Study on Adsorption of Toluene Waste Gas by Acid -base Modified Waste Activated Carbon

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Abstract: Activated carbon is inactivated due to pore blockage in the process of using. Modification of activated carbon to improve adsorption capacity is a hot research issue.By using the method of impregnation modification with acid and alkali, the effect of different concentrations of acid and alkali on the physicochemical properties of activated carbon and toluene adsorption performance.The results showed that the BET specific surface area, micropore area and pore volume of activated carbon were increased by both acid and base modification.Acid modification increased the number of surface acidic functional groups, while alkali modification showed the opposite change.With the increase of acid-base concentration, the saturated adsorption capacity increased first and then decreased, with the maximum of 80.63 mg • g-1 and 74.21 mg • g-1.The saturation time of penetration and adsorption is 20 min and 260 min after modification with 15% nitric acid, and 15 min and 240 min after modification with 10% sodium hydroxide.

1. Introduction

Activated carbon as an excellent adsorbent is widely used in industrial waste gas treatment[1-6]. However, in the process of adsorption and desorption, pore blockage and material damage will occur, resulting in a large number of activated carbon becoming hazardous waste (hereinafter referred to as waste carbon)[7-8].Its processing cost is high and causes waste of resources. Toluene is a typical volatile organic compound, which poses a great threat to human health[9-11]. Among the technologies for its treatment, activated carbon adsorption has a better performance in terms of operation, maintenance and economic cost[12-14]. In order to make the purification process of toluene waste gas more economical and easy to popularize, the simple and easy method to improve the adsorption efficiency is preferred for the selection of activated carbon modification methods. In this study, nitric acid and sodium hydroxide impregnation modification method[15-19] was used to treat the waste carbon, and the saturated adsorption capacity was improved by changing the pore structure and surface chemical characteristics of the waste carbon. Through the static and dynamic

adsorption test methods, we compare and analyze the influence of different concentrations of the modified solution on the toluene saturation of the waste carbon to find the best concentration and the most economical and effective modification method to reduce the actual process cost.

2. Materials and Methods

2.1. Experimental Materials

The original waste activated carbon is represented by AC, ACA5%、ACA10%、ACA15%、ACA20% represent the waste carbon modified by nitric acid solution with different mass fraction, ACB5%、ACB10%、ACB15%、ACB20% represent waste activated carbon modified by sodium hydroxide solution with different mass fraction. The operation method is as follows: take 10 g of pretreated waste carbon into 150 mL modified solution, shake it in a water bath shaker at 30 ℃ for 3 h, stand for 24 h, filter and wash it with deionized water to neutral, dry it at 110 ℃ for 12 h, and seal it for standby.

2.2. Sample Modification

The original waste activated carbon is represented by AC, ACA5%、ACA10%、ACA15%、ACA20% represent the waste carbon modified by nitric acid solution with different mass fraction, ACB5%、ACB10%、ACB15%、ACB20% represent waste activated carbon modified by sodium hydroxide solution with different mass fraction. The operation method is as follows: take 10 g of pretreated waste carbon into 150 mL modified solution, shake it in a water bath shaker at 30 ℃ for 3 h, stand for 24 h, filter and wash it with deionized water to neutral, dry it at 110 ℃ for 12 h, and seal it for standby.

2.3. Sample Characterization

Scanning electron microscopy (SEM, Hitachi S-4800, Japan) was used to analyze the surface morphology and surface elements of the samples.The number of oxygen-containing functional groups on the surface of activated carbon was determined by Boehm titration.The specific surface area analyzer (Micromeritics, ASAP2020C) is used to determine the specific surface area, pore volume and the sample parameters such as pore size distribution.Before the sample test, vacuum and high-temperature drying at 200 ℃ for 12 hours to remove residual moisture in the sample micropores, and then use -196 ℃ N2 as the adsorption medium to obtain the N2 adsorption desorption isotherm.BET method is used to calculate the specific surface area, microporous and mesoporous pore size distribution is calculated using HK and BJH methods respectively.

