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In-depth study of desorption kinetics in adsorption process

Ning Qiang[1], Tianzhe Shi[1], Yiqi Cao[1], Haichao Miu[1], and Tao Liu[1*]

[1]Departments of Environmental Science and Engineering, University of Tongji, Shanghai 200092, China

*Corresponding Author: Tao Liu   Email: liutao45@163.com

Abstract. In this paper, open-loop desorption experiments were carried out by hot gas sweeping. The effects of different concentrations of methylene chloride and temperatures in the sweeping gas on the desorption process were investigated from three perspectives: average desorption rate ($\overline{V_{30}}$, $\overline{V_9}$), instantaneous desorption rate (V_{max}) and desorption kinetics. It was concluded that the maximum instantaneous desorption rate could better represent the desorption rate required by the experiment at different sweeping concentrations and temperatures. The maximum instantaneous desorption rate V_{max} increased with the rising temperature and decreased with the increasing concentration of inlet methylene chloride. The concluded law was the same as the average desorption rate ($\overline{V_{30}}$) of 30 min. Thereinto, the temperature had a significant influence on V_{max}. As the temperature increased, the concentration of inlet methylene chloride also inhibited the maximum instantaneous desorption rate V_{max} more obviously. This provided important reference data for the optimization design of desorption equipment in the activated carbon adsorption process.

1. Introduction

With the development of the global economy and population growth, the energy crisis and environmental pollution have increasingly become the two most concerned focuses, and sustainable development has become the goal pursued by countries for economic development. In recent years, the phenomenon of haze has become more frequent, and VOCs, as a photochemical reaction and an important precursor of PM2.5, have become a hot issue in society [1, 2]. Air pollutants VOCs are mainly derived from the production process emissions of major industries. At present, the VOCs produced by many processes are characterized by high air volume, medium and low concentrations and mostly intermittent emissions. Direct emission without treatment will cause great environmental pollution [3].

Activated carbon adsorption-desorption process has been applied in many places to deal with the purification organic gases with high air volume and low concentration [4]. According to the literature review on the research progress of VOCs pollution control technology and related engineering experience, combined with the actual engineering process analysis, many studies are mainly on adsorption methods currently, aiming to improve the effect of adsorption systems [5-8]. The key to the application of adsorption method is the selection of adsorbent and the control of the adsorption and desorption conditions. Activated carbon is the most used adsorbent due to its large specific surface area and strong adsorption capacity, and the related research reports are also the most [9,10]. However, in actual application, activated carbon still has problems of flammability safety, secondary pollution to condensed water and low energy utilization efficiency in the desorption process [11]. Therefore, the research and improvement of these emerging processes will further improve the application of

activated carbon in the treatment of VOCs by adsorption, which is of great significance to the major industries that currently emit VOCs.

In this study, the fully adsorbed activated carbon was desorbed at different apparent wind speeds, to study the effect of apparent wind speed on the open-loop desorption process. Then, one apparent wind speed of desorption was selected to measure VOCs concentrations at the outlet of fully adsorbed activated carbon desorption under the conditions of sweeping gases with VOCs of different concentration and under different temperatures during open-loop desorption. The breakthrough curve was drawn, and the desorption rate was calculated. The effects of different concentrations of VOCs in sweeping gas and temperature on the desorption rate were studied from three perspectives of the average desorption rate, the maximum instantaneous desorption rate and desorption kinetics, which provides important reference data for the optimal design of desorption equipment in the adsorption method.

