Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2020.25220

182 (2020) 118–126
April

Tertiary treatment of biologically treated effluents from pulp and paper industry by microwave modified activated carbon adsorption

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Received 13 June 2019; Accepted 23 November 2019

ABSTRACT

Nowadays, biologically treated effluents (BTW) from pulp and paper industry still contain a significant organic load, which makes it unsuitable to discharge directly into the waterway. Therefore, a tertiary treatment by activated carbon adsorption was investigated. To improve the treatment efficiency of BTW in the pulp and paper industry, wood-based activated carbon (WAC) was modified by microwave irradiation (MWAC). WAC and MWAC were characterized by scanning electron microscopy, N_2 adsorption, elemental analysis, Fourier transform infrared and X-ray photoelectron spectroscopy. Compared with WAC, MWAC has a higher surface area and lower oxygen-containing groups. The BTW adsorption capacity of MWAC is higher than that of WAC. WAC and MWAC were used to remove chemical oxygen demand (COD) in BTW and the effects of adsorbent dosage, contact time, pH and temperature on the removal of COD in BTW were studied. The adsorption isotherms of WAC and MWAC revealed that the Langmuir models applied to the adsorption process. Molecular weight analysis showed that 1,531 Da was the main component in untreated and treated BTW. MWAC seemed to be more effective in adsorbing small molecular organics due to more micropores. The result indicated that microwave radiation was an efficient method to modify activated carbon for BTW tertiary treatment.

Keywords: Pulp and paper effluent; Wood-based activated carbon; Microwave modification; Adsorption

1. Introduction

The vigorous development of the pulp and paper industry is accompanied by a large number of highly polluted wastewater. Pulp and paper industry can discharge about 3 billion m^3 of wastewater annually, accounting for 30% of the global industrial wastewater production. In China, chemical oxygen demand (COD) generated by the pulp and paper industry from all industrial sectors is the largest, accounting for 32.37% of total COD emissions [1]. The effluent from the pulp and paper industry has caused a series of problems, such as slime growth, thermal impacts, scum formation, color problems, loss of aesthetics in the environment [2] and decline of species diversity [3]. Therefore, it's urgent to clean up the pulp and paper effluent before entering the aquatic environment.

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Conventional wastewater treatment plants generally use primary treatment and secondary biological treatment, which can reduce most of the organic matter [2,4,5]. However, residues of refractory organic compounds [6,7], such as lignin and derivatives [8,9], are still unable to meet the discharge limits due to increasingly stringent regulations [10]. Meanwhile, water resources are increasingly scarce, and water consumption has become a major problem restricting the development of the pulp and paper industry. Many regions stipulate that a certain proportion of papermaking wastewater must be reused. Hence, biorefractory organic matter for further reduction requires a tertiary treatment.

Many physicochemical methods have been applied to the tertiary treatment of pulp and paper mill effluent, such as ozone oxidation [11], Fenton reagent oxidation [12], adsorption [13], membrane separation [14,15], coagulation [16], electrochemical oxidation [17] and biological treatments [18]. Among these methods, adsorption is widely used because of its versatility, high separation efficiency, and easy operation. Many adsorbents, such as activated carbon [13], fly ash [19], biological castoff [20], diatomite [21], bentonite [22] and macroporous adsorption resins [23], have been used in the tertiary treatment of industrial wastewater or municipal wastewater. Activated carbon adsorption has a good removal effect on low concentration pollutants [24]. Although the effects of activated carbon treatment have been investigated before [13,25–28], the useful data of the properties and characteristics of activated carbon in the case of tertiary treatment of biologically treated effluents (BTW) from pulp and paper industry are not available. Microwave modification can improve the adsorption efficiency of activated carbon, however, the application of microwave surface modification activated carbon in real wastewaters is rare [29,30].

Therefore, the objectives of this study were (1) to change the adsorption capacity of activated carbon by microwave irradiation; (2) to characterize the profile of the modified activated carbon; (3) to evaluate the treatment performance of the modified activated carbon for real pulp and paper effluent; (4) to optimize the treatment performance by testing contact time, adsorbent dosage, pH and temperature; (5) to analyze adsorption isotherm and adsorption mechanism.

2. Materials and methods

2.1. Sampling

The biologically treated wastewater from a pulp and paper mill in Zhejiang Province, China, was used in the experiments. The main properties of the wastewater are COD 115–125 mg/L, biochemical oxygen demand (BOD_5) 13–17 mg/L, suspended solids (SS) 17–23 mg/L, pH 7–8 and color 50–60 Pt/Co. The wastewater was stored in refrigerator at 4°C before analysis.