2.4. Toluene Adsorption Experiment

2.4.1. Static Adsorption Experiment

One gram of modified and unmodified waste carbon was put into a sealed quartz tube filled with toluene standard gas (purity 99.5%, 100ppm) respectively for 48 hours, and then the waste carbon was taken out and weighed. The mass difference before and after modification was the adsorption saturation of the waste carbon for toluene.

2.4.2. Dynamic adsorption experiment

The experimental device consists of three parts: VOCs generation device, reactor and VOCs concentration detection device (as shown in Figure 1).The high purity air and toluene vapor pumped out of the nitrogen cylinder are fully mixed in the buffer cylinder (the concentration can be controlled by adjusting the flow ratio of the two gas channels).The inlet sampling point is connected with the adsorption pillar through a three-way valve. After the inlet gas concentration is stable, the mixed gas is switched to the adsorption column branch, and the outlet gas concentration is analyzed by timing sampling.When the outlet concentration was the same as the inlet concentration and kept for 30 min, the adsorption experiment ended.

After gas sampling, toluene concentration was determined by gas chromatograph with built-in FID detector (SHIMADZU GC-2014C).Each experiment was repeated three times, and the average concentration of toluene was taken to reduce the experimental error.
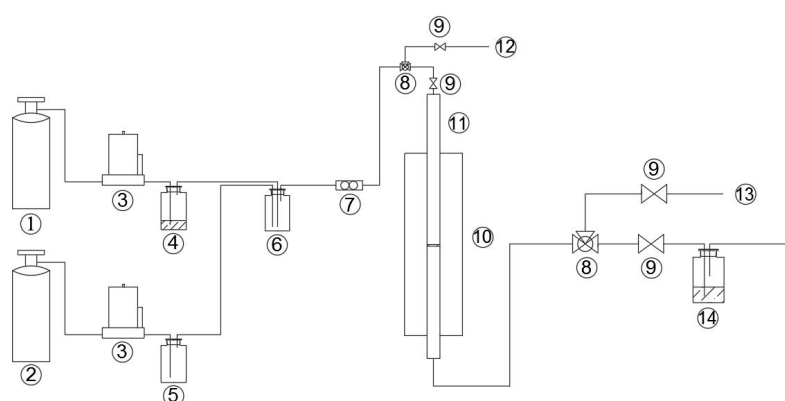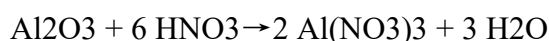

1. Pure nitrogen; 2. Pure air; 3. Mass flowmeter; 4. Toluene solution; 5. Buffer bottle; 6. Mixing cylinder; 7. Rotor flowmeter; 8. three-way connector; 9. One way valve; 10. Tubular furnace; 11. Quartz sand core pipe; 12. Inlet sampling port; 13. Outlet sampling port; 14. Toluene absorption device
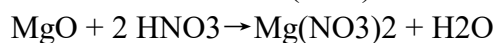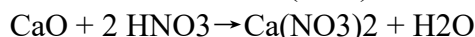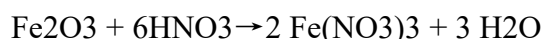
Figure 1: Composition diagram of adsorption device.

3. Experimental Results and Discussion

3.1. Structural Characterization Results and Analysis

The surface structure of the waste carbon before and after modification was analyzed by SEM, and the results were shown in Figure 2. Before modification, the waste carbon (Figure. 2a) presents a porous shape, with densely distributed small holes and interspersed macroporous channels. Impurities were clearly visible on the surface of the waste carbon, and macropores and micropores were blocked by ash impurities. This part of impurities should be hydroxides and metal salts, such as SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, etc. The ash that constitutes the waste carbon affects the adsorption quality of the waste carbon. After the nitric acid modification (Figure. 2b) and sodium hydroxide modification (Figure. 2c), the surface structure of the waste carbon becomes uniform and the pore structure is obvious. The number of macropores decreases and the number of micropores increases, showing an intensive structure of micropores. Impurities in the pores are dissolved and removed to make the pores become transparent, thus improving the quality of waste carbon and increasing the saturated adsorption capacity, which is consistent with the research of scholars such as Zhang Lidan[20]. The reaction equation between impurity and nitric acid is as follows:

$$Al_2O_3 + 6\ HNO_3 \rightarrow 2\ Al(NO_3)_3 + 3\ H_2O$$

$$Fe_2O_3 + 6HNO_3 \rightarrow 2\ Fe(NO_3)_3 + 3\ H_2O$$
$$CaO + 2\ HNO_3 \rightarrow Ca(NO_3)_2 + H_2O$$
$$MgO + 2\ HNO_3 \rightarrow Mg(NO_3)_2 + H_2O$$

The reaction equation between impurity and sodium hydroxide is as follows：
$$SiO_2 + 2\ NaOH \rightarrow Na_2SiO_3 + H_2O$$
$$2\ Al_2O_3 + 2\ NaOH + 3\ H_2O \rightarrow 2\ NaAl(OH)_4$$
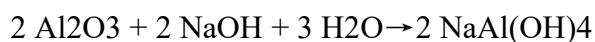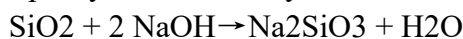
The pore structure parameters of waste carbon before and after modification are shown in Table 1. The BET specific surface area, micropore area and micropore volume are all increased.
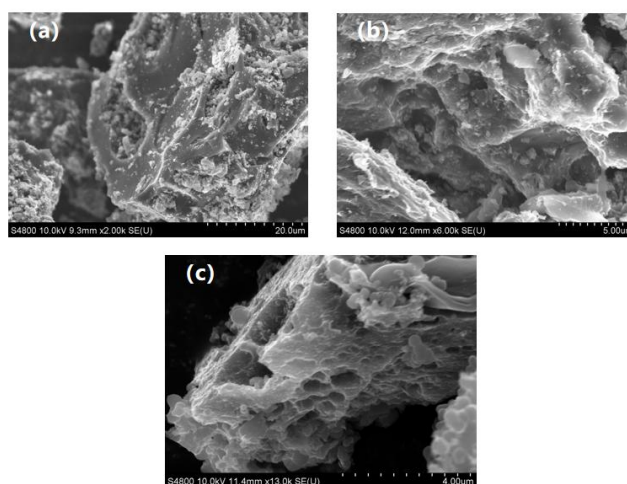

Figure 2: SEM analysis results before and after modification.

Table 1: Pore structure parameters of waste carbon before and after modification.

Modified way	Project	AC	5%	10%	15%	20%
Acid modified	BET specific surface area/$m^2 \cdot g^{-1}$	165.69	186.34	190.68	203.45	193.65
	Micropore surface area /$m^2 \cdot g^{-1}$	80.93	108.65	120.81	140.96	125.43
	The distributed capacitance/$cm^3 \cdot g^{-1}$	0.218	0.267	0.301	0.314	0.293
	The average pore diameter/nm	1.873	1.982	1.977	1.943	1.905
Alkali modification	BET specific surface area/$m^2 \cdot g^{-1}$	165.69	173.96	187.36	180.65	178.77
	Micropore surface area /$m^2 \cdot g^{-1}$	80.93	87.69	110.98	98.6	94.37
	The distributed capacitance/$cm^3 \cdot g^{-1}$	0.218	0.223	0.273	0.259	0.246
	The average pore diameter/nm	1.873	1.756	1.912	1.803	1.855

The content of oxygen-containing groups on the surface of the waste carbon modified by nitric acid and sodium hydroxide was calculated by the Bohem titration method (Table 2 and Table 3).

Table 2: Content of oxygen functional groups on the surface of waste carbon before and after the modification with different concentrations of nitric acid (mmol · g-1) .