2. Open-loop desorption experiment system

The open-loop desorption experiment device is shown in Figure 1. The open-loop desorption experiment system was basically the same as the dynamic adsorption experiment system, mainly composed of a gas distribution system and a desorption system. Ambient air was used as the gas source in the experiment, and after being dried by the silica gel (relative humidity RH≤5%), it served as the blank experimental gas to desorb the adsorption unit.
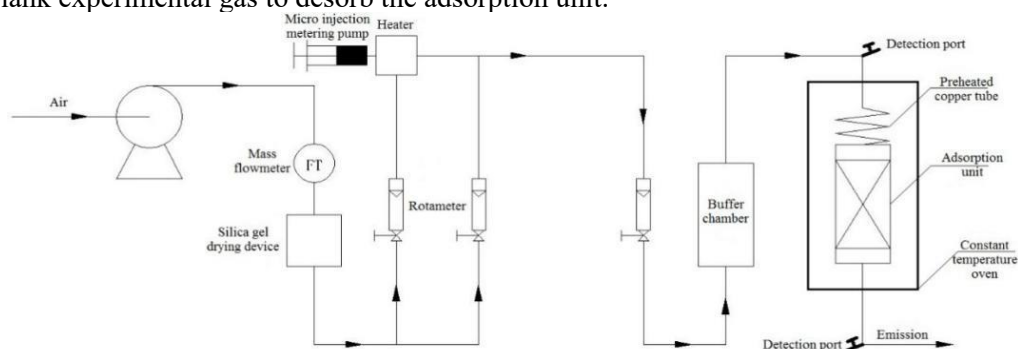

Figure 1. Schematic diagram of the open circuit desorption experiment system

The gas distribution system was divided into: a blower (Haley, ACO-9730), a silica gel dryer, a set of micro injection metering pump (LongerPump, LSP01-2A), a heater and a mixing buffer chamber of 2L. The dried air was divided into two lines, which were adjusted by a rotameter and accurately quantified by a mass flow meter (TSI, 4000Series). The two lines of gases were mixed in the mixing buffer chamber and entered the adsorption system with set dichloromethane concentration and flow rate.

The adsorption system consisted of a gas preheating pipeline and a glass-tube adsorption column. The adsorption column was a glass column with an inner diameter of 37 mm and a length of about 110 mm, with a filling height of 100 mm and a quartz sand cushion at the bottom of the adsorption column. The gas preheating pipeline was a copper coil. The adsorption system was placed in a constant temperature oven, and the temperature of the gas flow was controlled by the copper coil to reach the experimental temperature (±0.5 ° C). Detection points were set before and after the adsorption system to detect the concentration and temperature of the experimental object in the gas pipeline.

3. Open-loop batch desorption curve analysis

In the open-loop desorption batch experiment, four concentrations (0 g/m³, 4.0 g/m³, 8.0 g/m³, 50.0 g/m³) at five temperatures (60 °C, 90 °C, 110 °C, 130 °C, 150°C) were selected to carry out desorption experiments. The measured desorption curves are shown in Figure 2.

In all batch desorption curves, starting from the first sampling point at 1 min after the start of desorption, the concentration of outlet methylene chloride was already significantly higher than the set inlet concentration. Then the outlet concentration gradually rose to the peak value with time and

gradually declined with time to near the inlet concentration to stabilize finally, and a relatively complete desorption curve was obtained. When the experimental temperature increased to 150 °C, because of the fast desorption rate, some curves directly appear a peak point at the first sampling point at 1 min, so it could only represent the peak concentration.
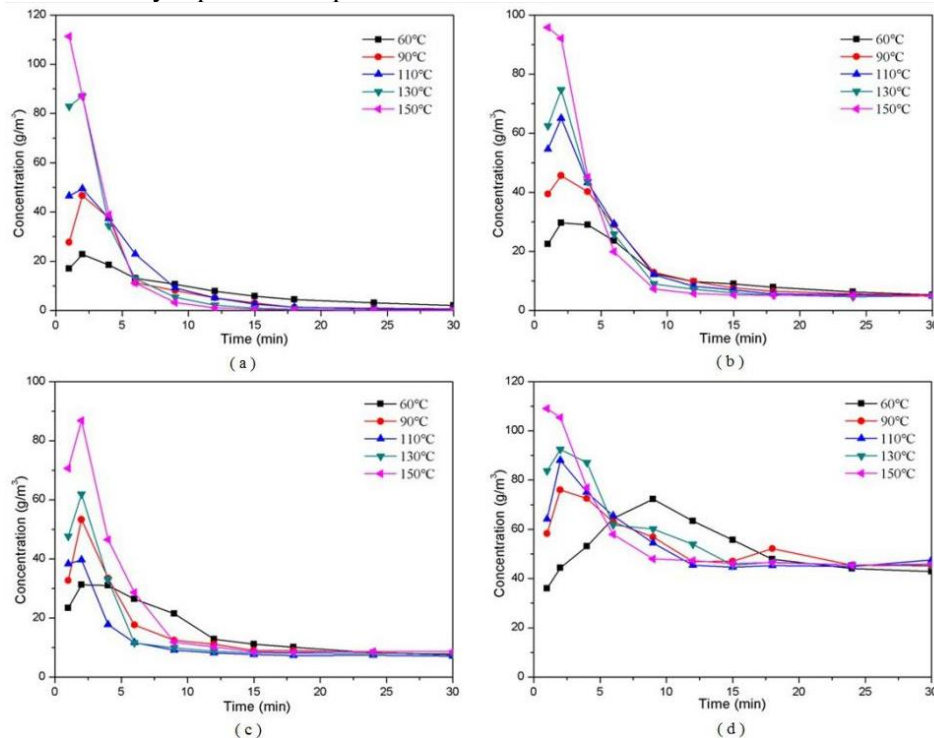