2.2. Preparation of activated carbon

The wood-based activated carbon (WAC) was purchased from Jiangsu Yiqing Activated Carbon Co., Ltd., China. The WAC was crushed, sieved to 200 mesh (size <75 μm), washed with distilled water, dried at 105°C, and stored in a sealed container. The samples were then placed in a silicon carbide drying pot and heated for 6 min in a 400 W microwave reactor (MCR-3E, Microwave Chemical Reaction Apparatus, China) under pure N_2 conditions. After cooling to room temperature, the samples were dried at 105°C for 3 h. The microwave modified WAC was labeled as MWAC.

2.3. Characterization of WAC and MWAC

The Brunauer–Emmett–Teller (BET) surface area and pore structure characteristic of WAC and MWAC was determined by N_2 adsorption/desorption at 77 K using a surface area analyzer (ASAP 2020, Micromeritics Instruments, USA). The surface texture of WAC and MWAC was observed by a scanning electron microscopy (SEM) (JSM 6480, JEOL, Japan). Elemental analysis (C, H, O, N, and S) of WAC and MWAC was determined by an elemental analyzer (Vario EL III, Elementar, Germany). The Fourier transform infrared (FTIR) spectra were recorded from 400 to 4,000 cm^{-1} by using an FTIR spectrometer (Tensor 27, Bruker, Germany). X-ray photoelectron spectroscopy (XPS) was employed to determine the number and type of functional groups present on the surface of the WAC and MWAC using an XPS (AXIS Supra, Kratos, UK).

2.4. Batch experiments

Batch experiments were performed to study the effects of initial adsorbate concentration, contact time, pH, and temperature on COD removal efficiency. For equilibrium adsorption, a certain amount of adsorbent was placed in 50 mL BTW in a conical flask. These conical flasks were placed in an air-temperature shaker at 150 rpm for 3 h under various operating conditions. The samples were then filtrated through a 0.45 μm membrane filter. The relative removal efficiency of COD (%) and q_e (mg/g) in BTW absorbed by WAC or MWAC were calculated based on Eqs. (1) and (2):

$$\text{Removal efficiency of COD}(\%) = \frac{\text{COD}_0 - \text{COD}_e}{\text{COD}_0} \times 100\% \quad (1)$$

$$q_e = \frac{\left(\text{COD}_0 - \text{COD}_e\right)V}{W} \quad (2)$$

where COD_0 and COD_e (mg/L) are the COD of the initial BTW and treated BTW after equilibrium, respectively. V (L) is the volume of the BTW and W (g) is the absorbent weight.

2.5. Characterization of molecular weight (MW)

High-performance size-exclusion chromatography (HPSEC) analysis was conducted according to the method described by Chow et al. [31]. A Waters 2690 Separation Module and Waters 996 photodiode array detector were used with UV detection at 260 nm. Separation of organic compounds based on size was conducted using a Shodex KW-802.5 column (Shoko Co. Ltd., Japan) and a 0.1 M phosphate buffer solution (pH 6.80, ionic strength adjusted to 0.1 M with NaCl). The flow rate was 1 mL/min and the injection volume was 100 μL. The column had an effective resolving range of 50–50,000 Daltons (Da) and the retention time was calibrated for apparent molecular weight (AMW) using polystyrene sulfonate (PSS) standards (Polysciences Inc., US) of molecular weights 35,000; 18,000; and 4,600 Da.

3. Result and discussion

3.1. Characterizations of activated carbon

3.1.1. BET analysis

BET analysis provides the structural characteristics of WAC and MWAC, as shown in Table 1. Microwave modification enhances the BET surface area, external surface area, total pore volume of pores and micropore volume of the adsorbent, which suggested that the modified samples are generally conducive to a well-developed pore structure of activated carbon [32]. The adsorption capacity of BTW is also expected to improve because the surface area and pore volume of the activated carbon increased for microwave modified treatment.

3.1.2. SEM analysis

SEM images of WAC and MWAC are shown in Fig. 1 to illustrate the surface morphology. As can be seen from Fig. 1, the surface of activated carbon before modification was smooth and its porosity was less. However, MWAC was observed a certain degree of collapse in some pores after modification, which may be explained that carbon is calcined at high temperature. The pore size of MWAC is increased and the surface is rough. Ge et al. [33] found a similar phenomenon on coal activated carbon modified by different microwave power.