Types of functional groups	AC	ACA5%	ACA10%	ACA15%	ACA20%
carboxyl	0.142	0.161	0.188	0.205	0.227
Phenolic hydroxyl	0.132	0.154	0.167	0.196	0.219
Acid oxygen-containing functional groups	0.285	0.323	0.365	0.421	0.456
Basic oxygen-containing functional groups	0.361	0.346	0.322	0.27	0.249
Total oxygen-containing functional groups	0.646	0.669	0.687	0.691	0.705

It can be seen from table 2 that with the increase of nitric acid concentration, the proportion of oxygen-containing functional groups and acid oxygen-containing functional groups (mainly carboxyl groups) on the surface of waste carbon increases, and the basic oxygen-containing functional groups are neutralized or oxidized, thus decreasing. The waste carbon shows stronger acidity. After modification with 5%, 10%, 15% and 20% nitric acid, the content of acidic oxygen-containing functional groups increased by 13.33%, 28.07%, 47.72% and 60% compared to waste carbon, and basic oxygen-containing functional groups decreased by 4.16%, 10.8 %, 25.21% and 31.02%. By analyzing the reasons, it can be seen that nitric acid has oxidizability and can neutralize with basic oxygen-containing functional groups. With the increase of nitric acid concentration, the oxidizability gradually increases, the proportion of oxygen-containing functional groups and acid oxygen-containing functional groups increases, and the waste carbon shows stronger acidity[21]. Due to the introduction of chemical functional groups on the surface, the chemical properties of the surface are changed. The introduction of surface oxygen functional groups can increase the adsorption active sites, which is conducive to increasing the amount of chemical adsorption.

Table 3: Content of oxygen functional groups on the surface of waste carbon before and after modification with sodium hydroxide at different concentrations (mmol • g-1).

Types of functional groups	AC	ACB5%	ACB10%	ACB15%	ACB20%
carboxyl	0.142	0.127	0.106	0.084	0.066
Phenolic hydroxyl	0.132	0.119	0.092	0.076	0.041
Acid oxygen-containing functional groups	0.285	0.254	0.203	0.176	0.109
Basic oxygen-containing functional groups	0.361	0.364	0.369	0.367	0.377
Total oxygen-containing functional groups	0.646	0.618	0.572	0.543	0.486

It can be seen from table 3 that the neutralization reaction between sodium hydroxide and the acidic oxygen-containing functional groups on the surface of waste carbon makes the acidic oxygen-containing functional groups gradually decrease with the increase of sodium hydroxide

solution concentration, and the decreasing percentages are 10.88%, 28.77%, 38.25% and 61.75%. Although the content of basic functional groups on the surface did not increase, the surface of the modified waste carbon showed stronger alkalinity with the decrease of the content of acidic oxygen-containing functional groups. The main reason for this change is that sodium hydroxide modification belongs to reductive modification, which reacts with acidic functional groups on the surface of activated carbon and consumes acidic oxygen functional groups. Although the content of basic groups on the surface of waste carbon increased less, the proportion of basic oxygen-containing groups increased, and the surface of waste carbon showed stronger alkalinity, which enhanced the non-polarity of the surface of waste carbon.Toluene is asymmetric in structure and belongs to polar molecule, but methyl is very small, so its polarity is weak and it can be regarded as non-polar molecule. Therefore, the waste carbon modified by sodium hydroxide improves the adsorption capacity of toluene[22].

