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ADSORPTION PROPERTIES OF ACIDIFIED ACTIVATED CARBON FOR REMOVING IMPURITIES FROM PHENOL

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ABSTRACT

2,4-diphenyl-4-methyl-1-pentene is a main impurity in phenol. In this paper, acidified activated carbon with sulfuric acid were used to remove the impurity from phenol. Combined with solid-phase microextraction (SPME) and gas chromatography-mass spectrometry (GC-MS), the adsorption capacity and mechanism of acidified activated carbon were analyzed. Unacidified and sulfated activated carbon was characterized by scanning electron microscopy (SEM). The adsorption mechanism of 2,4-diphenyl-4-methyl-1-pentene on sulfuric acid acidified activated carbon was investigated. The acidified activated carbon of sulfuric acid has much better adsorption capacity than the unacidified activated carbon on 2,4-diphenyl-4-methyl-1-pentene. The sulfuric acid acidified activated carbon has no obvious adsorption effectiveness on mesityl oxide and 2-methylbenzofuran. The optimum adsorption time of sulfuric acid acidified activated carbon for 2,4-diphenyl-4-methyl-1-pentene was 1 h, the removal rate was 82%. The Freundlich isothermal adsorption model can describe the adsorption behavior of 2,4-diphenyl-4-methyl-1-pentene on sulfuric acid acidified activated carbon. The adsorption process conforms to the pseudo-second-order kinetics model and is a chemical adsorption. The sulfuric acid acidified activated carbon can remove 2,4-diphenyl-4-methyl-1-pentene form phenol very well, which provide a theoretical basis and technical support for the phenol industry.

KEYWORDS

Acidified activated carbon, 2,4-diphenyl-4-methyl-1-pentene, adsorption capacity, adsorption mechanism.

1. INTRODUCTION

Phenol is also known as carbolic acid, its appearance is white crystals. It will turn into pink when placed in the air or under light. It can be miscible in ethanol, ether and glycerin. Phenol is widely used, mainly for the production of phenolic resins, bisphenol A and caprolactam, of which the production of phenolic resins is the largest use of phenol [1]. Phenol can also be used as drugs raw material for the production of aspirin, salicylic acid and sulfa [2-4]. Dilute aqueous solutions of phenol can also be used directly as a preservative and disinfectant [5]. Before World War I, the only source of phenol was extracted from coal tar. With the progress of the times, most of the phenol is obtained through a chemical synthesis process. At present, the main methods for producing phenol are isopropyl benzene, toluene oxidation, and benzene direct oxidation [6-9]. More than 92% of the world's phenols are produced using the cumene process [10]. However, due to the decomposition and oxidation of cumene during the production process, a large number of side reactions are accompanied, resulting in a large amount of organic impurities in the phenol products [11, 12]. The presence of impurities not only affects the color of phenol, but also affects the production and application of phenol downstream products, which in turn affects the economic benefits of the company. Therefore, improving the purity of phenol is an urgent problem to be solved at present. In recent years, the main methods of purifying phenol are azeotropic distillation, extractive distillation and ion exchange resin method. Among them, the ion exchange resin method is a used relatively widely method and has the advantages of simple operation and convenient and quick, but the procurement period of these resins is long and the price is high, causing many inconveniences and cost pressures for the manufacturers. Therefore, there is a need to find an adsorbent that can be used to purify phenol and that has a wide range of sources and low cost.

Activated carbon is an adsorbent artificially processed from carbon-containing raw materials. It has the advantages of strong adsorption, well-developed pore structure, abundant surface chemical groups, sufficient raw materials, high safety, and easy regeneration [13-15]. The surface chemical groups of activated carbon can be controlled by activating chemical processes or chemical post-treatment methods. That is, different chemical reagents are used to treat activated carbon, change the chemical or physical structure of the surface, and enhance the adsorption characteristics [16]. Because different adsorbates have different requirements for activated carbon. In order to achieve adsorption requirements for different adsorbates, activated carbon is usually subjected to targeted treatment to obtain desired physical and chemical properties. Therefore, because phenol is acidic, this article uses 50% sulfuric acid to treat activated carbon. Combined with solid-phase microextraction (SPME) and gas chromatography-mass spectrometry (GC-MS) technology to explore the adsorption capacity of acidified activated carbon for organic impurities [17, 18]. Further examine the adsorption mechanism of sulfuric acid acidified activated carbon to 2,4-diphenyl-4-methyl-1-pentene, provides an effective method and relevant basis for the purification of phenol by enterprises.