Table 1
BET surface area and pore structure data of WAC and MWAC

Properties	WAC	MWAC
BET surface area (m^2/g)	1,128	1,441
Micropore area (m^2/g)	629	727
External surface area (m^2/g)	499	714
Total pore volume of pores (cm^3/g)	0.891	0.925
Micropore volume (cm^3/g)	0.260	0.294

3.1.3. Elemental analysis

Table 2 shows the elemental composition of WAC and MWAC, including C, H, O, N, and S content. Microwave treatment increased carbon content and decreased oxygen content, resulting in a drastic increase in C/O ratio from 4.58 to 15.13, suggesting that microwave radiation can decompose and remove acidic groups in the form of CO or CO_2 [34]. At the same time, the hydrogen and sulfur content in MWAC also decreased to a certain extent.

3.1.4. FTIR spectra analysis

The representative FTIR spectra of WAC and MWAC are shown in Fig. 2a. Compared with WAC, the surface chemistry of MWAC illustrated some peak shifts. The band at approximately 3,410 cm^{-1} has been proposed to the O–H stretching vibration of hydroxyl functional groups including hydrogen bonding. The band at approximately 2,920 cm^{-1} is attributed to the C–H stretching vibration, which decreased slightly for MWAC, indicating that hydrogen was removed after microwave modification [35]. The results were consistent with the above element analysis (Table 2). The band centered around 1,700 cm^{-1} in the MWAC sample, which proposed C=O stretching vibration, decreased significantly compared with that of WAC, suggesting the reduction of carboxyl group by microwave treatment [36]. The intense band at approximately

Table 2
Elemental composition of the carbon samples used in the experiment

Samples	Relative content (%)					C/O
	C	H	O	N	S	
WAC	76.10	1.10	16.61	0.31	0.23	4.58
MWAC	88.76	0.61	5.87	0.37	0.20	15.13

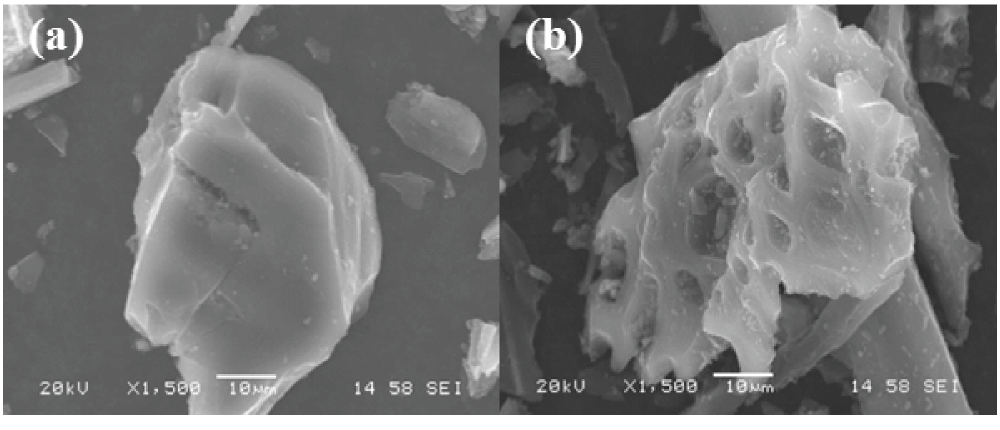

Fig. 1. SEM of activated carbon (a) WAC and (b) MWAC.

