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Feasible treatment of epoxy methyl ester wastewater using activated carbon as an adsorbent

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ABSTRACT

A feasible method for treatment of wastewater generated during epoxy methyl ester production was provided in this study, which consisted of four parts, i.e., neutralization, heat pump distillation, evaporation crystallization, and adsorption. For this treatment process, adsorption was a key step. The major pollutants of epoxy methyl ester wastewater after neutralization and distillation were determined as methanol, ethyl alcohol and epoxy propane. Activated carbon was used as an adsorbent for the wastewater treatment and the adsorption behavior was mainly studied. The adsorption experiments of methanol as the model compound to actual wastewater using virgin activated carbons (VAC) and HNO_3 modified activated carbons (MAC) were carried out. FTIR and Boehm titration results indicated the increased oxidation groups were obtained through modification. Several isotherm and kinetic models were adopted to fit the experimental data by non-linear regression method. Results showed that Langmuir isotherm and pseudo-second order kinetic models can well describe the adsorption behavior. Various thermodynamic parameters such as standard free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0) showed that the adsorption of methanol onto carbon was favored at lower temperature. In addition, breakthrough curves were determined using the column adsorption, which were fitted well by the Thomas model. Furthermore, the COD of initial actual wastewater (about 35000 mg/L) was significantly reduced to 293 mg/L after treatment. Finally, regeneration experiments demonstrated the potential of this method.

Keywords: Epoxy methyl ester wastewater; Activated carbon; Methanol; Adsorption; Non-linear regression

1. Introduction

As an important chemical plastic additive, plasticizer provides durability, elasticity and flexibility for polymeric products. Nowadays, phthalate esters are still the dominant raw material to produce plasticizers, although more and more evidence proves its suspected carcinogenicity and toxicity to animals and in humans [1,2]. With growing concern about health and environment, the application of phthalate esters in toys, medical supplies, and food packaging has been limited by many countries through legislation, which causes a sharp decrease in the market share of phthalate ester containing products [3]. Therefore, in order to meet product quality and specification requirements, alternative plasticizers to phthalate esters, such as epoxy soybean oil and epoxy fatty acid methyl ester (EFAME), have attracted much interest due to their low migration level and toxicity [4]. As a new environmentally friendly plasticizer, EFAME is generally produced using formic acid autocatalytic process, where fatty acid methyl ester, formic acid and hydrogen peroxide are well mixed at a constant temperature for certain time [5–7]. After reaction,

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the primary product is washed by water, and hence wastewater is generated. The epoxy wastewater mainly contains formic acid, hydrogen peroxide and other complex grease-like matters, making it difficult to be treated.

Biodegradation and advanced oxidation methods have been adopted for EFAME wastewater treatment. You et al. [8] used Fenton reagent and membrane bioreactor (MBR) to treat epoxy plasticizer wastewater, reaching 94% COD removal rate. The method can thoroughly deal with the wastewater, but the sludge and smell from biodegradation remained an issue. In order to reduce the cost, Zhao et al. [9] used calcium carbonate to recycle formic acid from wastewater. Nevertheless, this method did not pay attention to the treatment of other pollutants. Therefore, an efficient, simple and cost-effective method for EFAME wastewater treatment is required.

Adsorption method has been proven to be a suitable technique for removal of various pollutants due to its efficiency, simple design, easy operation, and capability to remove wide range of contaminant concentrations [10]. Numerous studies have evaluated the efficiency of adsorption technique in the removal of emerging contaminants, such as synthesis dyes, drugs, pesticides, etc. Activated carbon is an extensively utilized adsorbent for removal of organic compounds from both potable water and wastewater, mainly due to its low cost, high surface area and well-developed pore structure. Materials rich in carbon, such as coals [11], wood [12], coir pith [13], peat [14], and agricultural by-products [15,16], can be used for activated carbon production. Different raw materials and activation conditions would lead to difference in pore structure, surface area and surface functional groups [17,18]. The adsorption affinity of the carbon adsorbent surface depends essentially not only on the chemical characteristics of carbon surface and the physical properties of pore structure, but also on the chemical structure of the adsorbate and the characteristics of surrounding solution. For example, methanol with strong polarity was unfavorable to be adsorbed by activated carbon which was generally nonpolar. Therefore, acid oxidation with the purpose of adding oxygen-containing functional groups was employed, because the nature and amount of oxygen surface groups are extremely important in the adsorption of polar molecules [19]. The method of HNO_3 oxidation was used to increase the polarity of carbon surface by increasing the number of oxygen functional groups [20]. In addition, the COD of wastewater can be largely reduced by carboneous materials [21].

Our group developed an effective method for EFAME wastewater treatment, which mainly consisted of four parts, i.e., neutralization, heat pump distillation, evaporation crystallization, and activated carbon adsorption and regeneration. The wastewater was separated into heavy part and light part through heat pump distillation. The major pollutants of the light part included methanol, ethyl alcohol and epoxy propane, which were further removed by activated carbon adsorption. For this treatment process, activated carbon adsorption was a key step. Hence, the objective of this work is to investigate the adsorption kinetics and equilibrium data of methanol as the model compound to actual wastewater on both virgin activated carbons (VAC) and HNO_3 modified activated carbons (MAC). Various adsorption models were applied to fit the experimental results. In addition, a fixed bed set-up was developed to evaluate the adsorption behavior of simulation wastewater and actual wastewater on MAC.