Figure 2. Open-loop batch desorption curve analysis
(a, b, c, and d are the desorption curves measured when the concentration of inlet methylene chloride is 0 g/m³, 4.0 g/m³, 8.0 g/m³, and 50.0 g/m³, respectively)

Under the same concentration of inlet methylene chloride, the time of desorption peak appeared to a decreasing tendency with the increase of temperature, and the peak concentration of dichloromethane tended to ascend. In terms of the desorption process, when the temperature was 60 ° C and 90 ° C, the outlet concentration of methylene chloride had dropped to the inlet concentration in about 20 min, and the desorption process was basically finished. When the temperature was 110 °C, 130 °C and 150 °C, the desorption process basically ended at 10-15 min. This could also preliminarily verify that the desorption rate increased when the temperature rose.

At the same desorption temperature, as the concentration of inlet methylene chloride increased, the peak time of desorption had no obvious increase or decrease, and there was no significant increase in the peak concentration of methylene chloride at 0 g/m³, 4.0 g/m³, and 8.0 g/m³. Only when the inlet concentration was greatly increased to 50.0 g/m³, the peak concentration showed a significant increase. From the view of the desorption process, with the increase of the concentration of inlet methylene chloride, the time for desorption to stabilize tended to accelerate. On the one hand, it is necessary to consider the influence of the change of the desorption rate, while on the other hand, the variation of the desorption equilibrium caused by the concentration change should be considered. Therefore, the specific influence of this aspect needs to be calculated and further analyzed from the perspective of the average desorption rate.

4. Dynamics analysis of open-loop desorption batches

4.1. Analysis of average desorption rate of open-loop desorption batches
The desorption weight loss was weighed after all the batch experiments, and the average desorption

rate $\overline{V_{30}}$(g/(g·m²·min)) per unit area of the activated carbon per unit mass in 30 min under different working conditions was calculated. Similarly, according to the batch desorption curves measured in the experiments, the average desorption rate $\overline{V_9}$ per unit area of the activated carbon per unit mass in 10 min was calculated by taking 9 min as the node. Then, taking time as the abscissa and desorption rate as the ordinate, Figure 3 was obtained.
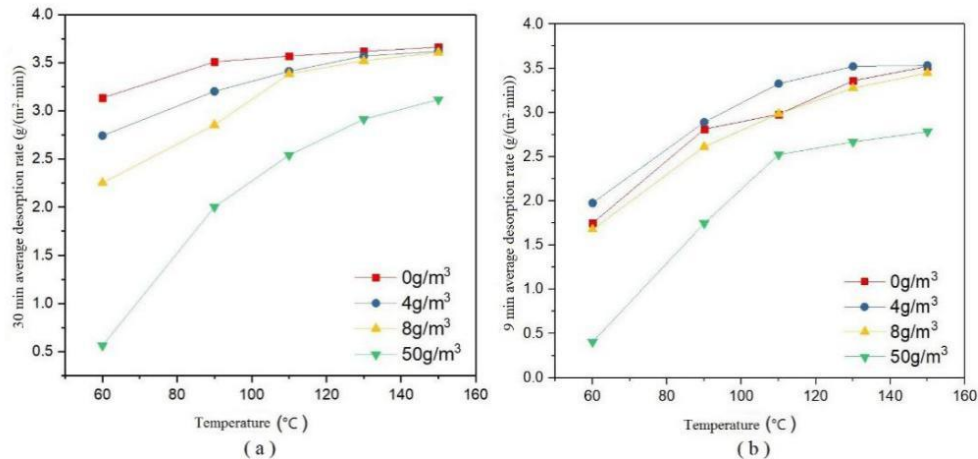