2. EXPERIMENTAL

2.1 Reagents

The activated carbon were obtained from Tianjin Damao Chemical Reagent Factory (Tianjin, China). The phenols were obtained from Sinopec Jilin Dyeing Factory (Jilin, China). Methanol, 2-methylbenzofuran, and mesityl oxide were chromatographic purity. 2-methylbenzofuran was purchased from Sigma-Aldrich (Shanghai, China). Mesityl oxide was purchased from Alfa Aesar Chemical (Shanghai, China). Methanol was purchased from Tianjin Yongda Chemical Reagent Development Center (Tianjin, China). 2,4-diphenyl-4-methyl-1-pentene was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). The ultrapure water was

purified by a Milli-Q system (Millipore, Redford, MA, USA).

2.2 Instrument

Extraction was performed on an SPME extraction head (Supelco, PDMS, 100 µl, 3 pk, USA). The analysis was performed on an M7 single quadrupole GC-MS (Beijing Purkinje General Instrument Co., Ltd., Beijing, China). The inlet temperature was 240 ℃. The reaction conditions were as follows: Program warming, the initial temperature was 50 ℃, kept for 0 min; the temperature was raised to 100 ℃ at 8 ℃/min; the temperature was then raised to 200 ℃ at 10 ℃/min and next the temperature was raised to 290 ℃ at 15 ℃/min and kept for 5 min. Pulsed split injection, with split ratio 10:1. The temperature of the ion source was 230 ℃, and the temperature of the transmission line was 250 ℃. SPME extraction was carried out on the DF-101S collector thermostatic heating magnetic stirrer (Gongyi Yuhua Instrument Co., Ltd., Henan, China). The static adsorption experiments were performed using a WE-1 water bath oscillator (Tianjin Uno Instruments Co., Ltd., Tianjin, China). The scanning electron microscopy (SEM) experiments were performed on a JSM-6490LV SEM (JEOL, Japan).

2.3 Acidification of activated carbon

For enhance the adsorption capacity of activated carbon, about 50 g activated carbon is placed in a beaker. The prepared sulfuric acid solution of 50% is put into the beaker. After mixing and treat for 48 h, the sulfuric acid solution in the beaker to pour out as much as possible. The activated carbon after the sulfuric acid acidification was cleaned by the distilled water. Until the water poured out after cleaning was neutral. The cleaned activated carbon was placed in a drying oven at 110 ℃ and dried for 12 h. Cool to room temperature.

2.4 Activated carbon static adsorption experiment

2.4.1 Adsorption capacity comparison experiment

Firstly, 2,4-diphenyl-4-methyl-1-pentene phenol sample 2.5 g with concentration of 1 ppm was added to 0.3, 0.5, 0.7, 1.0, 1.2, and 1.5 g of untreated activated carbon. Adsorption 2 h in a water bath at a temperature of 50 ℃. Then take out the sample and put it into the sample tube, test sample the next day. Then take 50% sulfuric acid acidified activated carbon with the same quality as above. Equal amount of 2,4-diphenyl-4-methyl-1-pentene phenol sample was added. Adsorption 2 h in a water bath at a temperature of 50 ℃. Take out the sample retain to the second day detection.

2.4.2 Acidified activated carbon adsorbs different impurities

In this work, 1 ppm of 2,4-diphenyl-4-methyl-1-pentene, 2-methylbenzofuran, and mesityl oxide phenol sample 2.5 g was added to 0.3, 0.5, 0.7, 1.0, 1.2, and 1.5 g of sulfuric acid acidified activated carbon, respectively. Adsorption 2 h in a water bath at a temperature of 50 ℃, and the sample was taken out in a sample tube and detected the next day.