2. Materials and methods

2.1. Materials

Nitric acid (HNO_3), methanol (CH_3OH) and reagents for chemical oxygen demand (COD) measurement were provided by Aladdin Industrial Corporation (China). Sodium hydroxide (NaOH, 96 wt%) was supplied by Hangzhou Xiaoshan Chemical Reagent Industrial Corporation. All solutions used during experiments were diluted to a certain concentration by previously prepared deionized water. Granular activated carbon based on coconut shell was bought from Lvlin Activated Carbon factory. Epoxy fatty acid methyl ester wastewater was obtained from Jiangyin Xiangyang Technology Co., Ltd. Unless otherwise stated, all of the chemicals are analytical reagent grade.

2.2. Modification of activated carbon

Prior to column packing in dynamic experiments, activated carbon was sieved to 1–2 mm, washed by deionized water, and dried in an oven at 110ºC for 24 h. To enhance the removal efficiency of strong polar compounds, the VAC were modified using HNO_3. The modification process was carried out by adding 500 g HNO_3 (10 wt%) to 100 g activated carbon for 8 h at a constant temperature of 60ºC and a constant stirring speed of 300 rpm. After oxidation, the MAC were filtered and washed with excessive deionized water and then dried in an oven at 110ºC for 24 h. The modified samples were kept in a sealed container until use.

2.3. Wastewater pretreatment process

As can be seen in Fig. 1, initially, the wastewater was neutralized by sodium hydroxide and separated by distilling apparatus, where the tower kettle temperature was controlled at 102ºC. For this part, heat pump distillation (i.e., the vapor stream leaving the top tray is compressed to a higher pressure and then used to heat the bottom liquid, or the liquid stream leaving the bottom tray is flashed in a pressure reducing valve and then used to cool the overhead vapor) can replace simple distillation in industry, which can largely reduce the energy. After distillation, the heavy part was enriched in the tower kettle, which was then washed by methanol followed by crystallization separation to get sodium formate which is a high value-added product. On the other hand, the light part after distillation, with COD value of about 2500 mg/L, was further treated by activated carbon adsorption.

2.4. Batch adsorption experiments

Batch adsorption experiments were performed by adding 0.1 g activated carbon powder into 40 mL methanol

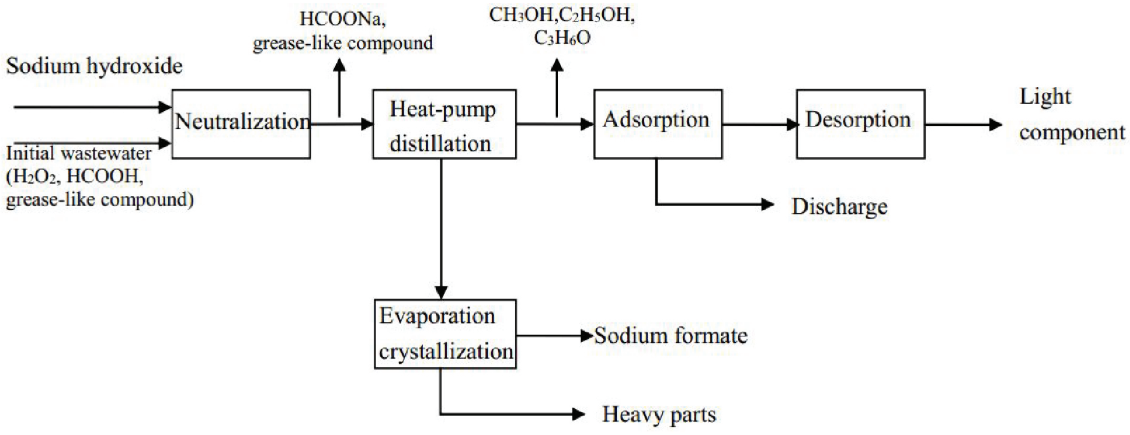

Fig. 1. Wastewater treatment process.

solution which was used to simulate the actual EFAME wastewater. The concentrations of the methanol solutions were 1 g/L, 5 g/L, 10 g/L, 20 g/L, 30 g/L, respectively. The mixtures were put in a 250 mL conical flask and shaken in an incubator shaker at a constant speed. In addition, adsorption experiments were carried out at different temperatures (30ºC, 40ºC, 50ºC). The equilibrium time was set at 4 h to ensure saturated adsorption. The solution after equilibrium was analyzed to determine the residual concentration. Additionally, a blank run without activated carbon was conducted for each concentration and temperature.

Kinetics adsorption experiments were performed by adding 0.1 g activated carbon powder into 40 mL methanol solution at various temperatures for 4 h, while samples were taken at preset time intervals for analysis. The concentration of methanol solution was determined as 1 g/L according to actual wastewater. The adsorption capacity data Q_e, Q_t (mg/g) were calculated using the following equation:

$$Q_t = \frac{(C_0 - C_t)V}{m} \tag{1}$$

where V (L) is the sample volume; C_o, C_t (mg/L) are the concentrations of adsorbate at initial time, and t time (min), respectively; Q_t (mg/g) are adsorption capacity at t time; m (g) is the dry weight of the adsorbent.

2.5. Column adsorption experiments

The model solution and actual EFAME wastewater were separately pumped into a fixed bed column with a diameter of 19 mm and height of 150 mm charged with 20 g activated carbon. Circulating water was introduced around the column to assure the adsorption at a constant temperature. The concentration of feed methanol solution was determined as 1g/L according to actual epoxy wastewater. The solution was pumped up-flow through the column at different flow rates using a peristaltic pump. The breakthrough curves were obtained by analyzing samples taken from the top outlet of column at preset time intervals. Furthermore, regeneration experiments were conducted to investigate the feasibility of carbon adsorption of actual wastewater.