Figure 3. Average desorption rate at different temperatures and inlet concentrations

It can be concluded from Figure 3 that both the temperature and the concentration of methylene chloride have a significant effect on the desorption rate. At the same temperature, as the concentration of the inlet methylene chloride increases, the desorption rate $\overline{V_{30}}$ gradually decreases; at the same inlet concentration, with the increase of temperature, the desorption rate $\overline{V_{30}}$ gradually ascends. The experimental conditions were divided into medium temperature (60 °C - 110 °C) and high temperature (110 °C - 150 °C) at a cutoff point of 110 °C. During the temperature rise in the medium temperature range, the desorption rate increases rapidly and is also greatly affected by the inlet concentration. As can be seen, $\overline{V_{30}}$ has significant differences between the four concentrations. In the high temperature range, as the temperature increases, the desorption rate changes tend to flatten out. When the concentration of inlet methylene chloride is less than 8 g/m³, the three curves gradually overlap, indicating that the effect of the concentration of methylene chloride on the desorption rate ($\overline{V_{30}}$) of activated carbon in this range is reduced. Only when the concentration of methylene chloride is greatly increased to 50 g/m³, the desorption rate is greatly reduced.

Comparing Figure 3(a) with Figure 3(b), it could be concluded that the variation of $\overline{V_9}$ was more obvious with the change of temperature than that of $\overline{V_{30}}$, that is, with the increase of temperature in the middle temperature range, the desorption rate also increased rapidly; In the high temperature range, as the temperature increased, the desorption rate chang tended to be gentle. There was a certain difference between the variation law of $\overline{V_9}$ with the concentration of methylene chloride and that of $\overline{V_{30}}$. At the same temperature, with the concentration increase of methylene chloride, $\overline{V_9}$ showed a certain decrease, while under different temperature conditions, the declining tendencies of $\overline{V_9}$ with the concentration increase of methylene chloride were basically the same, and the variation tendencies of the four curves were basically the same. Here, a conclusion different from $\overline{V_{30}}$ was obtained that under different temperature conditions, the inhibition of the desorption rates ($\overline{V_9}$) of activated carbon by the methylene chloride concentration were basically the same. In addition, with the increase of the concentration of methylene chloride, $\overline{V_{30}}$ showed a continuous decline, while $\overline{V_9}$ increased first and then decreased, reaching a maximum value at 4 g/m³.

Combined with the batch desorption curves in Figure 2, it can be seen that the outlet concentration is basically stabilized at the inlet concentration value at the end of desorption after 20-30 min, indicating that the desorption has reached equilibrium, so the results of $\overline{V_{30}}$ were more affected by the desorption equilibrium. Combined with the adsorption isothermal analysis of methylene chloride on activated carbon, the effect of methylene chloride on the capacity of activated carbon in the desorption

equilibrium is higher in the high temperature range. Therefore, when $\overline{V_{30}}$ represented the desorption rate, the desorption rate $\overline{V_{30}}$ of activated carbon at medium temperature was large inhibited by methylene chloride, while the desorption rate $\overline{V_{30}}$ of activated carbon at high temperature was less inhibited by methylene chloride.

In summary, $\overline{V_{30}}$ mainly reflected the average desorption rate in the desorption process from the perspective of desorption equilibrium, and $\overline{V_9}$ was more representative of the desorption rate in the early stage of the desorption process when the driving force was large.