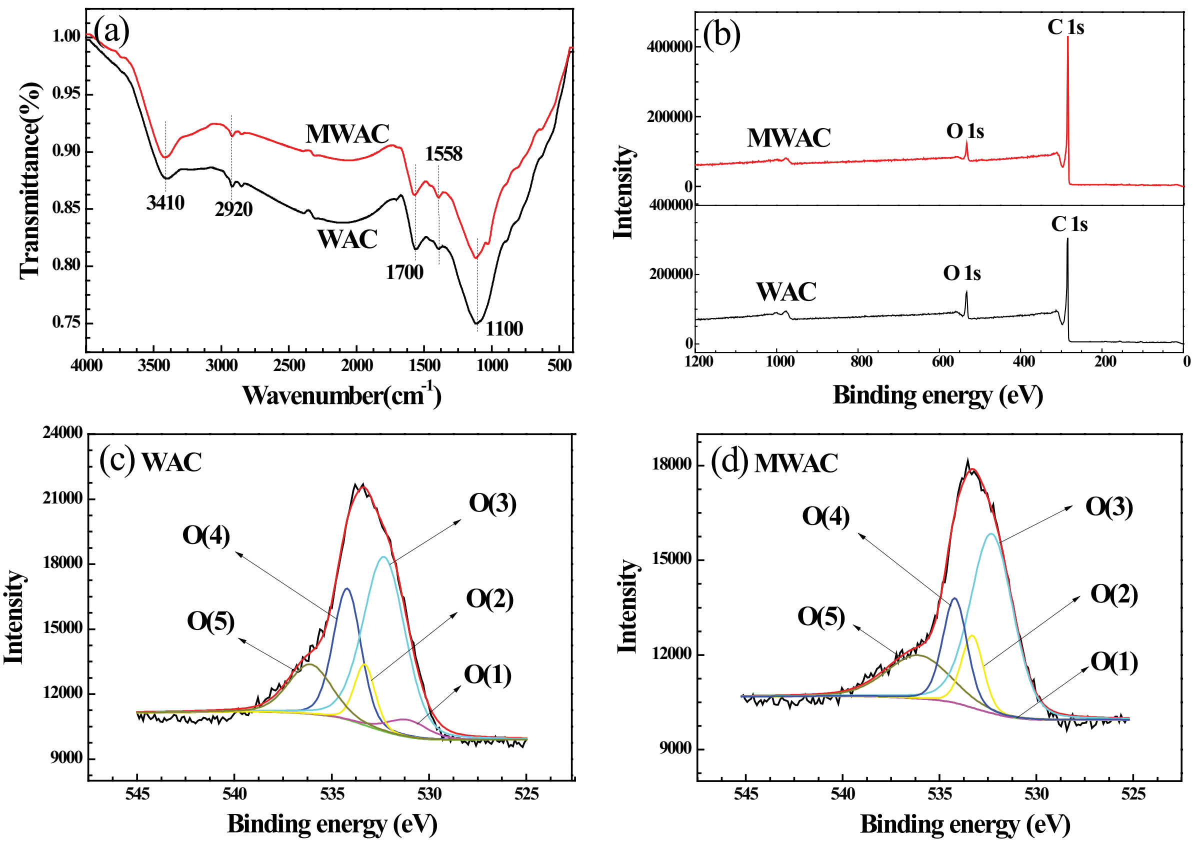

Fig. 2. (a) FTIR spectra of the WAC and MWAC, (b) XPS survey spectra of WAC and MWAC, (c) deconvolution of the core level O1s spectra of WAC, and (d) deconvolution of the core level O1s spectra of MWAC.

1,100 cm^{-1} decreased significantly for MWAC, which may be due to the decrease of the hydroxyl group and the reduction of the peak value of 3,410 cm^{-1}.

3.1.5. XPS analysis

The XPS spectra of WAC and MWAC are shown in Fig. 2b. Two main peaks were identified and labeled as C1s and O1s of WAC and MWAC. It can be seen that the C content increased, and the O content decreased obviously after microwave modification, which indicated that the oxygen group of MWAC was eliminated in the process of microwave modification. Figs. 2c and d show the high-resolution spectrum of the O1s using a curve-fitting program, which was based on the Gaussian-Lorentzian function subtracted from the baseline using Shirley's method. Information on the components, peak position, and their concentrations are summarized in Table 3. Four different O functions and a contribution of chemisorbed water were determined [37]. The O peaks were divided into five peaks at 531.1, 532.3, 533.3, 534.2, and 536.1 eV; representing O=C (carbonyl oxygen atoms), O–C (carbonyl oxygen atoms in esters, amides and anhydrides, and oxygen atom in hydroxyls or ethers), R–O*–C=O (ether oxygen atoms in esters and anhydrides), O*=C–OH (oxygen atoms in the carboxyl groups) and H_2O, respectively. In unmodified WAC, the oxygen functional groups were attributed to chemical activation processes [38]. For the oxygen component, the C=O group of modified carbon decreased, and the C–O group increased, which was consistent with the analysis C1s spectrum and FTIR. MWAC increased the number of R–O*–C=O group and decreased the number of O*=C–OH group. According to Menéndez et al. [39], thermal treatment can produce highly active carbon atoms at the edge of crystals, which re-exposure to air can lead to oxygen adsorption and the formation of new oxygen groups.

3.2. Batch adsorption experiment

WAC and MWAC were used to remove COD in BTW and the effects of adsorbent dosage, contact time, pH and temperature on the removal of COD in BTW were studied. The results are shown in Fig. 3.