2.6. Analytical methods

The concentrations of formic acid and hydrogen peroxide were determined by titration using standard sodium hydroxide solution and potassium permanganate solution, respectively. Chemical oxygen demand (COD) was analyzed according to the Chinese National Standard GB-11914–89. The concentrations of methanol, ethyl alcohol and epoxy propane were determined using Shimadzu 2014C gas chromatograph (GC) equipped with a DB-5 column (30 m × 0.25 mm × 0.25 µm) and a flame ionization detector (FID). The injection amount and split ratio were 0.5 µL and 50:1, respectively. The oven temperature was initially 50ºC, kept at 50ºC for 4 min, and then increased to 100ºC at a rate of 15ºC/min. The quantification was carried out using external standard method.

2.7. Characterization of activated carbon

Nitrogen adsorption is a standard procedure for the determination of porosity of carbonaceous adsorbents. The textural properties of VAC and MAC were analyzed using static volume method on a 3H–2000PS1 specific surface & pore size analysis instrument. The functional groups on the surface of activated carbon were determined on a Bruker Tensor II Fourier Transform infrared spectroscopy (FT-IR), with a resolution of 4 cm^{-1} and scanning time of 64.

The Boehm titration method was used to determine the number of oxygen- containing surface groups [22]. The sample (1 g) was placed in 50 mL of the following 0.05 mol/L solutions: hydrochloric acid, sodium hydroxide, sodium carbonate, and sodium bicarbonate. The vials were sealed and stirred for 48 h, and then the carbon suspensions were filtered. An aliquot of each filtrate (5 ml) was titrated with HCl or NaOH, depending on the original titrant. The number of acidic sites of various types was calculated under the assumption that NaOH neutralizes carboxylic, phenolic, and lactonic groups, $NaCO_3$ neutralizes carboxylic and lactonic groups, and $NaHCO_3$ neutralizes only carboxylic groups. The number of basic sites was calculated from the amount of HCl that reacted with the carbon.

3. Results and discussion

3.1. Wastewater component

The wastewater was neutralized and distilled, with the light part collected at the top and heavy part kept at the bottom analyzed separately. The results showed that heavy part contained C_3–C_{10} alcohol compounds, aldehydes, ketones and other cyclic compounds, which may be produced from ring-opening reactions of epoxy compounds. On the other hand, light part was mainly composed of methanol, ethyl alcohol, and epoxy propane, with the contents about 0.1%, 0.01%, 0.003%, respectively. It was speculated that methanol was produced from the hydrolysis of epoxy methyl ester. Since methanol was the main compound in light part, it was used as the model compound to simulate the wastewater for activated carbon adsorption.

3.2. Characterization of activated carbon

The surface area of porous adsorbents is the most commonly described factor affecting adsorption if there are no special interaction sites on the adsorbent surface. As shown in Table 1, the BET specific surface area of MAC was a little lower than that of VAC, which was mainly due to the collapse and blocking of pore structure resulting from the oxidation process. Similar results were obtained for the total pore volume and average pore diameter, yet the pore channel was still large enough for the adsorption of methanol molecules.

The results of Boehm Titration shown in Table 2 indicated the oxygen-containing surface functional groups significantly increased due to the HNO_3 oxidation. The total number of acidic groups on MAC was obviously larger than these on VAC, while the number of basic groups on MAC was relatively small, which would be favorable to the wastewater adsorption onto MAC.

FTIR spectra of VAC and MAC is shown in Fig. 2. As can be seen, both curves had similar shapes showing vibration bands characteristic of carbonaceous materials. The bands at c.a. 1161 cm^{-1}, 1560 cm^{-1} and 3447 cm^{-1} were assigned to C–O–C or C–O group, –COOH group, and O–H (from carboxyl, phenol and water) group, respectively. The surface oxygen-containing functional groups contribute significantly to adsorption processes, especially for polar compounds. It can be noticed from Fig. 2 that MAC possessed more oxygen-containing functional group than VAC, indicating larger adsorption capacity of MAC for polar compounds [19].

Table 1
Textural properties of VAC and MAC

Textural properties	VAC	MAC
S_{BET} (m^2/g)	571.80	533.23
$S_{Langmuir}$ (m^2/g)	689.02	658.14
Total pore volume (mL/g)	0.3066	0.2673
Average pore diameter (nm)	2.6251	2.3637

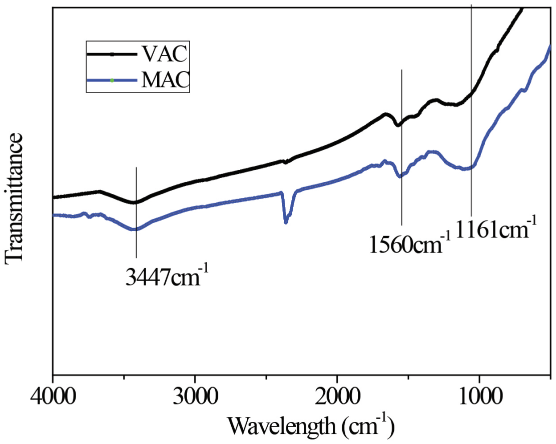

Fig. 2. FTIR spectra of VAC and MAC.