4.2. Instantaneous rate analysis of open-loop desorption batches
The outlet concentration curves of open-loop batch desorption were integrated to obtain the curves of the weight loss of activated carbon with time in the desorption process. The curves of all the batches were summarized by taking the time as the abscissa and the weight loss of the activated carbon as the ordinate, shown as Figure 4.

According to the curves in Figure 4, the slopes of the curves become substantially flat after 9 minutes, and the rate of desorption rapidly decreases. Therefore, comparing the average desorption rate and the instantaneous desorption rate in Figures 3 and 5, the instantaneous desorption rate was much larger than the average desorption rate, which could obviously represent the desorption rate under different temperatures and different concentrations of inlet methylene chloride expected in this experimental study.
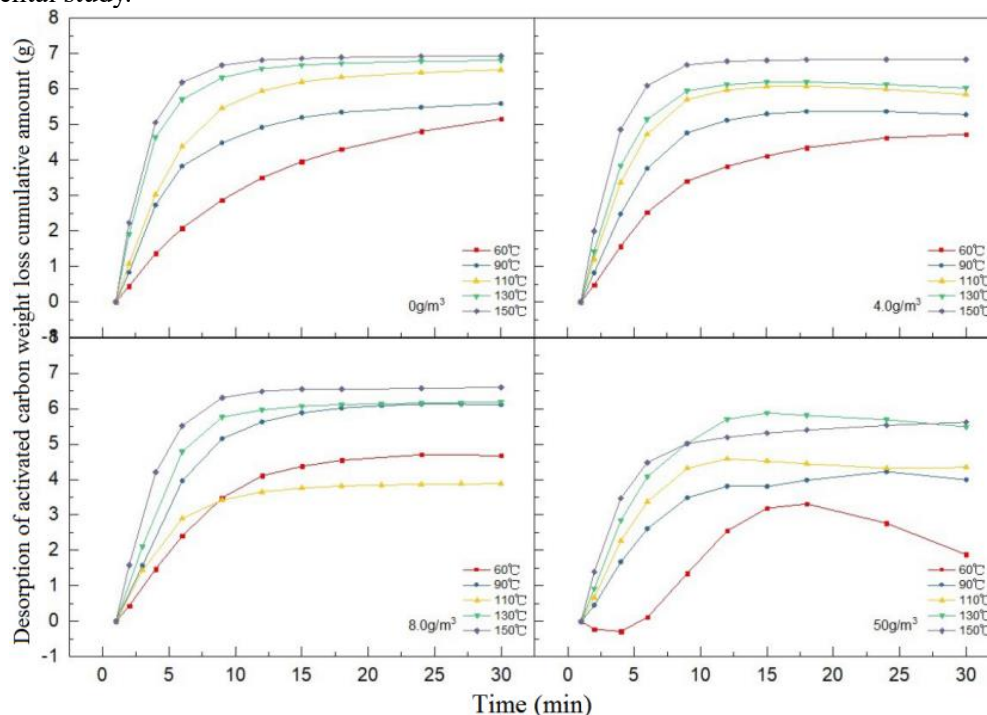

Figure 4. The cumulative amount of de-weight loss for each working condition

The tangent slopes of all the curves of each batch were calculated for the first three sampling points in Figure 4, and the instantaneous desorption rates (g/min) under various working conditions of different conditions and different temperatures were obtained. The maximum instantaneous desorption rate of each working condition was taken to calculate the desorption rate V_{max} $g/(g \cdot m^2 \cdot min)$ per unit area of the corresponding activated carbon per unit mass, Figure 5 was plotted with V_{max} as the ordinate and desorption temperature as the abscissa.