2.5 Adsorption time

Firstly, 5 parts of 0.5 g sulfuric acid acidified activated carbon into five 40 mL brown vials. Then 2.5 g 25 ppm of 2,4-diphenyl-4-methyl-1-pentene phenol sample was added to the vials, Take another 2.5 g of 2,4-diphenyl-4-methyl-1-pentene phenol sample as control. numbered 1-6, placed in a 50 ℃ water bath thermostat oscillator, according to the time gradient adsorptions of 0.5, 1, 2, 3 and 4 h. Finally the samples were take out one by one and placed in a sample tube. The next day test.

2.6 Adsorption process

Take 5 parts of 0.5 g sulfuric acid acidified activated carbon. 2.5 g of 2,4-diphenyl-4-methyl-1-pentene phenol sample at a concentration of 14, 16, 18, 20 and 22 ppm were added to activated carbon, respectively. Adsorption 1 h in a water bath at a temperature of 50 ℃. The samples were take out one by one and placed in a sample tube and detected the next day.

3.RESULTS AND DISCUSSION

3.1 Activated carbon characterization

SEM has been a primary tool for characterizing the surface morphology and fundamental physical properties of the adsorbent surface. SEM of untreated activated carbon and activated carbon was treated sulfuric acid are shown in Figure 1. It can be seen from Figure 1(A), has considerable numbers of pores on the surface of activated carbon. Compared with Figure 1 (A), As shown from the Figure 1(B), the activated carbon surface has more pores and larger pore size. This is due to the fact that during the acidification of activated carbon by sulfuric acid, closed pores are opened, fine pores are enlarged. This makes the average pore diameter of the activated carbon larger and increases the specific surface area of the activated carbon.

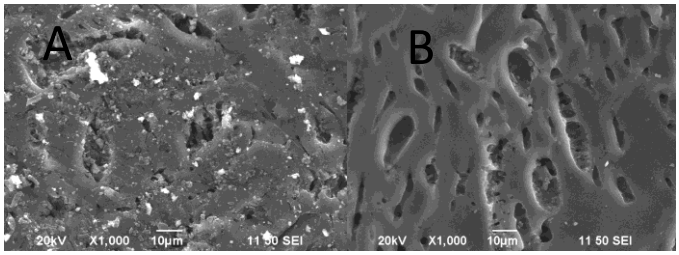

Figure 1: SEM image comparison of activated carbon (A. SEM image of untreated activated carbon; B. SEM image of sulfuric acid acidified activated carbon)

3.2 Adsorption capacity of activated carbon

The mass ratio of activated carbon under different acidifying conditions to phenol is 0.3:2.5, 0.5:2.5, 0.7:2.5, 1.0:2.5, 1.2:2.5, 1.5:2.5. At this mass ratio, the adsorption capacity of activated carbon for mesityl oxide, 2-methylbenzofuran and 2,4-diphenyl-4-methyl-1-pentene in phenol was investigated. The mass of activated carbon and the adsorption rate are plotted in Figure 2. As shown in the figure 2(A), the untreated activated carbon has low adsorption capacity for 2,4-diphenyl-4-methyl-1-pentene. The adsorption effectiveness of the sulfuric acid acidified activated carbon for 2,4-diphenyl-4-methyl-1-pentene is significant. The mass ratio is 0.5:2.5 and adsorption rate can reach 80%. Therefore, sulfuric acid acidified activated carbon has a good adsorption capacity for 2,4-diphenyl-4-methyl-1-pentene. As seen from figure 2(B), The adsorption rates of mesityl oxide and 2-methylbenzofuran, with the increase of the mass of sulfuric acid acidified activated carbon are basically unchanged and the adsorption rate is lower. At the same time, compared with the adsorption capacity of sulfuric acid acidified activated carbon for mesityl oxide and 2-methylbenzofuran, sulfuric acid acidified activated carbon has a better adsorption capacity for 2,4-diphenyl-4-methyl-1-pentene. Therefore, sulfuric acid activated carbon can be used to remove 2,4-diphenyl-4-methyl-1-pentene.