3.3. Methanol adsorption experiments

3.3.1. Batch adsorption

Adsorption isotherms are considered essential while designing the adsorption systems, since it could clearly depict the distribution of adsorbate between the liquid and solid phases at various equilibrium concentrations. To date, the isotherm models of Langmuir [23] and Freundlich [24] are generally accepted to assess the adsorption equilibrium behavior of different substances onto activated carbons. Those two isotherm models can be represented by Eq. (2) and Eq. (3), respectively.

$$Q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{2}$$

$$Q_e = K_F C_e^{(1/n)} \tag{3}$$

where C_e is the equilibrium concentration (mg/L); Q_e is the amount of adsorbate adsorbed onto per unit mass of ACs (mg/g); q_m is the theoretical maximum monolayer adsorption capacity (mg/g); K_L is the Langmuir isotherm constant (L/mg); K_F (mg/g(L/mg)$^{1/n}$) and n are Freundlich

Table 2
Surface chemistry of carbons (Boehm titration)

Sample	Acidic (mmol/g)	Carboxylic (mmol/g)	Lactonic (mmol/g)	Phenolic (mmol/g)	Basic (mmol/g)
VAC	0.1127	0.01781	0.07157	0.02331	0.2721
MAC	0.7044	0.3232	0.1694	0.2118	0.0000

constants with n as a measure of the deviation of the model from linearity of the adsorption and K_F as an indicative of the adsorption capacity of the adsorbent. Generally speaking, n is used to verify types of adsorption, if n is equal to unity, the adsorption is linear. Moreover, adsorption is a chemical process when n is below unity, while a favorable adsorption and a physical process are suggested when n is above unity [25].

In this study, the adsorption behavior of methanol with various initial concentrations at different temperatures was studied. As can be clearly seen in Fig. 3, the equilibrium adsorption uptake on the adsorbent obviously increased with increasing initial methanol concentration, which is due to the more contact of methanol molecules with the adsorbent surface. For both VAC and MAC, Q_e decreased with increased temperature, indicating that the process was exothermic. As temperature increased, the desorption of methanol from activated carbon resulting from stronger molecular thermal motion improved. Moreover, the largest Q_e observed for MAC and VAC were 243 mg/g and 224 mg/g, respectively, both of which were larger than the results obtained by Casas et al. [26]. According to the results of Boehm titration, the amount of oxygen-containing functional groups obviously increased, which may slightly enhance the capacity of adsorbent, leading to a larger Q_e for MAC than VAC [18].

The error distribution changes worse depending on the way adsorptive equation linearized [27], and hence it is more appropriate to use the non-linear method for estimating the adsorptive model parameters instead of the linear one. As a result, non-linear regression method was employed to fit experimental data in this work. The obtained fitting curves and isotherm model parameters are summarized in Fig. 3 and Table 3, respectively. Higher correlation coefficient (R^2) values were obtained for Langmuir model than Freundlich model at all three temperatures, which indicated Langmuir model was more suitable to describe the adsorption behavior of methanol solution onto both VAC and MAC. It suggested that the adsorption mainly occurred in a monolayer on the well distributed active sites of the adsorbent.

3.3.2. Batch kinetic studies

Kinetic models are helpful to provide valuable information for better understanding adsorption mechanism and determining the rate of adsorption process. In this paper, pseudo-first order, pseudo-second order kinetic models were used to fit experimental results. The Lagergren pseudo-first order model [28] can be expressed by Eq. (4)

$$q_t = q_{e1}\left(1 - e^{-k_1 t}\right) \tag{4}$$

where q_{e1} (mg/g) indicates the capacity of equilibrium adsorption of methanol on adsorbent, q_t(mg/g) is adsorption capacity at the time of t, and k_1 is rate constant for pseudo-first order based on min^{-1}.