It can be seen from Figure 5 that, in terms of the overall trend, the maximum instantaneous desorption rate increased with the increase of temperature and declined with the increase of the concentration of inlet methylene chloride, wherein the temperature had a significant effect on V_{max}. At 60 °C, under the inlet gas concentrations of 0 g/m³, 4.0 g/m³, 8.0 g/m³ and 50 g/m³, V_{max} were

0.0454, 0.513, 0.493, and 0.406 (g/min), respectively, with not much differences in the range of 0.04-0.05 (g/min). At 90 °C, V_{max} showed a significant reduction with the increase of the concentration of inlet methylene chloride, and when the inlet concentration range is < 8.0mg/m³, the V_{max} under the three working conditions had less reduction; While at the operating point of 50 g/m³, V_{max} showed a significant decrease, which was only 68.2% of that at 8 g/m³. At 110 °C, combined with the desorption outlet concentration curves in Figure 5-3, the V_{max} were relatively small at 0 and 8 g/m³, probably because the sampling point missed the desorption outlet concentration peak. At this temperature, V_{max} at 8.0 g/m³ and 50 g/m³ were significantly less than that at 0 and 4.0 g/m³. At high temperature of 130 ° C and 150 ° C, the V_{max} at each concentration has been greatly improved compared with those under the previous medium and low temperature conditions, and with the increase of the inlet concentration, V_{max} decreased significantly. Thereinto, under the working condition of 50g/m³, V_{max} was only 62.7% of that at 0 g/m³.
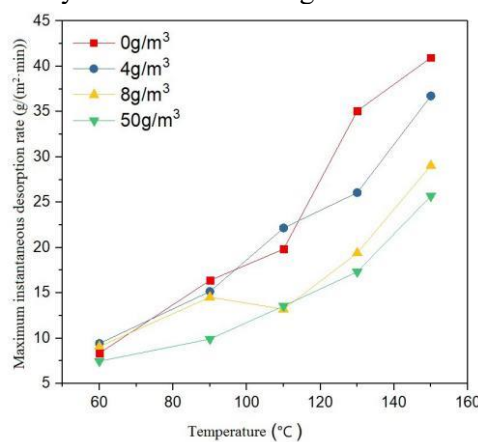

Figure 5. Maximum instantaneous desorption rate per unit area of mass activated carbon per working condition V_{max}

4.3 Dynamics analysis of open-loop desorption batches

In this paper, the linear driving force (LDF) model was used to calculate the desorption kinetics, and the gas desorption kinetic equation under dynamic desorption was derived and obtained:

$$\ln(q - q_*) = -kt + \ln(q_0 - q_*) \tag{1}$$

The experimentally measured data (c_i, t_i) was integrated to obtain (q_i, t_i). $\ln(q_i - q_*)$ was plotted against t, and the desorption rate constant k of the experiment was obtained by linear fitting according to Equation (1). The linear fitting curves of different temperature conditions under four concentrations were plotted on four graphs, as shown in Figure 6(a), (b) and (c), corresponding to 0 g/m³ and 4.0 g/m³, 8.0 g/m³, respectively. The obtained desorption rate constant k and the correlation coefficient R^2 are shown in Table 1.