3.2.1. Effect of activated carbon dose

In the experiment, BTW and activated carbon were stirred with a constant temperature oscillator. Fig. 3a shows the effect of WAC and MWAC doses on COD reduction. With the increase of adsorbent dosage from 0.4 to 1.8 g/L, the adsorption rate of WAC increased from 61.03% to 75.05%, and that of MWAC increased from 69.50% to 79.24%. When the dosage of adsorbent was less than 1.2 g/L, the adsorbent surface was saturated by compound, and the residual

Table 3
Assignments and peak parameters of the different O1s components

Component	Assignment	Binding energy	Concentration of each sample (%)	
			WAC	MWAC
O(1)	O=C	531.1	4.6	~0.0
O(2)	O–C	532.3	48.6	52.5
O(3)	R–O*–C=O	533.3	8.4	11.0
O(4)	O*=C–OH	534.2	24.2	17.7
O(5)	H_2O	536.1	14.2	18.8

Table 4
Isotherm equation parameters for COD adsorption using WAC and MWAC

Adsorbent	Langmuir isotherm			Freundlich isotherm			Temkin isotherm		
	q_m	K_L	R^2	K_f	$1/n$	R^2	B	A	R^2
WAC	110.636	0.009	0.992	4.728	0.785	0.977	41.781	0.167	0.951
MWAC	120.128	0.011	0.982	5.481	0.788	0.959	44.742	0.187	0.945

concentration in the solution was higher [40], therefore, the amount of adsorption increased with the increase of the dosage. When the dosage reached 1.2 g/L, any increase will not significantly increase the reduction of COD, which was known that with the increase of adsorbent dosage, the decrease of adsorption density is mainly due to the unsaturation of adsorptive sites in the adsorption reaction [41]. Another reason may be due to particle interaction, such as aggregation, resulting from a high adsorbent dose. Such aggregation would lead to a decrease in the total surface area of the adsorbent and an increase in diffusional path length [42]. The results showed that the removal efficiency of BTW by MWAC was better than that of the original MAC. When the dosage reached 1.2 g/L, the removal efficiency of MWAC is 13.87% higher than that of WAC.

3.2.2. Effect of contact time

Fig. 3b shows the effect of the contact time on COD reduction of BTW for WAC and MWAC. Both activated carbons can reach adsorption equilibrium quickly. WAC achieved adsorption equilibrium in 30 min, the removal efficiency was 76.5%, while MWAC reached adsorption equilibrium in 20 min with the removal efficiency of 80.7%. Similar results have been reported in the literature on BTW [13,40]. In batch adsorption systems, a monolayer of adsorbate is usually formed on the surface of the adsorbent, and the removal efficiency of adsorbate species in aqueous solution was mainly controlled by the transport rate of adsorbate species from the external/external sites to the internal site of adsorbent particles [43].

3.2.3. Effect of pH

As shown in Fig. 3c, the effect of solution pH on COD reduction by WAC and MWAC was studied. The solution pH had a significant effect on the reduction of COD when varied from 2 to 12. It can be seen that the adsorption rate of BTW on two kinds of activated carbon decreased gradually with the increase of pH value. The removal efficiency of WAC decreased significantly when the pH was higher than 4, while MWAC decreased when the pH was higher than 10. The pH effect can be described in terms of pH_{pzc}. When the solution pH < pH_{pzc}, the positively charged species start dominating and the surface tends to acquire a positive charge. When the solution pH > pH_{pzc}, the surface tends to acquire a negative charge. The pH_{pzc} of WAC was found to be 4.2 when solution pH < 4.2, the increasing electrostatic attraction between negatively charged adsorbate species and positively charged adsorbent particles would lead to increased adsorption of the acidic lignin compounds with negative charge [21,46,47]. And studies have shown that there was little competition between the adsorbed molecules and hydroxyl ions at low pH [44]. When the solution pH > 4.2, the electrostatic exclusion leads to decreased adsorption of the acidic lignin compounds with a negative charge. The pH_{pzc} of MWAC was found to be 9.5, so microwave radiation increased the surface potential of WAC. Those led us to the dual adsorption of BTW onto WAC/MWAC: physical adsorption and chemical adsorption. The chemical adsorption mechanism includes the reaction between hydroxyl and carbonyl functional groups on the surface of the WAC/MWAC and acidic lignin derivatives [45].

