁻¹
Lagergren	k ₁ (min ⁻¹)	0.037	0.045
	R ²	0.714	0.934
	q _{e,mea} (mg g ⁻¹)	13.39	22.69
Pseudo-second-order	q _{e,cal} (mg g ⁻¹)	13.44	23.25
	k ₂ (g (mg min) ⁻¹)	0.08676	0.03031
	R ²	0.999	0.999
	q _{e,mea} (mg g ⁻¹)	13.39	22.69
Elovich	αE (g (mg min) ⁻¹)	379.73	312.25
	βE (mg g ⁻¹)	0.738	0.411
	R ²	0.799	0.901

Table 3: Kinetic parameters of Cu(II) on MBAC-N at different initial concentrations. The fitted parameters are from linearized Lagergren, Pseudo-second-order, and Elovich models. This table has been modified from Wan and Li²⁷.

Adsorbents	pH	q _e (mg g ⁻¹)	References
Wood-based granular activated carbon	5.5	6.016	34
Baobab fruit shell-derived activated carbon	6	3.0833	35
Olive stone AC (COSAC)	5	17.08	36
Activated carbon from date stones	5.5	18.68	37
Walnut shell based activated carbon	5	9.3	38
Plasma modified activated carbon		21.4	
MBAC-N	5	25.12	This study

Table 4: Comparison of the adsorption capacity of Cu(II) on different adsorbents. The ability of activated carbon to remove Cu(II) is significantly affected by the pH of the solution, so the adsorption capacity of the contrast biomass-based carbon materials should be obtained close to pH 5.

Discussion

In this protocol, one of the critical steps is the successful preparation of mesoporous carbon with better physicochemical properties by the one-step approach, where optimal experimental conditions need to be determined. So, in a previous study²⁸, we have carried out orthogonal array microwave pyrolysis experiments, considering the effect of the impregnation ratio of bagasse and phosphoric acid, pyrolysis time, microwave oven power, and drying time. Besides, great care must be taken in tedious Cu(II)-adsorption experiments, especially when the pH value of the solution is adjusted, because the pH value has a great influence on Cu(II) removal by activated carbon (**Figure 3**). It is imperative to test the actual copper concentration of the CuSO₄ solution with a defined initial concentration and use this value as C₀ in Equation (1).

A larger specific surface area and higher pore volume of biomass-based activated carbon can be obtained by chemical activation. However, the specific surface area and total pore volume both decrease during the subsequent pyrolysis and modification process, which is likely due to the collapse and blockage of the pores²⁷, resulting in a reduction of the adsorption capacity. Therefore, further work is required to prepare biomass-based mesoporous carbon with both a high surface area and abundant functional groups.

Microwave pyrolysis is verified to more adequately synthesize biomass-based mesoporous carbon with a higher nitrogen/oxygen-chelating adsorption for Cu(II), which has many advantages over widely used conventional heating methods. However, it is not possible to control the instantaneous temperature accurately during the microwave pyrolysis process. Biomass is a good microwave absorption material, whose temperature can rapidly increase under the effect of a microwave. Clearly, future work needs to examine how the pyrolysis temperature affects the physicochemical properties of the biomass-based carbon.

A detailed description of the modification mechanism is beyond the scope of this article, but it can be found in earlier published literature²⁷. The potential importance of nitrification and reduction modification which can effectively introduce more N/O functional groups concurrently on the surface of carbon samples is worth appreciating. However, the modification process contains numerous experimental steps and the utilization

of dangerous concentrated strong acid. A simpler and more effective nitrogen/oxygen modification method may be tested and adopted in further studies.

We have demonstrated an environment-friendly energy-efficient method for preparing biomass-based mesoporous carbon by microwave pyrolysis and dope N/O groups simultaneously on the carbon using a nitrification and reduction route. Such N/O dual-doped activated carbon owns a higher adsorption capacity of heavy-metal ions in an aqueous solution, which is applicable for wastewater remediation. We expect that this protocol will provide ideas for the rapid preparation of high-adsorptive carbon from biomass by time-saving, effective microwave pyrolysis and will be optimized in the future.

Disclosures

The authors have nothing to disclose.

Acknowledgements

The authors acknowledge the Fundamental Research Funds for the Central Universities of China (No.KYZ201562), China Postdoctoral Science Fund (No. 2014M560429) and the Key research and development plan of Jiangsu Province (No. BE2018708).

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