Combined with Figure 6 and Table 1, the fitting linearity of the desorption kinetic equation obtained by LDF in this experiment was good, and R^2 was basically above 0.95. Overall, the linear correlation of the fitting at 60 °C-110 °C at medium temperature was better. When the sweeping concentration of methylene chloride was 0, that is the commonly understood hot-air open-loop desorption process, the desorption kinetic constant k of the experiment grew up with the increase of temperature, and the range of k varied from 0.11355 to 0.27148. The same increasing trend was also observed at 4 g/m³ and 8 g/m³. Comparing the k of different concentrations at the same temperature, it could be obtained from the table that when the concentration of inlet methylene chloride was 4 g/m³, k was the largest; the value of k climbed first and then decreased with the increase of the concentration of the sweeping methylene dichloride, which was the same as the variation law of $\overline{V_9}$ with the concentration change of methylene dichloride.
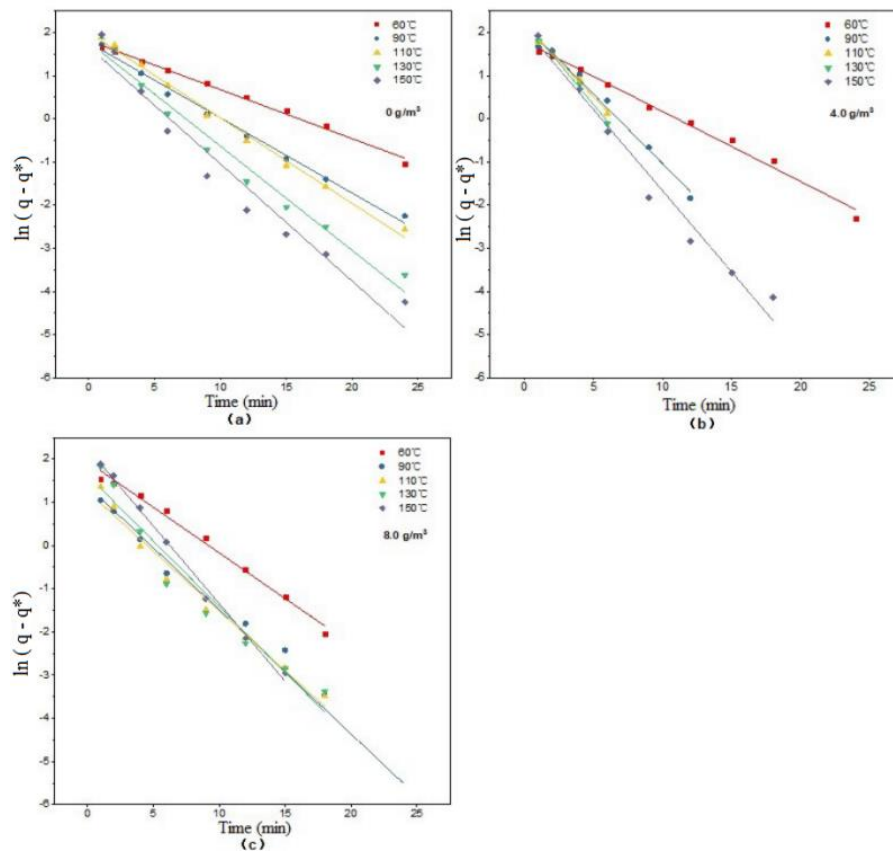
Figure 6. kinetic equation fitting of open-loop desorption batches

Table 1. Kinetic equation fitting parameters of open-loop desorption batches

Temperature	Dichloromethane inlet concentration g/m³					
	0		4		8	
	k	R^2	k	R^2	k	R^2
60°C	0.11355	0.9935	0.1623	0.9919	0.21128	0.9902
90°C	0.17436	0.9926	0.32155	0.9876	0.28753	0.979
110°C	0.19753	0.9945	0.33104	0.9916	0.27677	0.97691
130°C	0.24155	0.9759	0.38621	0.9924	0.30451	0.94774
150°C	0.27148	0.95678	0.37595	0.97759	0.35939	0.9936

5. Conclusions

Open-loop batch desorption experiments were analyzed from three perspectives of average desorption rate, desorption rate kinetics and maximum instantaneous desorption rate. It was concluded that the maximum instantaneous desorption rate could better represent the desorption rate required by the experiment at different sweeping concentrations and temperatures. The maximum instantaneous desorption rate V_{max} increased with the rising temperature and decreased with the increasing concentration of inlet methylene chloride. The concluded law was the same as the average desorption rate $(\overline{V_{30}})$ of 30 min. Thereinto, the temperature had a significant influence on V_{max}. As the temperature increased, the concentration of inlet methylene chloride also inhibited the maximum instantaneous desorption rate V_{max} more obviously. This provided important reference data for the

optimization design of desorption equipment in the activated carbon adsorption process. At 60 °C, under the inlet gas concentrations of 0 g/m³, 4.0 g/m³, 8.0 g/m³ and 50 g/m³, V_{max} were 0.0454, 0.513, 0.493, and 0.406 (g/min), respectively, with not much differences in the range of 0.04-0.05 (g/min). As the temperature increased, the concentration of inlet methylene chloride inhibited the maximum instantaneous desorption rate V_{max} more obviously. Among them, under the working condition of 50g/m³, V_{max} was only 62.7% of that at 0 g/m³.

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Acknowledgements

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