3.2.   Effect of Modified Waste Carbon on Adsorption of Toluene

3.2.1. Effect of Acid-base Concentration on Static Adsorption of Toluene by Waste Carbon

The waste carbon modified by nitric acid and sodium hydroxide was used to carry out adsorption experiments on toluene for many times under the same conditions, and the saturated adsorption capacity was taken as the average value of many experiments. The results are shown in Figure 3.
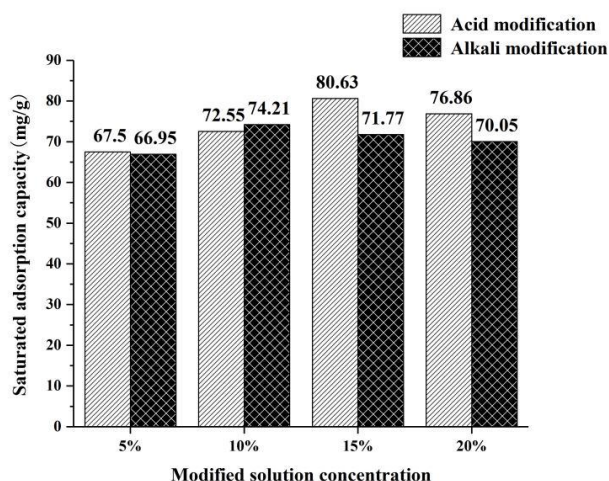

Figure 3: Saturated adsorption capacity of waste carbon after impregnation of modified solution with different concentration.

The results show that the saturated adsorption capacity of toluene on waste carbon before modification is 65.45 mg·g-1 . It can be seen from Fig. 3 that the saturated adsorption capacity of toluene on acid and alkali modified waste carbon has increased, and the growth amount first increases and then decreases with the increase of modified solution concentration. The acid modified saturated adsorption capacity increased by 3.13%, 10.85%, 23.19% and 17.43% respectively, and the highest adsorption capacity reached 80.63 mg·g-1 . The order of adsorption capacity for toluene was aca15% > aca20% > aca10% > aca5% > AC.The saturated adsorption capacity of alkali modification increased by 2.29%, 13.38%, 9.66% and 7.03% respectively, and the highest adsorption capacity reached 74.21 mg·g-1 . The order of adsorption capacity for toluene was acb10% > acb15% > acb20% > acb5% > AC.From the analysis of saturated adsorption capacity, the modification of nitric acid and sodium hydroxide is an effective method to improve the

adsorption performance of waste carbon and improve the quality of waste carbon, which can be applied to the treatment process of waste gas containing toluene.

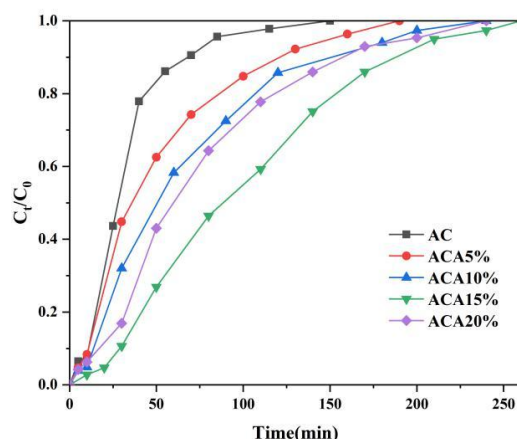### 3.2.2. Effect of Acid-base Concentration on Dynamic Adsorption of Toluene by Waste Carbon

Figure 4: Adsorption breakthrough curves of different concentrations of acid-modified waste carbon.
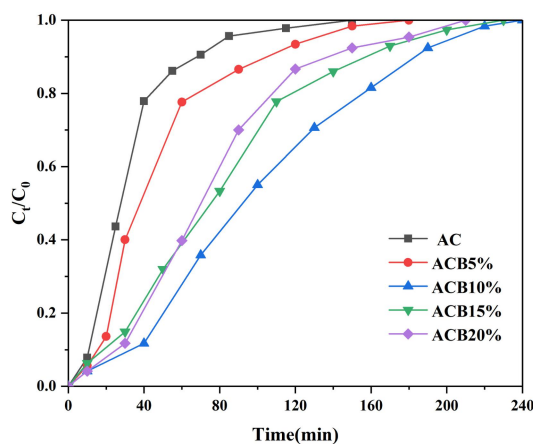

Figure 5: Adsorption breakthrough curves of modified waste carbon with different concentrations of alkali.