3.2.4. Effect of temperature

Fig. 3d illustrates the effect of temperature on COD removal from BTW by WAC and MWAC. The COD removal efficiency from BTW by both activated carbon increased with the increase of temperature from 15°C to 20°C. Then the COD removal efficiency began to decrease as the temperature increased. This was explained by the adsorption mechanism, there was mainly physical adsorption at lower temperatures, and higher temperature can provide greater activation energy for chemical adsorption, thus improving the removal efficiency of COD. However, when the

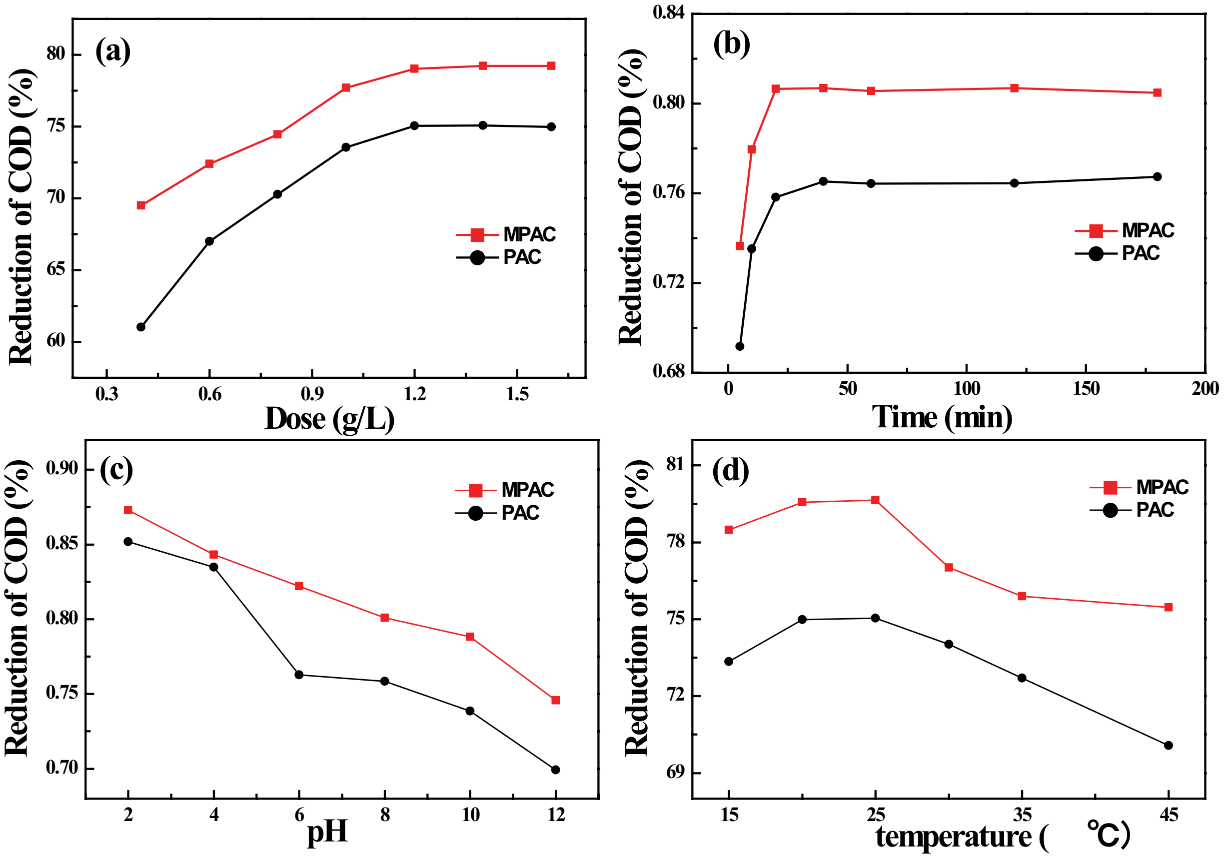

Fig. 3. Effect of different conditions on the adsorption of COD onto WAC and MWAC (initial COD concentration: 118 mg/L and $V = 50$ mL); (a) adsorbent dosage (3 h, pH 7.35, and 25°C), (b) contact time ($m = 60$ mg/50 ml, pH 7.35, and 25°C), (c) pH ($m = 60$ mg/50 ml, 1 h, and 25°C), and (d) temperature ($m = 60$ mg/50 ml, 1 h, and pH 7.35).

temperature continued to rise, the molecular thermal movement intensified, and the physically adsorbed molecules left the surface of activated carbon and resolved into wastewater, resulting in a decrease in COD removal efficiency [46]. Therefore, the proper increase of adsorption temperature can improve the removal of COD from BTW by activated carbon.

3.3. Isotherm studies

In this study, the most commonly used two-parameter isotherms [47], Langmuir and Freundlich and Temkin were used to describe the adsorption characteristics of adsorbents.

