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New Activated Carbon with High Thermal Conductivity and Its Microwave Regeneration Performance

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Abstract: Using a walnut shell as a carbon source and $ZnCl_2$ as an activating agent, we resolved the temperature gradient problems of activated carbon in the microwave desorption process. An appropriate amount of silicon carbide was added to prepare the composite activated carbon with high thermal conductivity while developing VOC adsorption-microwave regeneration technology. The experimental results show that the coefficient of thermal conductivity of SiC-AC is three times as much as those of AC and SY-6. When microwave power was 480 W in its microwave desorption , the temperature of the bed thermal desorption was 10 ℃ to 30 ℃ below that of normal activated carbon prepared in our laboratory. The toluene desorption activation energy was 16.05 $kJ \cdot mol^{-1}$, which was 15% less than the desorption activation energy of commercial activated carbon. This study testified that the process could maintain its high adsorption and regeneration desorption performances.

Key words: activated carbon with high thermal conductivity; activation energy for desorption; VOCs; microwave radiation

1 Introduction

Activated carbon has a porous structure and a high specific surface area, which develops benefits such as fast adsorption with a high capacity, good stability and mechanical strength, low preparation cost, as well as simple and recyclable preparation process . It is widely used in decoloration processing, purification reagents producing, solvent recovery, and elimination of pollutants, *etc*. For the disposal of volatile organic gas has recently become a worldwide problem and the demand for activated carbon is increasing by years, it is currently the most widely used adsorbent material in the world[1-3].

If the used activated carbon is not renewable in time, it will cause serious waste and subseqent pollution. The key factor in activated carbon adsorption technology is whether the activated carbon can be efficiently regenerated and reused for multiple times, which determines the efficiency and economy of the whole process of adsorption. However, conventional activated carbon adsorption technology has a few disadvantages-low regeneration efficiency and high regeneration cost; for example, the traditional Thermal Regeneration method is of serious time and energy consuming, as well as severe damage to the activated carbon structure[2,3]. Microwave, having characteristics of unique heating method and rapid selective heating with no need for certain media, is holding a bright future in enhanced desorption and regeneration of adsorbents, *eg*, activated carbon[4-7].

However, activated carbon has a low volume density and a poor thermal conductivity-with a thermal conductivity coefficient of about 0.17 $W \cdot m^{-1} \cdot K^{-1}$ to 0.28 $W \cdot m^{-1} \cdot K^{-1}$, even lower than that of ordinary refractory brick, which is generally recognized as a non-conductive material[5]. Because the adsorption process is an exothermic process in terms of thermodynamics, a low temperature condition is in favor of adsorption process. In large industrial adsorption bed, the amount of adsorption heat generated by activated carbon adsorption will not only affect the adsorption efficiency, but also lead to overheating caused by excessive accumulation of heat. Therefore, the temperature became an important factor affecting the effects of adsorption[7]. As for the desorption regeneration, the poor thermal conductivity

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of activated carbon usually causes the following problems in large-scale thermal regeneration processes: low thermal conductivity process, slow heat transfer, low energy efficiency, *etc*, thus laying down a safety loophole.

Therefore, developing a new type of activated carbon with high thermal conductivity is in the urgent need to overcome the negative effects caused by the temperature gradient.

Adopting walnut shell powder as the carbon source together with silicon carbide (the thermal conductivity coefficient is 83.6 $W \cdot m^{-1} \cdot K^{-1}$), a composite activated carbon with high thermal conductivity coefficient was prepared. On the premise of guaranteeing the adsorptive performance of activated carbon as much as possible, the heat conduction was improved to ameliorate that of activated carbon in microwave field , so as to reduce or eliminate the negative factors of temperature gradient. Subsequently, typical toluene adsorption was adopted as the adsorbate to observe its adsorptive property and microwave regeneration performance. In this paper, the research work might significantly promote the large-scale industrial application of microwave desorption and regeneration.

2 Experimental

2.1 Preparation of the activated carbon with high thermal conductivity

Weighed a certain amount of walnut shell powder with a size ≤80 mesh after crushing, grinding, cleaning, washing, and screening of the walnut shells. Then mixed in proportion with a 0.3 $g \cdot mL^{-1}$ $ZnCl_2$ solution fully and evenly , added a certain amount of silicon carbide (400 mesh) and placed the mixture in the ultrasonic instrument for 30 min so that the silicon carbide can be better dispersed in the walnut shell powder. Put the mixture in a water bath with a temperature of 80 ℃ and stirred for 3 h.

