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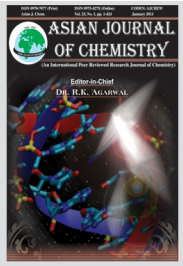

# Properties of LPG Carbon Residue Prepared with the Activated Method at High Temperature

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In this paper, activated carbon is prepared form the carbon residue of Lugi pressurized gasifier slag (LPG carbon residues) with KOH solution as activating agent with the chemically activated method at high temperature. This work reports the influence of activation temperature, activation time and the mass ratio of raw materials and activating agent on the properties of activated carbon. The experimental results show that the great specifc surface area and interspace of activated carbon prepared from the coal residue has a great property of adsoption of phenol.

**Key Words: LPG carbon residuem, Activated carbon, Chemical activation, Phenol.**

## INTRODUCTION

Mainly composed of carbon and containing some oxygen, hydrogen and ash, activated carbon is the porous carbon material. With highly developed pore structure and special surface characteristics, it is widely used in environmental protection, chemical industry, food processing, hydrometallurgy, medicine, electronics and other fields and is an essential product of daily life in the national economy and national defense building[1]. A chemical fertilizer plant in Kaiyuan of Yunnan Province uses low calorific value of low quality coal to synthesize ammonia by Lugi pressurized gasification process and achieves good results. However, it produces gas slag, coal gangue approximately 100,000 t/a, which contains 35~40 % carbon, 14.38 % volatile matter. The value of low heating is 10660~13850 kJ/kg. Therefore, reasonable use of the carbon residue of Lugi pressurized gasifier slag (LGP carbon residual) has very important economic and social benefits. In this research, activated carbon was prepared form the LPG carbon residues by heat activated method and researched its adsorption properties of phenol. In this paper, the thermodynamic functions ($\Delta G^\circ$, $\Delta H^\circ$ and $\Delta S^\circ$) of adsorption with the changes of the adsorption temperature were evaluated.

## EXPERIMENTAL

The light photometer (The Third Shanghai Analysis Instrument Factory)721 cents, the HQ45A-II constant temperatures shake bed (Wuhan Scientific Instrument Factory in Chinese Science), dynamoelectric leave scheming (The Medical Treatment apparatus factory of Longgang in Jiangsu Province), flap to concuss machine, the magnetic force mixer, Philip EM420 electrical mirror in Holland, the American ASAP2000 specific surface analyze instrument automatically, *etc.*

Carbon residues of stove residue, passing through 250 meshes, stoved by 110 ºC before using and stored in desiccator. All except potassium hydroxide materials are analytically pure.

**Preparation of activated carbon in chemical method:** This paper introduces the preparation of activated carbon from the LPG carbon residue with the potassium hydroxide in chemically activated method, in resistance furnace at high temperature and investigates the influence of adsorption on activate parameter. The basic step is as follows:

Raw material → broken up → pass through 250 meshes → mix with the potassium hydroxide → dehydrate at the low temperature condition → microwave activation → soak in acid → wash by water → dry → product.

**Characteristics of activated carbon:** The iodine absorption value of activated carbon is analyzed and tested according to stipulations in The coal quality grain activated carbon iodine absorption value measurement method (GB/T7702.7 - 87). The Philip EM420 electric mirror in Holland is used to observe the condition of surface carbon residue. BET liquid nitrogen adsorption technique is used to admeasure specific surface with America ASAP2000 specific surface automatic analyzer.

**Absorption experiment:** After adsorption balance, 4-amino antipyrine direct photometric method is used to measure the concentration of phenol. The adsorption quantity was calculated according to the following equation:

TABLE-1
SELECTION OF ACTIVATED TEMPERATURE

| Temperature (ºC) | 110 | 500 | 600 | 700 | 750 | 780 | 800 | 850 | 900 | 950 | 1000 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Iodine value (mg/g) | 503.3 | 508.4 | 547.1 | 668.9 | 734.5 | 805.0 | 904.7 | 1009.3 | 1054.8 | 1079.3 | 1141.4 |
| Productivity (%) | 65 | 54 | 50 | 44 | 40 | 40 | 39 | 38 | 34 | 34 | 32 |