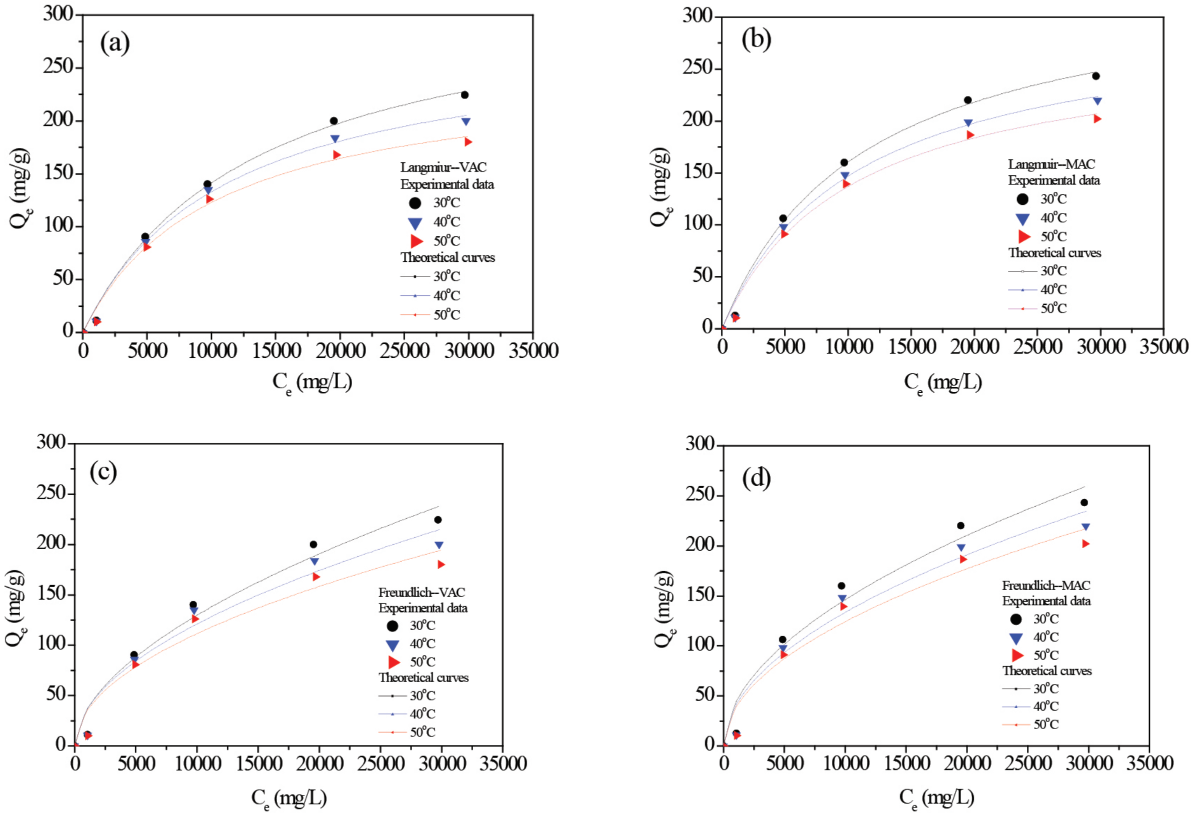

Fig. 3. Adsorption isotherm of methanol onto VAC and MAC at different temperatures and non-linear adjustments of (a) Langmuir model to VAC; (b) Langmuir model to MAC; (c) Freundlich model to VAC; and (d) Freundlich model to MAC.

Table 3
Isotherm parameters for methanol adsorption onto activated carbon

Temperature		Langmuir model			Freundlich model		
		q_m (mg/g)	$K_L \times 10^5$ L/mg	R^2	K_F (mg/g (L/mg)$^{1/n}$)	$1/n$	R^2
30°C	VAC	330	7.47	0.9901	0.78	0.56	0.9482
	MAC	340	8.89	0.9873	1.16	0.53	0.9323
40°C	VAC	282	8.88	0.9863	0.96	0.52	0.9274
	MAC	304	9.36	0.9856	1.14	0.52	0.9257
50°C	VAC	248	9.77	0.9833	1.05	0.51	0.9148
	MAC	279	9.63	0.9837	1.11	0.51	0.9186

The pseudo-second order model [29] is based on the assumption that the rate of used adsorbent sites is proportional to the square of the number of sites. Also, it is acknowledged as a special kind of Langmuir kinetics, supposing that the adsorbate concentration is constant in relation to time and the total number of binding sites depends on the amount of adsorbate adsorbed at equilibrium. It can be expressed as:

$$q_t = \frac{k_2 q_{e2}^2 t}{1 + k_2 q_{e2} t} \tag{5}$$

where q_{e2} (mg/g) indicates the capacity of equilibrium adsorption of methanol on adsorbent, q_t (mg/g) is adsorption capacity at the time of t, the pseudo-second order rate constant k_2, is based on g/mg/min too.