Place the mixture in a vacuum drying oven with a temperature of 110 ℃ for 12 h when the reaction was finished. Ground the dried prepared materials and silicon carbide powder to evenly mixed materials, feed them into a heat-resisting quartz tube, and placed it in a tubular furnace. The temperature program was set to increase from room temperature up to 400 ℃ to 750 ℃ at a rate of 4 $℃ \cdot min^{-1}$ and maintained for 4 h to 8 h. Nitrogen was introduced into the system throughout the whole procedure (the flow rate was maintained at 80 $mL \cdot min^{-1}$ to 100 $mL \cdot min^{-1}$) until the tubular furnace heating was completed and cooled to room temperature. The sample was removed after cooling to room temperature, washed with distilled water to neutral pH value. It was then placed into the drying oven with a temperature of 110 ℃ for 12 h to finally obtain the composite activated carbon with high thermal conductivity. The composite activated carbon with high thermal conductivity was marked as SiC-AC. The self-prepared activated carbon under the same conditions without silicon carbide was marked as AC, whereas the commercial carbon was marked as SY-6.

2.2 Testing of the thermal performance

A Hot Disk (TPS2000) thermal constants analyzer produced by the Swedish Company. Hot Disk AB was employed to test the thermal conductivity of the composite activated carbon with high thermal conductivity.

2.3 Comparison of area and pore size distribution

An ASAP2010M analyzer produced by American Micrometrics Company was utilized to determine the surface features of the specific surface area and pore structure of the activated carbon. The physical adsorption system was employed to measure the said factors.

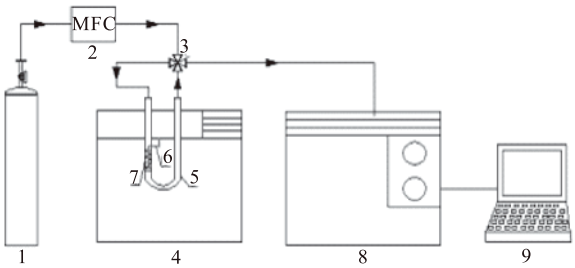
2.4 Boehm titration of surface acid-base functional group of the activated carbon

Boehm titration is a qualitative and quantitative analysis method based on the reactivity of acid and alkaline surface oxide of different intensities. This method is currently the easiest and most commonly used one for porous carbon surface chemistry analysis. Boehm titration can better distinguish the quantity of strong acid, moderately-strong acid, weak acid, and basic group on the activated carbon surface[8].

2.5 Measurement of adsorption isotherm

An IGA-003 intelligent gravimetric analyzer was utilized to measure the adsorption-desorption isotherm of methylbenzene on the different activated carbon samples.

2.6 Flow diagram of the microwave desorption experiment



(1) N_2; (2) Mass flow controller; (3) Four-channel valve; (4) Microwave oven (Mars5 microwave accelerating reactor Made by CEM Corp. USA); (5) Adsorption tube; (6) Thermoscope; (7) Adsorbent; (8) Gas chromatography; (9) Chromatography working station

Fig.1 Schematic diagram of the experimental setup

When the microwave desorption was performed, 0.05 g of the activated carbon samples saturated with methylbenzene was placed into the desorption column

(inner diameter of 0.5 cm) exclusively for the use of microwave energy. While microwave radiation was processing, nitrogen was utilized as the carrier gas with a flow rate of 30 mL·min^{-1}. Methylbenzene molecules were desorbed from the activated carbon samples in a certain time, and washed by carrier gas to a hydrogen flame ionization detector in gas chromatograph for measurement. Optical temperature measuring equipment in the microwave reactor was used to measure how the temperature of the carbon bed varied with time in this experiment. The device for the microwave desorption experiment is shown in Fig.1[9,10].

3 Results and discussion

3.1 Structural characteristics of the microwave-adapting composite activated carbon

Tables 1 and 2 show how the amount of silicon carbon influenced the coefficient of thermal conductivity of activated carbon. The result shows that if the amount of silicon carbon is 40%, the coefficient of thermal conductivity of SiC-AC is seven times larger than that of AC and approximately eight times larger than that of SY-6. Considering the adsorptive property of high thermal activated carbon, we finally determined the amount of silicon carbon to be 20% (SiC-AC-20).