TABLE-2
SELECTION OF OPTIMAL ACTIVATION TIME

| Time (min) | 0 | 5 | 10 | 15 | 20 | 25 | 30 | 40 |
|---|---|---|---|---|---|---|---|---|
| Iodine value (mg/g) | 575.3 | 659.5 | 827.1 | 938.8 | 1009.5 | 1015.5 | 886.0 | 874.2 |
| Productivity (%) | 65 | 42 | 40 | 38 | 38 | 34 | 32 | 28 |

TABLE-3
SELECTION OF RATIO OF MATERIAL AND REAGENT

| Ratio of material and reagent ($M_{activated\ carbon}/M_{KOH}$) | 1 : 0 | 1 : 0.5 | 1 : 0.75 | 1 : 1 | 1 : 1.25 | 1 : 1.5 | 1 : 2 | 1 : 3 |
|---|---|---|---|---|---|---|---|---|
| Iodine value (mg/g) | 565.8 | 570.4 | 722.5 | 1009.5 | 1032.2 | 1052.0 | 1087.5 | 1255.6 |
| Produce rate (%) | 62 | 52 | 58 | 58 | 55 | 56 | 58 | 42 |

TABLE-4
COMPARISON OF SPECIFIC SURFACE AREA OF RESIDUE ANDMODIFIED CARBON

| LPG carbon residue dosage (g) | Iodine value (mg/g) | Specific surface area ($m^2/g$) | Volume (cc/g) | Average diameter (Å) | Micropore area ($m^2/g$) | Micropore volume (cc/g) |
|---|---|---|---|---|---|---|
| 10 | 1009.30 | 1032.0 | 0.68 | 20 | 571 | 0.26 |
| 40 | 1048.00 | 1896.0 | 1.24 | 26 | 905 | 0.40 |
| LPB Carbon residue | 350.15 | 249.7 | 0.25 | 29 | 83 | 0.038 |

$$A = \frac{(C_0 - C_e)V}{1000 * W} \quad (1)$$

$C_0$ and $C_e$ in the equation represent the equilibrium concentration (mg/L) before and after adsorption respectively; W represents the mass (g) of adsorbent used; V represents sampled volume, 50 mL. Take a group of plugged conical flask with accurately measured adsorbent. At a specific temperature, stirred it for different periods of time, get the upper-layer clear solution after centrifugal separation, measure the concentration of phenol, calculate adsorption quantity and finally determine the time for adsorption equilibrium. At 25 ºC, with pH between 2.5~11.5, examine the influence of pH on adsoption according to the method above and measure isotherm of absorption at different initial concentration.

## RESULTS AND DISCUSSION

As is shown in Tables 1-3, prepare activated carbon, integrating factors like activation temperature, activation time, ratio of material and agent and selecting temperature at 850 ºC and time at 20 min, ratio of material and reagent at 1:1.

**Analytical result of general performance of activated carbon:** In the LPG carbon residue micro structure drawing, the particals stack and knit closely while in the prepared activated carbon micro structure drawing, it is a loose porous network structure (Figs. 1 and 2). The specific surface area is multiplied.

As is shown in Table-4, the activated charcoal surface area is multiplied nearly three times of the original slag. Other indicators, such as pore size and pore volume are grealy increased, which is consistent with the results of previous iodine value and TEM.

**Adsorbability of phenol:** Selection of the adsorption equilibrium time from (Fig. 3) adsorption at 25 ºC, phenol adsorption capacity increases with time rapidly in the first 1 h.