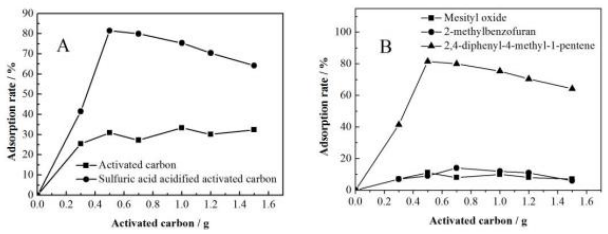

Figure 2: Adsorption effectiveness of mesityl oxide and 2-methylbenzofuran, and 2,4-diphenyl-4-methyl-1-pentene by different acidified activated carbons (A. Adsorption capacity of 2,4-diphenyl-4-methyl-1-pentene on activated carbon under different acidification conditions; B. Adsorption capacity of mesityl oxide and 2-methylbenzofuran, and 2,4-diphenyl-4-methyl-1-pentene on sulfuric acid acidified activated carbon

3.3 Adsorption time

The effect of adsorption time on the adsorption of 2,4-diphenyl-4-methyl-1-pentene by sulfuric acid acidified activated carbon cannot be ignored. Adequate adsorption time can equilibrium the adsorption and improve the adsorption efficiency. As shown in the figure 3, the adsorption process show a very rapid rate in the beginning of adsorption, with the increase of time, the adsorption rate achieves the equilibrium after adsorption for 1h. Therefore, the best adsorption time was 1 h.

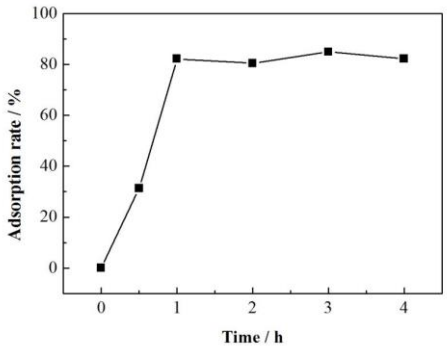

Figure 3: Effect of adsorption times on the adsorption of the 2,4-diphenyl-4-methyl-1-pentene on sulfuric acid acidified activated carbon

3.4 Adsorption isotherms

The adsorption isotherms were fitted using the Langmuir equation and the Freundlich equation [19, 20]. The Langmuir isothermal adsorption model describes that the adsorption is a monolayer adsorption process. The Freundlich isothermal adsorption model describes an multi-layer adsorption process on the adsorbent surface. These two equations are as follows:

Langmuir equation:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{Q_m K_L} \quad (1)$$

Freundlich equation:

$$\ln Q = \frac{1}{n}\ln C_e + \ln K \quad (2)$$

In the equations, Q_e represents the equilibrium adsorption capacity per unit weight of sulfuric acid acidified activated carbon, C_e represents the equilibrium concentration, K_L represents the Langmuir equilibrium adsorption constant, Q_m represents the maximum adsorption capacity per unit mass of the sulfuric acid acidified activated carbon, K represents Freundlich equilibrium adsorption constant, and n represents the intensity coefficient.

From Eq. (1) and (2), the fitting results of the isothermal adsorption model fitting experimental data are shown in Figure 4, and the isothermal adsorption model parameters in Table 1. The results show, the correlation coefficient of the Freundlich isothermal adsorption equation for 2,4-diphenyl-4-methyl-1-pentene was 0.99, which was larger than the correlation coefficient of the Langmuir isotherm equation of 0.96. So the Freundlich equation can accurately describe the adsorption characteristics of 2,4-diphenyl-4-methyl-1-pentene on sulfuric acid acidified activated carbon, indicating that the adsorption is multi-layer.