Table 1 Influence of the silicon carbon amount on the thermal conductivity coefficient

Sample	AC	SiC-AC			SY-6
		SiC/wt%			
κ/(W·m^{-1}·K^{-1})	0.738	10	20	30	40	0.666 1
		1.136	2.408	3.871		5.246

Table 2 Structure parameters of the three activated carbons

Adsorbent	S_{BET} /(m^2·g^{-1})	L_{H-K} /nm	V_{micro} /(cm^3·g^{-1})	V_{meso} /(cm^3·g^{-1})	L_{BJH} /Å
AC	1 419	0.712	0.367	1.23	31
SiC-AC-20	1 074	0.491	0.352	0.301	31
SY-6	1 171	0.485	0.357	0.251	30

The results in Table 2 show that these three types of activated carbon have large specific surface area, and their micropore volume difference is not great. SiC-AC-20 and AC have larger micropore volume and micropore diameter than that of SY-6. Furthermore, SiC-AC-20 and AC also have a considerable large mesopore volume that does not exist in SY-6, which is attributed to the pore structure of activated carbon prepared through zinc chloride activation. Hence, the composite activated carbon with high thermal conductivity produced in this experiment has a similar specific surface area and pore volume to commercial activated carbon, moreover, contains abundant mesopore structures suitable for the use as an adsorbent.

The test result of the Boehm titration in Table 3 shows that SiC-AC-20 has more lactone and carbonyl groups, and the amount of the acidic and basic groups are higher than that of SY-6. The basic group of AC is similar to that of SiC-AC-20, but the acidic group is slightly lower than that of SiC-AC-20. This condition is mainly due to $ZnCl_2$ being adopted at a high temperature as activating agent with a stronger activation performance, which removes the carbonyl group in the activated carbon to form hydrogen and oxygen into water vapor to be expelled. The active point is also improved and the acid-basic groups are increased.

3.2 Adsorption power of the activated carbon with high thermal conductivity

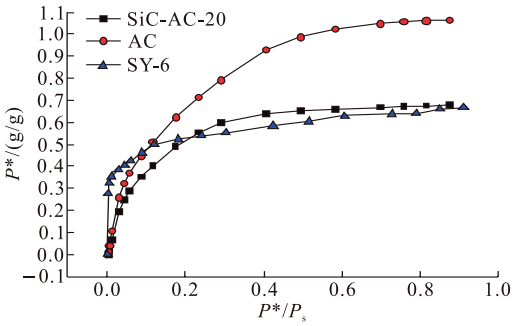


Fig.2 Adsorption-desorption isotherms of toluene at 25 ℃ for the different activated carbons

According to Tables 2 and 3, the relationship between the specific surface area of the three kinds of adsorbent is AC > SY-6 > SiC-AC-20. The basic group content of the three types of activated carbon is SiC-AC-20 ≈ AC > SY-6, consistent with the law of

Table 3 Concentrations of the surface functional groups measured by Boehm titration/(mmol·g^{-1})

Sample	Acidic/(mmol·g^{-1})					Basic/(mmol·g^{-1})
	Carboxyl	Lactones	Carbonyl	Phenols	Total	
SY-6	0.714	0.979	0.244	0.148	1.937	0.471
SiC-AC-20	0.125	1.452	0.556	0.768	2.901	0.824
AC	0.473	0.802	0.457	0.877	2.609	0.831

equilibrium adsorption capacity of toluene on these types (Fig. 2). The activated adsorption site of toluene is a basic site; the more basic functional groups, the stronger adsorbing capacity of toluene. The adsorption capacity of SY-6 is greater than that of SiC-AC-20 and AC at a low pressure, which is mainly ascribed to the abundant cellular structure contained in SY-6. As the pressure increases, the quantity of mesopores puts more and more effect on the adsorption performance. The adsorption capacity of AC at high pressure is much higher than that of SiC-AC-20 and SY-6 because of the abundant mesoporous structure of AC.

3.3 Microwave regeneration

3.3.1 Microwave radiation desorption rate

As microwave power increases, the peak point time slightly moves forward and the peak point increases. More heat is generated as microwave energy is absorbed by activated carbon, which improves the desorption rate.