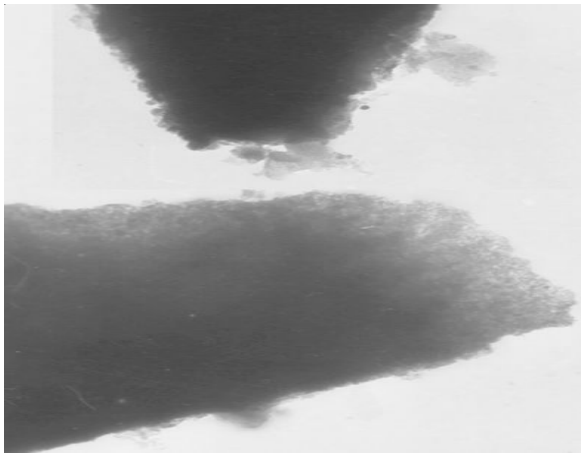

Fig. 1. Micro-structure of LPG carbon residue 1

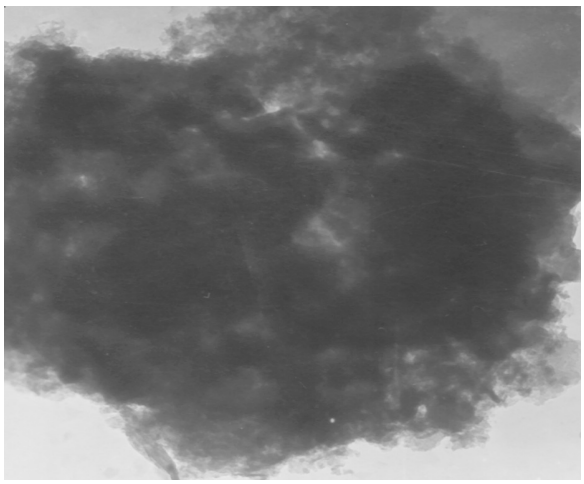

Fig. 2. Micro-structure of activated carbon

After 1 h, absorbtion capacity increase relatively smoothly. Adsobtion maily occurs in an hour. In order to ensure full absorption for adsorbent, with the time factor taken into consideration at the same time, adsorption time is selected as 2 h.

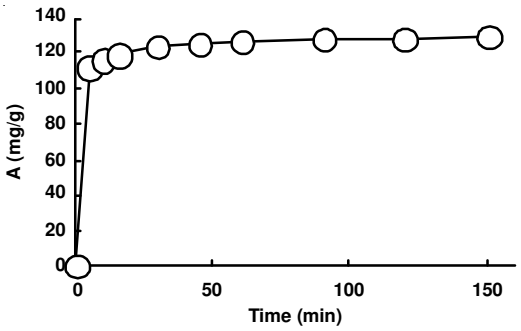


Fig. 3. Adsorption velocity curve at 25 ºC

**Influence of the pH value on adsorption equilibrium:** Fig. 4. shows that when the solution pH value is from 5.9 to 7, the equilibrium adsorption quatity of phenol on activated carbon increases with pH value and reaches it maximum when pH value is close to neutral. When the pH value is greater than 8, the capacity of adsorption of phenol decreases significantly. It indicates that the adsorption capacity of phenol in the acidic condition is greater than that in the alkaline condition.

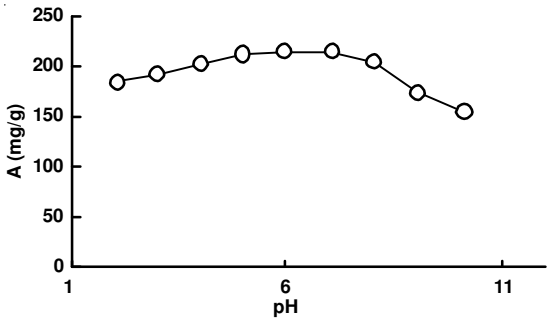


Fig. 4. Influence of the pH value on adsorption

**Analysis of adsorption kinetics**: The kinetic curve of the adsorption of phenol by prepared activated carbon is shown in Fig. 5. use the measured data in the first order adsorption kinetics Lagergren[2] eqn.:

$$\ln (A_m\text{-}A) = \ln A_m\text{-}k_a^t \quad (2)$$

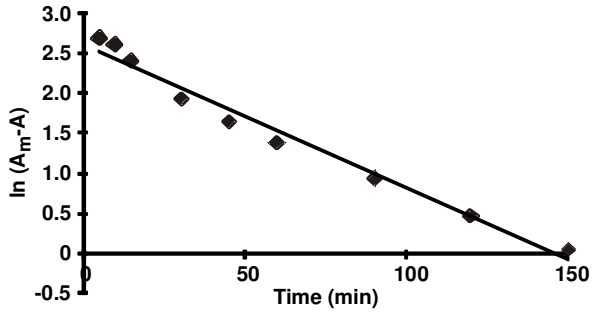


Fig. 5. Adsorption kinetic curve

In the equation, $A_m$, A represents the adsorption quantities at the equilibrium and at the time t, $K_a$ is the constant of adsorption rate. Make a figure for t with ln ($A_m$-A). The result shows that adsorption kinetics accord with this equation. Calculated by the straight slope, the value of $K_a^{298}$ is 0.126 $h^{-1}$.

**Analysis of adsorption thermodynamics:** From the adsorption isotherm at different temperatures, the adsorption quantities decrease with the increase of temperature. This may be due to the factor that solid releases heat in the process of adsorbing solute. Therefore, either in physical adsorption or chemical adsorption, the adsorption quantity decreases with the increase of temperature. There are both physical and chemical adsorption in the process of processing phenolic wastewater with activated carbon, which is characterized by high speed of adsorption and easy equilibrium. Use the measured data in Fig. 6 in the Langmuir straight line equation: $C/A = C/A_m + 1/A_m*b$. The result shows that the adsorption of phenol by activated carbon accords with Langmuir Law. Calculate the maximum adsorption quantity $A_m$ and adsorption equilibrium constant B with the straight slope and intercept. According to the method[3,6], the standard thermodynamics function ΔGº, ΔHº and ΔSº of the adsorption of phenol by residue activated carbon can be calculated as follows:

$$\Delta G^{\Theta} = -RT \ln(\frac{A_m b}{st}) \quad (3)$$

$$\ln(\frac{b_1}{b_2}) = (\frac{\Delta H}{R})(\frac{1}{T_2} - \frac{1}{T_1}) \quad (4)$$

$$\Delta H^{\Theta} = \Delta G^{\Theta} - T\,(\frac{\partial \Delta G^{\Theta}}{\partial T}) \quad (5)$$

$$\Delta S^{\Theta} = \frac{\Delta H^{\Theta} - \Delta G^{\Theta}}{T} \quad (6)$$

$A_m$ and b is Langmuir constant, S is residue activated carbon specific surface area, t is the thickness of adsorption monolayer on the solid surface, or more exactly the height to which adsorbate's thermal motion of adsorbate molecule can reach after being adsorbed. It is not equal to the height of adsorbate molecular and does not necessarily vary with the size of adsorbate molecular. In this work, t is considered 5.17 according to the size of phenol. The calculating result of all the thermodynamics functions in the adsorption process is shown in Table-5.

TABLE-5
CALCULATION RESULT OF EACH THERMODYNAMICS FUNCTION IN THE ADSORPTIVE PROCESS

| T (K) | 298 | 308 |
|---|---|---|
| $A_m$ (mg/g) | 178.57 | 156.25 |
| b (L/mg) | 0.024 | 0.019 |
| $_{\Delta}G^{\theta}$ (KJ $mol^{-1}$) | -41.52 | -41.98 |
| $_{\Delta}H^{\theta}$ (KJ $mol^{-1}$) | | -9.20 |
| $_{\Delta}S^{\theta}$ (J $mol^{-1}K^{-1}$) | 108.47 | 106.42 |

According to the general rules of surface chemistry, solid releases heat when it adsorbs matter molecule while it absorbs heat when matter molecule desorbs from its surface. The specific area of carbon residue is relatively great, which strengthens the adsoption forces between them. This makes the system stable after adsorption. Therefore, in the process of adsorption