The Langmuir adsorption model assumes that the adsorption is monolayer and the adsorbate molecules are adsorbed at specific sites on the adsorbent surface [48]. The non-linear equation of Langmuir isotherm model is expressed as follow:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{3}$$

where C_e is the equilibrium liquid concentration, q_e (mg/g) is the equilibrium amount of adsorbate per unit mass of adsorbent, while q_m (mg/g) and K_L (L/mg) are Langmuir constants related to adsorption capacity and adsorption rate.

Freundlich isothermal model assumes that adsorption occurs on heterogeneous surfaces and is applied to describe multilayer systems and reversible adsorption [49]. The empirical Freundlich isotherm equation is expressed as follows:

$$q_e = K_f C_e^{1/n} \tag{4}$$

where C_e is the equilibrium liquid concentration, q_e (mg/g) is the equilibrium amount of adsorbate per unit mass, while K_f is the adsorption capacity (mg/L), and $1/n$ is the adsorption affinity of the adsorbent. The slop of $1/n$ is between 0 and 1, which indicates that there is a strong interaction between adsorbent and adsorbate with favorable adsorption. Generally, n at the ranges of 2–10, 1–2 and less than 1 represent good adsorption, moderate adsorption, and poor adsorption, respectively [50].

The Temkin isotherm model [51] contains a factor that explicitly takes into account adsorbing species-adsorbate interactions. By ignoring the extremely low and large concentration values, this model assumes the following: (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and that (ii) the adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. The derivation of the Temkin isotherm assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation. The Temkin isotherm has commonly been applied in the following form:

$$q_e = B\ln\left(AC_e\right) \tag{5}$$

where A and B are Temkin isotherm constants.

A comparison of non-linear fitted curves from experimental data and isotherm is shown in Fig. 4. The coefficients of determination (R^2) and isotherm parameters from the non-linear regressive method are listed in Table 4. Since the value of R^2 nearer to 1 indicates that the respective equation better fits the experimental data. The representations of the experimental data by all model's equation result in a non-linear curve with R^2 values of a least 0.94 as tabulated in Table 4. The experimental data yielded excellent fits within the following isotherms order: Langmuir > Freundlich > Temkin. We can see that the models which best represented the data obtained were the Langmuir model (with higher $R^2 > 0.992$) for BTW.

3.4. Variety of molecular weight

HPSEC analysis was used to investigate changes in the BTW of dissolved organic compounds caused by adsorption treatment. The HPSEC chromatograms of each organic samples were quantitatively analyzed by the mathematical fitting of overlapping peaks as described previously [52]. Each chromatogram was fitted to the sum of up to four Gaussian functions (Eqs. (6) and (7)) which were defined by three parameters: position (p), height (h) and width (w).

$$I_x = \frac{h\times\exp\left(\frac{-4\ln\left(2\right)\left(x-p\right)^2}{w^2}\right)}{\sqrt[w]{\frac{\pi}{4\ln\left(2\right)}}} \tag{6}$$

$$I_{\text{fit}} = \sum_{i=1}^{4} I_x \tag{7}$$

To facilitate the comparison between samples, the positions and widths of the fitting peaks remained unchanged in all chromatograms, and only the peak heights could vary in the fitting (including the zero value of the missing peak). For multivariate analysis, the trace of the chromatograms was used; AMW values were log-transformed, and the absorbance at 260 nm was baseline corrected and normalized.

Fig. 5a shows the HPSEC chromatograms of untreated wastewater, wastewater adsorbed by WAC, and wastewater adsorbed by MWAC. The result showed that the untreated or treated wastewater contained organic compounds with AMW in the range 100–3,000 Da, which was consistent with the research of Leiviskä et al. [53]. The content of dominant AMW changed greatly and the distribution of dominant AMW changed little.

Fig. 5b shows the results of a fitting process. Four peaks of fixed molecular weight and peak width were identified in the molecular weight range from 100 to 3,000 Da. The molecular weights of these peaks were 276; 528; 1,039; and 1,531 Da, respectively. The main molecular weight was 1,531 Da in all wastewater. The average absorbance by WAC adsorption was significantly lower than that of untreated BTW, while higher than that of MWAC adsorption. In addition, the organic component of the lowest molecular weight 276 Da was almost completely removed after MWAC adsorption, which corresponds to the higher micropore area of MWAC than of WAC (Table 1). According to Moore et al. [54], organic components with molecular weight less than 3,000 Da were more suitable for microporous adsorption of activated carbon.