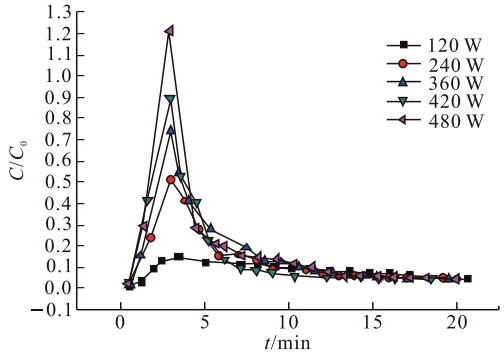


Fig. 3 Spectra of toluene desorption on SiC-AC-20 by microwave radiation at different M_W powers

A peak is observed respectively to appear under these different levels of microwave power in a relatively short period of time. A large amount of microwave energy is also absorbed to generate a lot of heat, which expels the toluene from the activated carbon channel.

It takes only 20 mins for almost all toluene to be desorbed from activated carbon in the desorption process under different levels of microwave radiation power. While, it takes 30 mins in conventional desorption process at a temperature rise rate of 12 ℃·min^{-1}, and 70 mins at a temperature rise rate of 4 ℃·min^{-1}. This result elucidates that the microwave desorption is far more effective than conventional thermal desorption.

When microwave radiation power is over 360 W, the desorption of SiC-AC-20 with a high thermal conductivity coefficient is more effective. Under 10 mins microwave radiation, the concentration of toluene outflowed from SiC-AC-20 bed is far less than that from AC and SY-6 bed. The reason is that the high thermal conductivity material (silicon carbide) is doped in SiC-AC-20, which improves the heat conduction property of activated carbon to evenly spread out the heat absorbed during microwave radiation process. Thus, sufficient energy is absorbed by adsorbed toluene to desorb, which saves energy consumption.

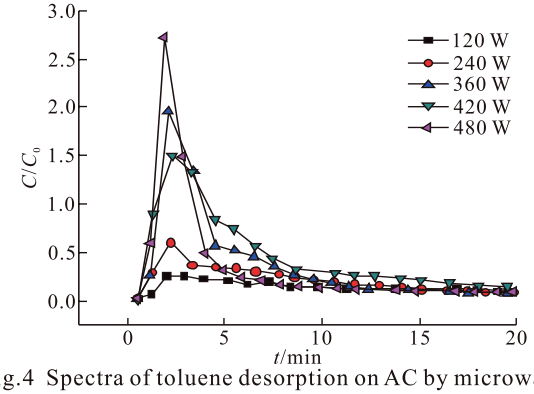


Fig.4 Spectra of toluene desorption on AC by microwave radiation at different M_W powers

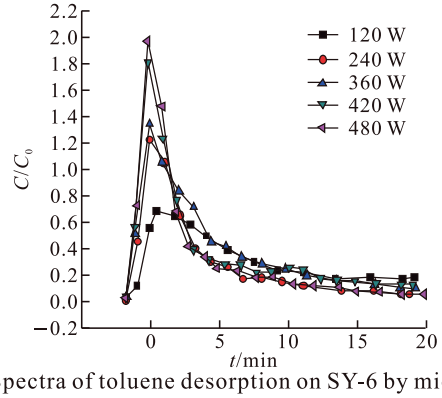


Fig.5 Spectra of toluene desorption on SY-6 by microwave radiation at different M_W powers

3.3.2 Comparison figure of the microwave desorption temperature rise of toluene on the different activated carbons

Figs.6 to 8 show the bed temperature rise curves of SiC-AC-20, AC, and SY-6 at different microwave power settings of 120, 240, 360, 420, and 480 W, respectively.

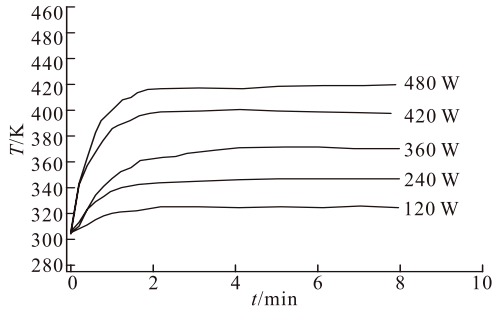


Fig.6 Temperature rise curves of the SiC-AC-20 bed during toluene desorption from SiC-AC-20 under microwave radiation

As microwave power increases, the bed temperatures of all the three kinds of activated carbon clearly increase. It is mainly for the reason that more

microwave-generated heat is absorbed by activated carbon, leading to the increase in bed temperature.

When a rather low microwave desorption power is set (*eg*, 120 and 240 W), the temperature rising of all the three kinds of activated carbon is relatively slow and the temperature differentiation is little. The bed temperature of SiC-AC-20 is higher than the other two after a while. It illustrates that under a low microwave desorption power SiC-AC-20 does not have the capacity to absorb too much heat and fails to present its superior performance.