of phenol, water turns to absorb less heat and release more heat and hence $\Delta H^{\circ} < 0$. The adsorption of solute molecule in the solid-liquid adsorption system is bound to be accompanied by desorption of a certain amount of solvent molecule. The amount of solvent molecule depends on the surface sectional area of the adsorbate molecule, *i.e.* the relative size of its molecule volume. The greater the molecule volume is, the greater the amount of molecules that desorb from the solvent is and the more positive is the entropy change. According to references, the radius of phenol is about 5.17 Å and the radius of phenol is about 1.12 Å and the calculated molar volume of phenol is about 3 to 5 times of that of water molecule. Therefore, the adsorption of per molar phenol will cause the desorption of 3 to 5 mol water molecule. And the solute is adsorbed on the adsorbent which causes the decrease of degree of freedom. It is a process of entropy decrease. The desorption of solvent molecule is a process of entropy increase. The entropy change in the adsorption process is a sum total of the above two process. As a result, the entropy increase caused by the desorption of water molecule is greater than the entropy decrease caused by the adsorption of phenol. Therefore, the entropy change in adsorption process is greater than 0. Thus, the entropy increase effect of the phenol adsorption in the water solution is caused by the desorption of solvent molecule adsorbed on the activated carbon surface.

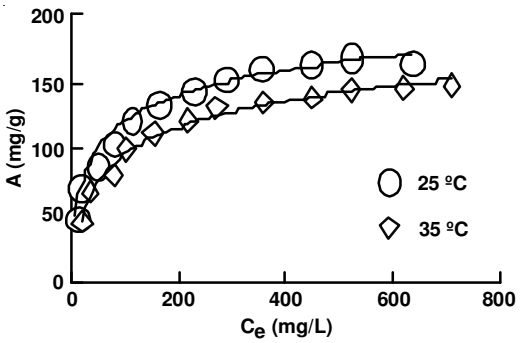


Fig. 6. Adsorption isotherm of activated carbon to phenol

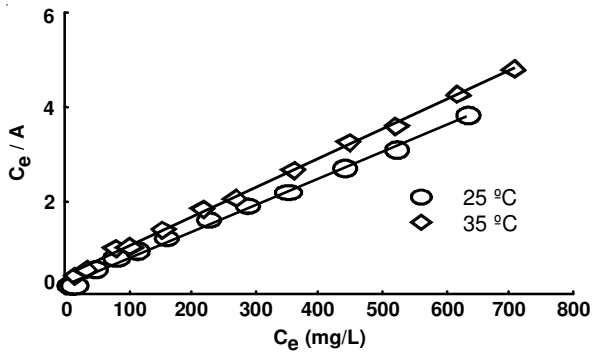


Fig. 7. The Langmuir equation curve of modified carbon residue adsorption phenol

## Conclusion

From the result of the experiment, it is an effective way to prepare activated carbon with high surface area and great amount of microspores in controlling activation temperature, time and increasing the dosage of KOH. Therefore, integrating factors like activation temperature, time and ratio of raw materials and agent, selecting activation temperature at 850 ºC time for 20 min and ratio of raw materials and agent as 1:1 can prepare high-quality activated carbon. The interspaces of residue activated carbon are abundant and the specific surface area is great with great capability of adsorption. The result of adsorption experiment shows that the adsorption of phenol by residue activated carbon accords with Langmuir isothemic adsorption mode with great relativity. The adsorption shows as monomolecular layer and the adsorption is easy to carry out. The process of adsorption includes physical and chemical adsorption. The effect of physical adsorption depends on the specific surface area and porosity of activated carbon. The greater the specific surface area is, the better is the effect of adsorption; the chemical adsorption can be explained by the ionization of oxygen on the surface of the modified residue carbon and phenol, the entropy increase effect of adsorption thermodynamics, enthalpy change and degree of freedom.

## ACKNOWLEDGEMENTS

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## REFERENCES

1. H.-B. Wang, M. Yang, Y.-J. Chen, J.-H. Lu and W.-P. Liu, *J. Yunnan Univ. Nationalities (Nat. Sci. Ed.)*, **12**, 221 (2003).
2. State Environmental Protection Administration, Water and Wastewater Monitoring Analysis Method, Beijing,China Environmental Science Press, edn. 3, pp. 408-412 (1989).
3. Z.-G. Zhao, *Chem. Res. Appl.*, **13**, 600 (2001).
4. A.E.J. Ofomaja, *Chem. Eng. J.*, **120**, 35 (2007).