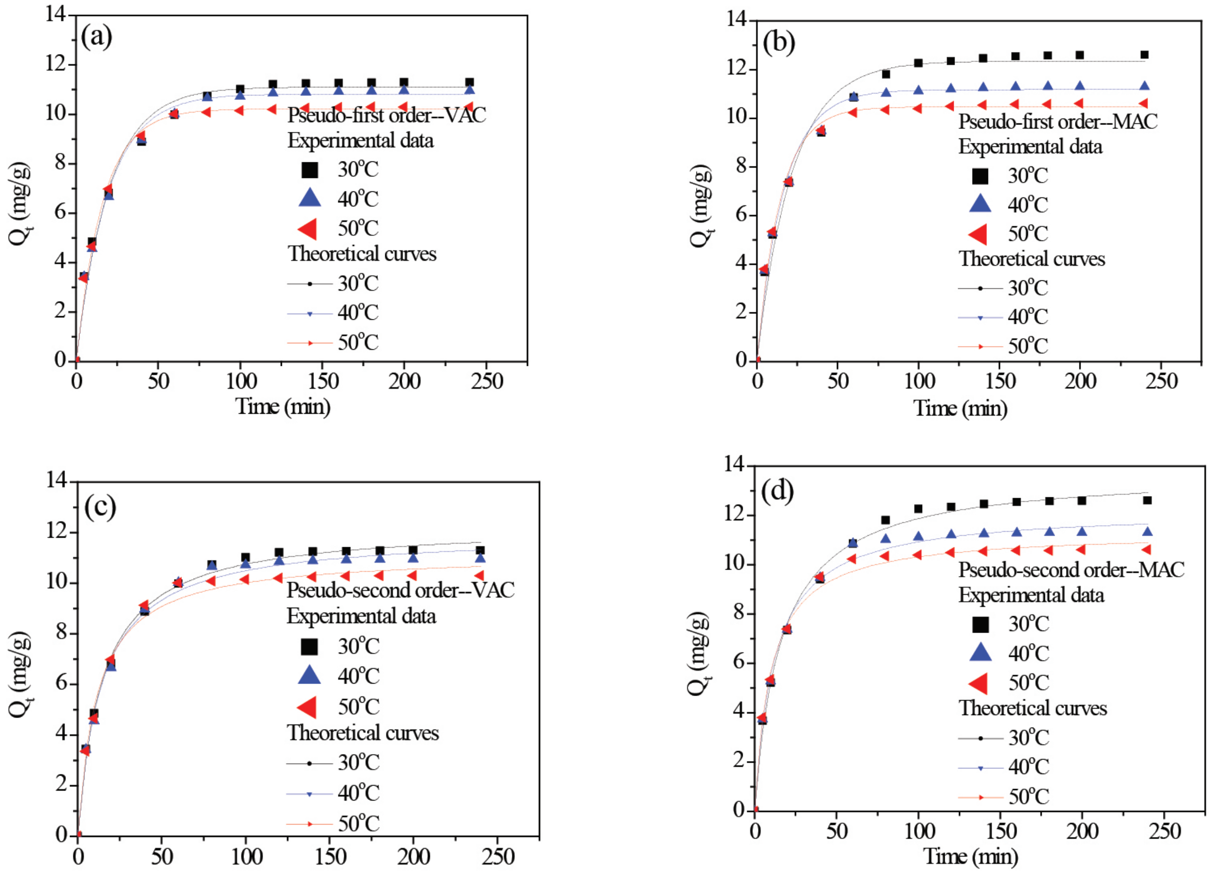

Fig. 4. Adsorption kinetic of 1 g/L methanol onto VAC and MAC at different temperatures and non-linear adjustments of (a) Pseudo-first order model to VAC; (b) Pseudo-first order model to MAC; (c) Pseudo-second order model to VAC; (d) Pseudo-second order model to MAC.

The parameters of the pseudo-first order and pseudo-second order models were determined using nonlinear regressive analysis. The experimental and fitting results are displayed in Fig. 4 and Table 4. It can be clearly seen that the adsorption took place quickly in first minutes, and then became slower and finally reached equilibrium. The high adsorption rate in the first step may be attributed to the presence of active sites, which can adsorb the methanol quickly, while the rate decreased as the active sites were gradually occupied. In addition, the adsorption rate increased with the increasing temperature, and the same results were found by Garcia et al. [30]. From Table 4, it is observed that the R^2 values gained for pseudo-first order model and pseudo-second order model ranged from 0.9667 to 0.9924, showing a general consistent trend with the experimental results. In addition, the R^2 values of pseudo-second order model were generally larger than pseudo-first order, which indicated that the pseudo-second order model was more suitable to describe the adsorption kinetics of methanol onto activated carbon.

3.3.3. Adsorption thermodynamic

The thermodynamic parameters regarding methanol adsorption onto activated carbon were determined using the experimental data obtained at 30°C, 40°C and 50°C. The changes in the standard Gibbs free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) were determined using the variation of solute distribution coefficient between the solid and liquid phases at equilibrium (k_d), using the following equations:

$$k_d = \frac{q_e}{C_e} \tag{6}$$

$$\Delta G^0 = -RT\ln\left(k_d\right) \tag{7}$$

$$\ln\left(k_d\right) = -\frac{\Delta G^0}{RT} = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{8}$$

where R is the universal gas constant (8.314 J/mol/K) and T is the absolute temperature of the system (K). The values of ΔH^0 and ΔS^0 were calculated from the slope and intercept of van't Hoff plots of ln(k_d) vs. 1/T in Fig. 5, respectively. The thermodynamic parameters are listed in Table 5. The ΔG^0 values were positive, reflecting the non-spontaneous nature of the adsorption processes at the range of temperature studied. The negative ΔH^0 confirmed the exothermic nature of the adsorption process, which further demonstrated that the adsorption was improved

Table 5
Thermodynamic parameters for the adsorption of methanol on VAC and MAC at different temperature

Material	ΔG^0 (kJ/mol)			ΔH^0 (kJ/mol)	ΔS^0 (J/mol/K)
	30°C	40°C	50°C		
VAC	12.31	13.02	13.74	–9.22	–71.04
MAC	12.11	12.78	13.41	–7.56	–64.90

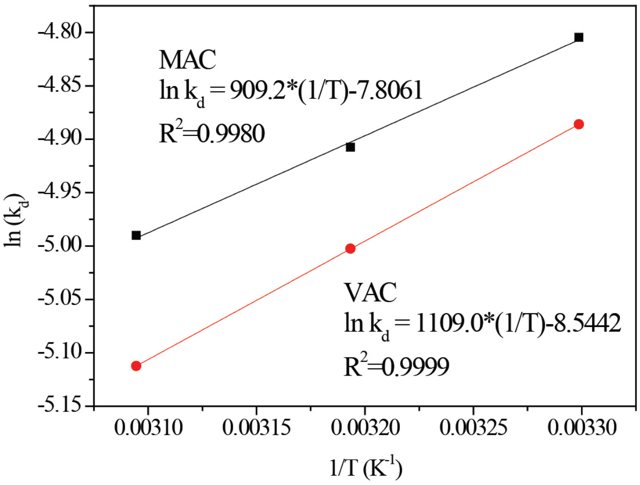

Fig. 5. Plot of ln k_d vs. $1/T$ for estimation of thermodynamic parameters for the adsorption of methanol onto VAC and MAC.

Table 4
Parameters of pseudo-first order, pseudo-second order at different temperature

	VAC			MAC		
Temperature	30°C	40°C	50°C	30°C	40°C	50°C
Experimental q_e	11.32	10.80	10.20	12.59	11.19	10.51
Pseudo-first order						
q_{e1}	11.11	10.83	10.22	12.35	11.17	10.47
k_1	0.0496	0.0511	0.0615	0.0454	0.0593	0.0694
R^2	0.9715	0.9811	0.9908	0.9667	0.9802	0.9837
Pseudo-second order						
q_{e2}	12.32	11.98	11.17	13.79	12.23	11.35
k_2	0.00553	0.00587	0.00777	0.00448	0.00686	0.00886
R^2	0.9924	0.9868	0.9790	0.9917	0.9861	0.9857

at lower temperature. The negative ΔS^0 suggested decreasing randomness at the solid/solution interface during the adsorption process. In addition, the values of ΔH^0 (< 20 kJ/mol) indicated that the adsorption was likely to be dominated by physical processes involving weak forces of attraction [31].