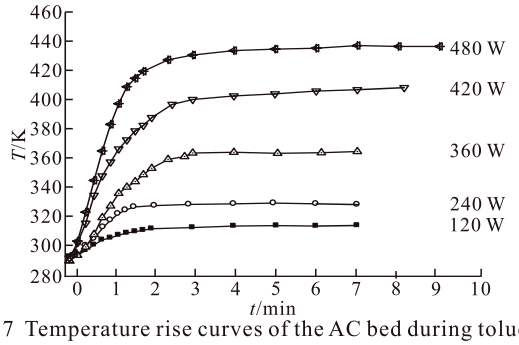


Fig.7 Temperature rise curves of the AC bed during toluene desorption from AC under microwave radiation

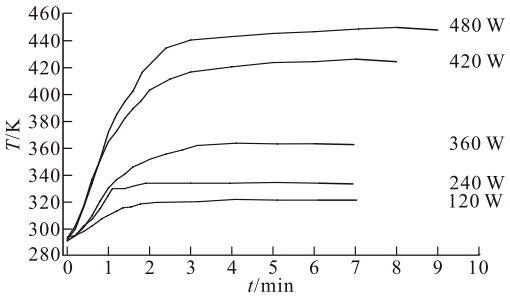


Fig.8 Temperature rise curves of the SY-6 bed during toluene desorption from SY-6 under microwave radiation

As microwave power continues to increase, the bed of SiC-AC-20 has an obviously slighter change in temperature than the other two. For instance, when the power is 420 W, the bed temperature of SiC-AC-20 is approximately 15 ℃ lower than that of SY-6 and AC, and more than 20 ℃ lower when the power is increased to 480 W. A lower bed temperature could prevent the pore structure of activated carbon from excessive damage for better recycling use. It is mainly because SiC-AC-20 has an excellent heat conduction property that could rapidly transfer the internally generated heat to the surface, which is taken away by the carrier gas, leading to a significantly lower bed temperature than that of SY-6 and AC.

3.3.3 Activation energy of toluene desorption on different activated carbons in microwave field

According to the spectrograms of microwave radiation desorption in Figs.3 to 5 and the temperature rise diagrams of the adsorbent bed under different microwave power radiation settings in Figs.6 to 8, the peak point temperature of desorption and dT/dt value under different microwave power settings can be obtained. The activation energy of desorption of toluene on the three kinds of adsorbents under microwave radiation can be calculated by applying the following formula:

$$\ln(RT_p^2) - \ln\left.\frac{dT}{dt}\right|_{t-t_z} = \frac{E_d}{RT_p} + \ln\frac{E_d}{k_0}$$

The peak point temperature of toluene desorption of SiC-AC-20, AC, and SY-6 under microwave radiation and the activation energy of desorption calculated utilizing the above formula are listed in Table 4. Figs.9 to 11 show the linear fit of calculating the activation energy for benzene desorption on the three activated carbons under microwave radiation.

The data in Table 4 show that under the action of microwave field, toluene has a less activation energy in microwave adaptive composite activated carbon AC-SIC-20 than in AC and SY-6. This elucidates that under the effect of microwave radiation, the toluene adsorbed in AC-SIC-20 is more likely to desorb than in AC and SY-6. It is due to the fact that the silicon carbide doped in AC-SIC-20 improves the performance of thermal conductivity and efficiently transfers the heat generated by activated carbon that has absorbed microwave to the whole adsorption bed, making the temperature of the adsorption bed rise faster and more evenly, thus more conducive to toluene desorption.

3.3.4 Adsorption capacity of activated carbon after repetitive microwave regeneration

Penetration times of adsorption that toluene needs after it undergoes three times of microwave regeneration in AC-SI, AC, and SY-6, respectively, are listed in Table 5.