4. Conclusion

Compared with WAC, the surface properties of MWAC were enhanced with the increase of BET surface area and C/O ratio. MWAC could effectively adsorb BTW at a dose of 1.2 g/L and 25°C. WAC showed 75.0% COD removal of BTW in 40 min, while MWAC removed 79.7% COD of BTW in 20 min. The adsorption isotherms of WAC and MWAC

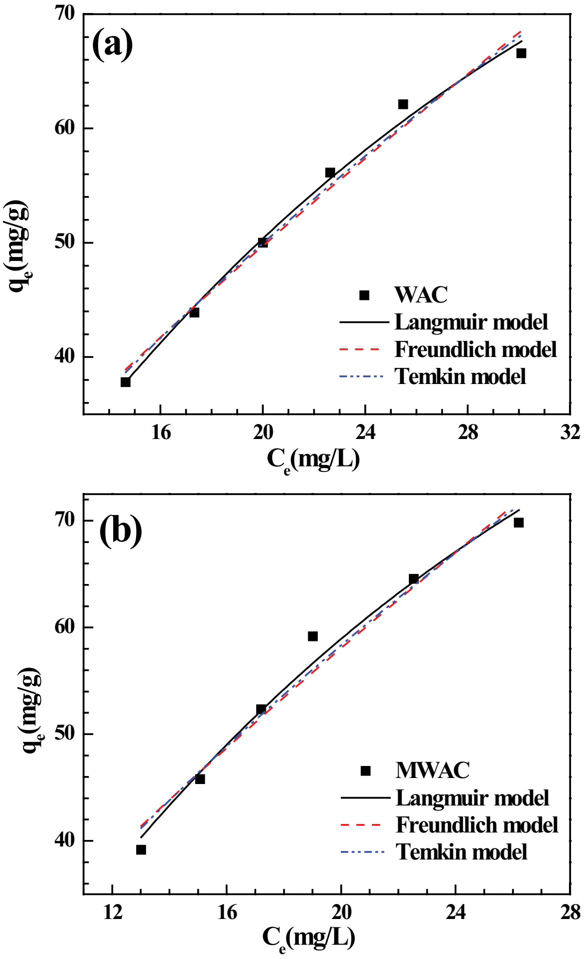

Fig. 4. (a,b) Non-linear adsorption isotherm of COD adsorption using WAC and MWAC (initial BTW concentration = 110–60 mg/L, dose = 1.2 g/L, and equilibrium time = 1 h).

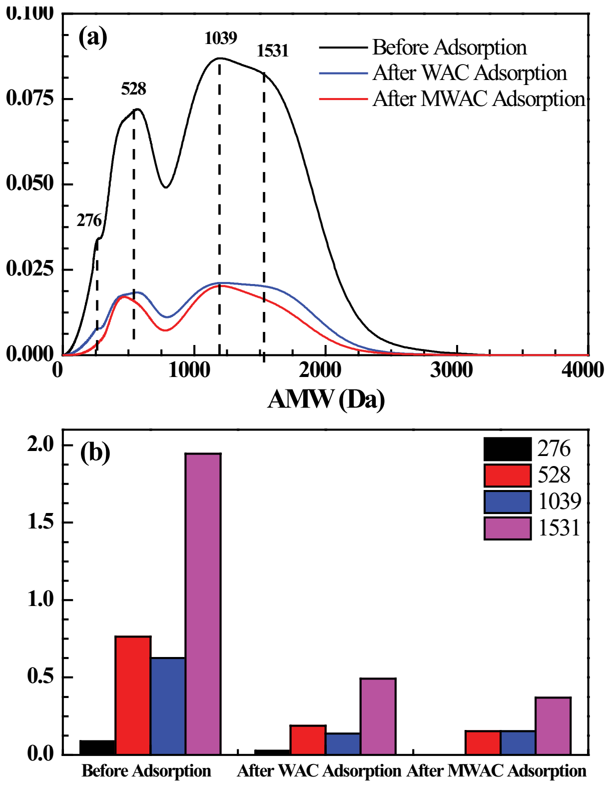

Fig. 5. (a) HPSEC of raw BTW, after adsorption by WAC and after adsorption by MWAC for optimum adsorption condition. (b) Relative proportions of the 4 peaks (MW showed in Da) identified in the peak fitting of HPSEC chromatograms.

both fit the Langmuir isotherm models. Molecular weight analysis showed that 1,531 Da accounted for the main part in untreated and treated BTW, MWAC seemed to be more effective in adsorbing small molecular organics due to more micropores. In summary, microwave radiation is a rapid and efficient method to modify activated carbons, and MWAC is a promising low cost and fast adsorbent to remove COD of BTW.

Acknowledgment

This work was supported by the National Science and Technology Major Projects Special for Water Pollution Control and Management (No. 2017ZX07206-002-03).

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