3.4. Column adsorption

In order to further understand the basics of adsorption for commercial applications, adsorption experiments on a fixed bed column were carried out to obtain the breakthrough curves. The wastewater was pumped from the bottom to the top through the column by a peristaltic pump, assuring sufficient contact of wastewater with adsorbent particles. The amount of adsorbate adsorbed by the adsorbent changes with time, causing the change of adsorbate concentration at the outlet. Breakthrough curve, i.e., the trend of adsorbate concentration at the outlet with time, is closely related to temperature and wastewater flow rate.

As shown in Fig. 6a, the adsorbate concentration at the outlet reached the breakthrough point in less time when the temperature reached up to 50ºC. The results can be explained by the related adsorption thermodynamic data. As temperature increased, the thermal motion of molecules increased, leading to the increase in systematic randomness, which went against this adsorption process ($\Delta S^0 < 0$). On the other hand, the desorption of adsorbate from activated carbon was improved at higher temperature. In addition, the effect of wastewater flow rate on breakthrough curve was examined at the temperature of 30ºC, with the results shown in Fig. 6b. At a higher flow rate, the adsorption capacity was lower due to insufficient residence time of the solute in the column and inadequate diffusion of the solute into the pores of the adsorbent. Overall, lower temperature and lower flow rate will lead to prolonged breakthrough time and saturation time.

Successful design of a column adsorption process requires prediction of breakthrough curve for the effluent. The Thomas model is a widely used model to predict adsorption in a column system at a constant flow rate and no axial dispersion. The model behavior assumes second-order reversible adsorption kinetics and the Langmuir isotherm [32]. The model is in the following basic form:

$$\frac{c}{c_0} = \frac{1}{1+\exp\left(K_T q_F \frac{m}{Q} - K_T c_0 t\right)} \tag{9}$$

where q_F is the adsorptive capacity (mg/g), K_T is the rate constant (L/g/min), Q is wastewater flow rate (L/min), C_0 is the initial concentration (g/L) of adsorbate pumped into column, t is time (min), and m is mass of the carbon bed (g).

In this paper, the experimental results of MAC were evaluated based on the Thomas model using the non-linear regression method. The fitting results are summarized in Table 6. According to the R^2 values and the fitting curves in Fig. 6, we can conclude that the model curves fit well with the experimental data. Furthermore, as temperature increased, both K_T and q_F decreased. However, as flow rate increased, K_T increased, while q_F decreased.

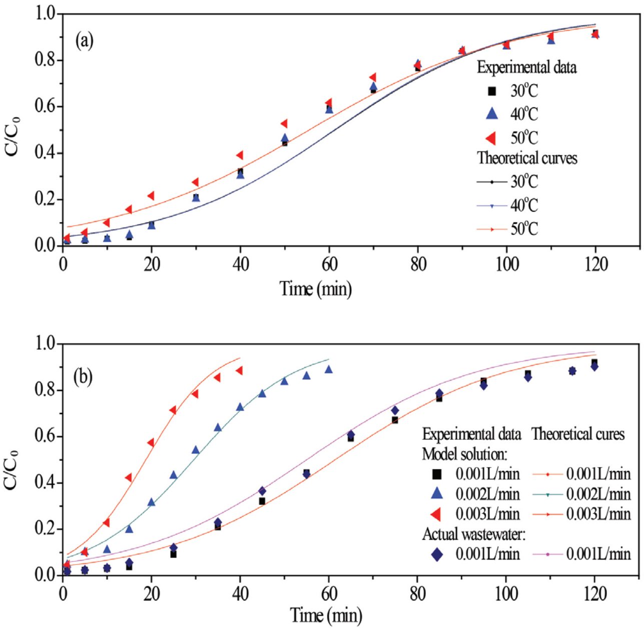

Fig. 6. Adsorption onto MAC: (a) Breakthrough curves of model solution with 0.001 L/min for flow rate at different temperatures; (b) Breakthrough curves of model solution and actual wastewater at 30°C for temperature with different flow rates.

Table 6
Parameters of Thomas model for column adsorption of methanol onto MAC

T (ºC)	C_0 (g/L)	Q (L/min)	K_T (L/g/min)	q_F (mg/g)	R^2
30	1	0.001	0.0513	3.07	0.9895
30	1	0.002	0.0866	2.96	0.9905
30	1	0.003	0.1294	2.81	0.9830
40	1	0.001	0.0509	3.06	0.9899
50	1	0.001	0.0444	2.77	0.9933
30	Actual	0.001	0.0519	2.75	0.9827

3.5. Adsorption of actual wastewater

In order to determine the potential application of this wastewater treatment method in industry, the column adsorption performance of actual wastewater that mainly contains methanol, ethyl alcohol, epoxy propane was also provided in Fig. 6b. GC results after adsorption in Fig. 7 showed that only methanol was detected, which indicated that ethyl alcohol and epoxy propane were completely adsorbed by activated carbon. As for the breakthrough curve of wastewater, it showed similar trend with the experimental and fitted results when using methanol solution to simulate the actual wastewater. It certified the feasibility of choosing methanol as the model compound