Table 4 Activation energy for desorption of toluene on different activated carbons

Adsorbent	Peak temperature (T_p, K) for different M_w powers/W					Activation energy for desorption of toluene/(kJ·mol^{-1})
	120	240	360	420	480	
SiC-AC-20	328.15	339.15	356.15	371.15	399.15	16.05
SY-6	318.15	329.15	352.15	416.15	439.15	18.76
AC	317.15	331.15	352.15	410.15	441.15	23.09

Table 5 Penetration time of adsorption of activated carbon to toluene after microwave regeneration

Adsorbent	Penetration time of first adsorption	Penetration time of second adsorption	Penetration time of third adsorption
SiC-AC-20	74	82	78
AC	64	58	50
SY-6	53	51	48

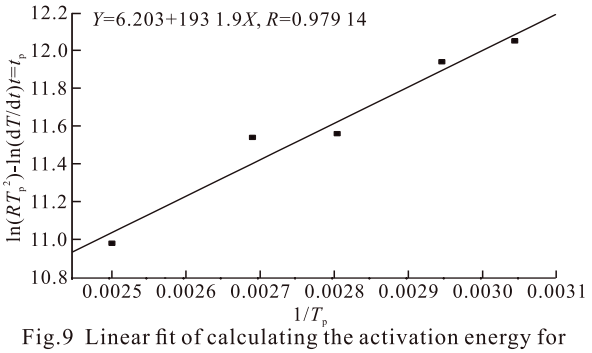


Fig.9 Linear fit of calculating the activation energy for benzene desorption on SiC-AC-20 under microwave radiation

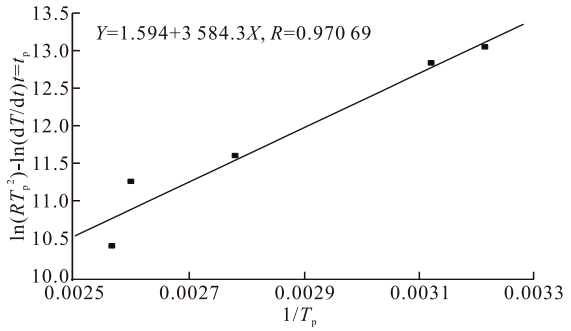


Fig.10 Linear fit of calculating the activation energy for benzene desorption on AC under microwave radiation

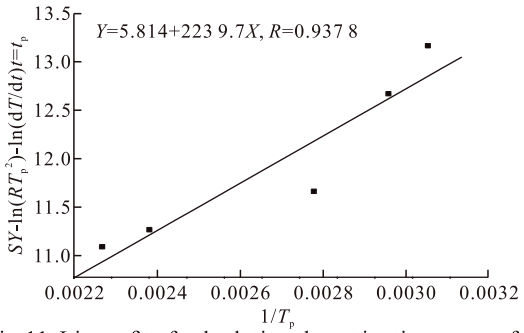


Fig.11 Linear fit of calculating the activation energy for benzene desorption on SY-6 under microwave radiation

According to Table 5, after three times of microwave regeneration, microwave adaptive composite activated carbon could still maintain a rather high adsorption capacity and adsorption penetration time did not decrease significantly. To the contrary, the adsorption penetration time of commercial activated carbon and ordinary activated carbon produced in the laboratory decreased by approximately 22% after undergoing three times of cyclic regeneration. This condition shows that the microwave adaptive composite activated carbon presents properties such as fast desorption, desorption at low temperature, and being regenerative for multiple times .

4 Conclusions

a)The composite activated carbon with high thermal conductivity was prepared with walnut shells as carbon source, $ZnCl_2$ as an activating agent, and an appropriate amount of silicon carbide. The prepared composite activated carbon was verified to have equivalent micropore area and toluene adsorption capacity as commercial activated carbon (SY-6). Furthermore, its thermal conductivity coefficient of high thermal conductivity is three times as much as those of AC and SY-6, if the amount of silicon carbon is 40%, it has a thermal conductivity coefficient six times as much as that of SY-6.

b) The microwave adaptive composite activated carbon (AC-SiC) has a less temperature rise in bed layer than common active carbon (AC) and commercial activated carbon (SY-6) under microwave radiation. Under the same microwave power, its desorption bed temperature is 10 to 30 ℃ lower than that of common activated carbon.

c)Toluene has a microwave desorption activation energy of 16.05 $kJ \cdot mol^{-1}$ in microwave adaptive composite activated carbon (AC-SIC), less than that in ordinary activated carbon (AC) prepared in laboratory and commercial activated carbon (SY-6), 15% less than the latter (18.76 $kJ \cdot mol^{-1}$).

d)After repetitive microwave regeneration, the composite activated carbon with high thermal conductivity could still maintain a good adsorption performance. However, the adsorption capacity of commercial activated carbon decreased significantly. It is shown that the composite activated carbon with high thermal conductivity has an excellent thermal conductivity capacity, and performs well in the regeneration process.

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