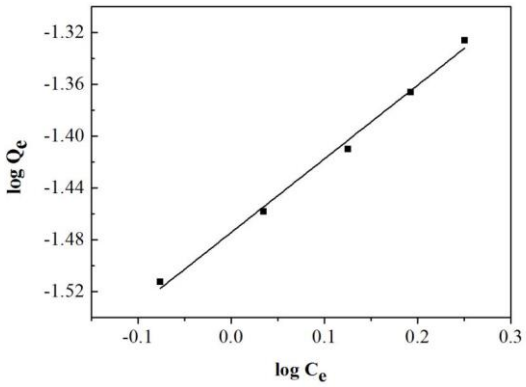

Figure 4: Freundlich isotherm model fitting results for 2,4-diphenyl-4-methyl-1-pentene

Table 1: Langmuir and Freundlich isotherm model parameters for 2,4-diphenyl-4-methyl-1-pentene

Langmuir			Freundlich		
Q_m (μg/g)	K_L (L/mg)	R^2	1/n	K	R^2
0.0908	0.5859	0.9645	0.5682	0.2289	0.9944

3.5 Adsorption kinetics

The pseudo-first-order kinetics model and pseudo-second-order kinetics model were used to fit the adsorption times of 2,4-diphenyl-4-methyl-1-pentene [21,22]. The correlation coefficient was used as the evaluation criterion. The pseudo-first-order kinetics model described the physical adsorption process; the pseudo-second-order kinetics adsorption model described the chemisorption process. These two kinetics expressions are as follows:

Pseudo-first-order kinetics model:

$$\ln(Q_e - Q_t) = \ln Q_e - K_1 t \quad (3)$$

Pseudo-second-order kinetics model:

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \quad (4)$$

Where Q_e is the amount of adsorption at equilibrium (mg g^{-1}), Q_t is the amount of adsorption at time t (mg g^{-1}), t is the adsorption time (h), K_1 is the pseudo-first-order kinetics model adsorption equilibrium rate constant (h^{-1}), and K_2 is the pseudo-second-order model adsorption equilibrium rate constant (g mg^{-1} h^{-1}).

A pseudo-first-order kinetics model and pseudo-second-order kinetics model were used (Eq. 3 and 4) for fitting 2,4-diphenyl-4-methyl-1-pentene experimental data. Pseudo-second-order kinetics fitting results are shown in Figure 5, and the fitting parameters in Table 2. The results show that the correlation coefficient 0.99 of the pseudo-second-order kinetics model of 2,4-diphenyl-4-methyl-1-pentene is greater than the correlation coefficient 0.62 of the pseudo-first-order kinetics model. So the pseudo-second-order kinetics model can better describe the adsorption process of 2,4-diphenyl-4-methyl-1-pentene on sulfuric acid acidified activated carbon. Therefore, the reaction process is a chemical adsorption process.

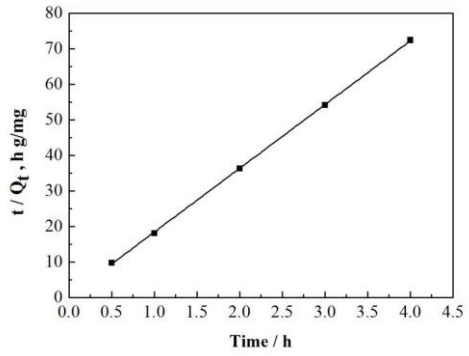

Figure 5: Fitting results of pseudo-second-order kinetics model to adsorption time on 2,4-diphenyl-4-methyl-1-pentene

Table 2: 2,4-diphenyl-4-methyl-1-pentene of pseudo-first-order and pseudo-second-order kinetics parameters

Pseudo-first			Pseudo-second		
$Q_{e,cal}$ (mg/g)	K_1 (h^{-1})	R^2	$Q_{e,cal}$ (mg/g)	K_2 (g/(mg·h))	R^2
0.1513	2.4259	0.6233	0.0556	688.6774	0.9999

4. CONCLUSIONS

In summary, we successfully found a method to remove impurities from phenol by using activated carbon as adsorbent. Sulfuric acid acidified activated carbon has good adsorption capacity for 2,4-diphenyl-4-methyl-1-pentene, and the removal rate is 82%. Both the Freundlich model and the pseudo-second-order kinetics model can well describe the behavior of 2,4-diphenyl-4-methyl-1-pentene in activated carbon. Acidified activated carbon can be used to remove 2,4-diphenyl-4-methyl-1-pentene. This provides a theoretical basis and a new approach for phenol companies purification of phenol.

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