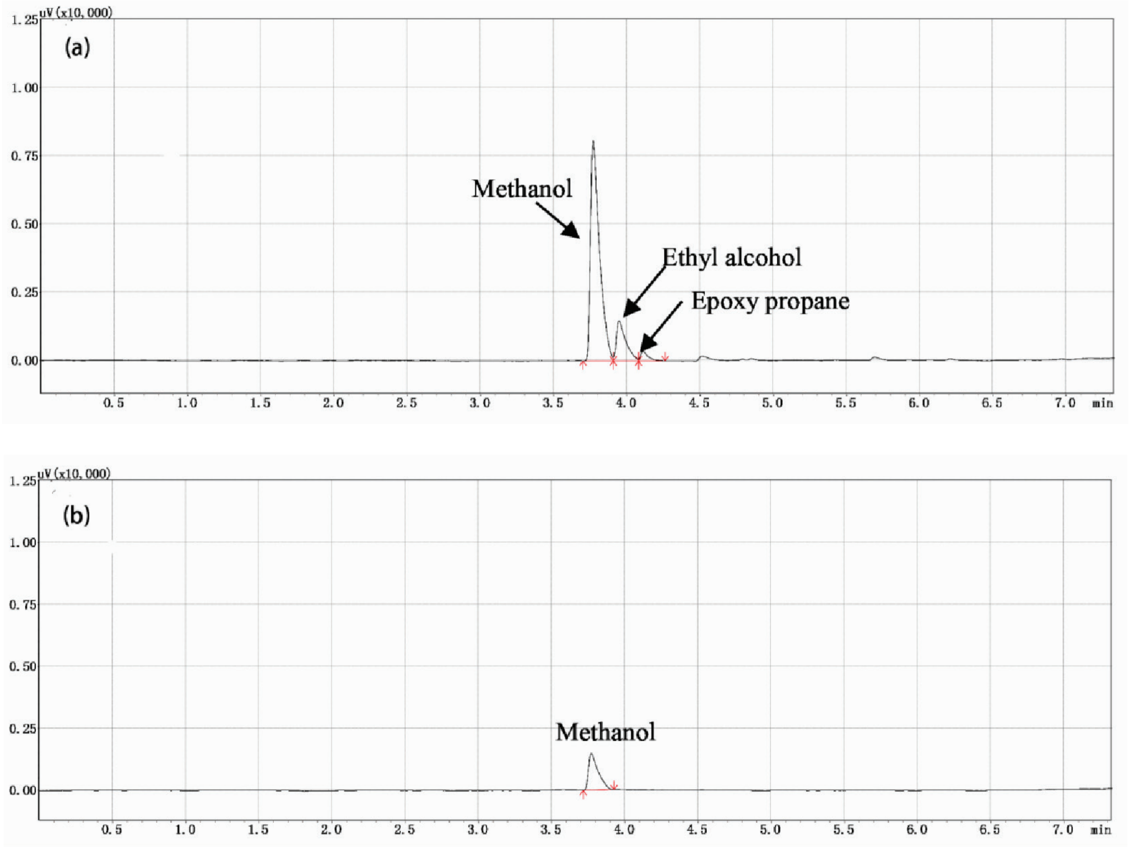

Fig. 7. GC profiles of actual wastewater (a) before and (b) after column adsorption.

in this study. In addition, a little offset of the breakthrough curve of actual wastewater was observed compared with that of simulated wastewater, which was mainly due to the competitive adsorption of other compounds in actual wastewater. This phenomenon can be also confirmed by q_F value of actual wastewater in Table 6, which was lower than that of model solution. Moreover, as essential index of emission standard, COD was determined when 40 mL wastewater was treated. The result showed that the COD value was significantly reduced from 2500 mg/L to 295 mg/L. Therefore, in this paper, breakthrough point was defined as the time when COD value of actual wastewater reached 300 mg/L after column treatment. Generally, the volume was about 40 mL. In addition, regeneration experiments shown in Fig. 8 revealed that little change in adsorption performance of activated carbon was observed after it was reused for several times, which indicated the feasibility of this treatment using activated carbon as an adsorbent. Overall, the experimental results can be used as guidance for actual wastewater treatment. The operating parameters of the activated carbon adsorption can be adjusted to meet various wastewater discharge standards.

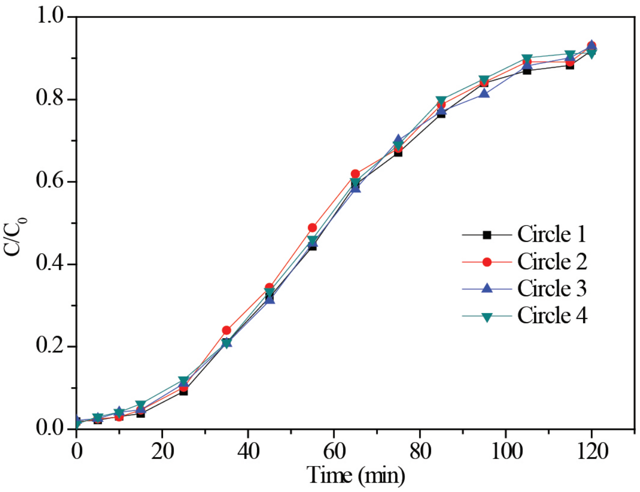

Fig. 8. Regeneration experimental results of actual wastewater adsorption onto MAC.

4. Conclusions

In this study, activated carbon adsorption method was used for the treatment of light part of EFAME wastewater after distillation. The adsorption behavior of methanol as the model compound to the actual wastewater was investigated through batch and column experiments. For batch adsorption, fitting lines obtained using Langmuir isotherm and pseudo-second order kinetic models were in good agreement with the experimental results. Thermodynamic study indicated lower temperature was favorable to the adsorption behavior. For column adsorption, breakthrough curves of model wastewater were determined, which can be well described by the Thomas model. In addition, column experiment of actual wastewater showed that the COD was greatly reduced using the activated carbon adsorption. In a word, the method offered can be a guidance for epoxy plasticizer wastewater treatment.

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