Using toluene as adsorbent, dynamic adsorption experiment was used to determine the adsorption breakthrough curve of waste carbon before and after modification. It can be seen from Fig. 4 and Fig. 5 that when the concentration of toluene vapor is constant, the adsorption capacity of acid and alkali modified waste carbon for toluene is improved. Before modification, the adsorption of p-toluene on the waste carbon penetrated in 5min and reached saturation in 150 min.The breakthrough time and adsorption saturation time increased first and then decreased with the increase of modified solution concentration. When the concentration of nitric acid was 15%, the modification effect was the best, the penetration time was 20min, the adsorption saturation time was 260 min, the sodium hydroxide concentration at 10% was the best, the breakthrough time was 15min, and the adsorption saturation time was 240 min.

4. Conclusions

(1) Compared with unmodified waste carbon, the specific surface area and pore volume of waste carbon treated by nitric acid and sodium hydroxide increased.The amount of oxygen-containing functional groups of waste carbon modified by nitric acid increased greatly, and the oxygen-containing functional groups of waste carbon modified by 20% nitric acid increased by 60%.The number of oxygen containing acid functional groups on the surface of the waste carbon modified by sodium hydroxide decreased and the alkalinity increased.

(2) In the static adsorption experiment, the order of acid modified adsorption saturation is ACA15% > ACA20% > ACA10% > ACA5% > AC, and the order of alkali modified adsorption saturation is ACB10% > ACB15% > ACB20% > ACB5% > AC. With the increase of acid and alkali concentration, the adsorption capacity first increased and then decreased.

(3) In the dynamic adsorption experiment, the breakthrough time for waste carbon, 15% nitric acid, and 10% sodium hydroxide were 5 min, 20 min, and 15 min, respectively, and the saturation time was 150 min, 260 min, and 240 min, respectively, all of which were extended backward.

Acknowledgments

References

[1] Jiming Hao, Guangtong Ma, Ke Yu, et al. Air pollution control engineering . Higher education press, 1989.

[2] Lixing Zhou . Performance and mechanism of adsorption of benzene and toluene by activated carbon . Kunming University of science and technology, 2011.

[3] Qigang Cen. Study on adsorption and separation of carbon dioxide from flue gas by activated carbon materials . Zhejiang University, 2017.

[4] Moli Qu. Pollution status and treatment technology of VOCs in the atmosphere .Environmental science and management. 37 (06) (2012) 102-104.

[5] Salager J L , Raquel E. Antón, Sabatini D A , et al. Enhancing solubilization in microemulsions―State of the art and current trends. Journal of Surfactants and Detergents. 8(1) (2005) 3-21.

[6] Mingzhe Li, Zhenghong Huang, Feiyu Kang, et al. Progress in control technology of volatile organic compounds . Chemical industry and engineering. 2 (3) (2015) 2-9.

[7] Xu Wei, Liu Junli, Sun Kang. Research progress on the application of activated carbon adsorption in the treatment of volatile organic compounds . Progress in chemical industry.35 (04) (2016) 1223-1229.

[8] Jie Li , Ning Qian. Research progress of adsorption and recovery of VOCs by activated carbon . Chemical environmental protection. 01 (2008) 24-28.

[9] Mohan N,Kannan G K,Upendra S,etal.Breakthrough of toluene vapours in granular activated carbon filled packed bed reactor.Journal of Hazardous Materials.168(2-3) (2009) 777-781．

[10] Yawei Fan, Qixing Zhou . Environmental behavior and ecotoxicology of BTEX . Journal of ecology.27 (4) (2008) 632-638.

[11] Ke Zhao ,Guo Liu , Zhigang Xue , et al. Research progress on temporal and spatial distribution, reaction characteristics and sources of atmospheric BTEX. Industrial safety and environmental protection. 04 (2013) 78-84.

[12] Hashisho Z,Rood M,Botich L.Microwave-swing adsorption to capture and recover vapors from air streams with activated carbon fiber cloth.Environ Sci Technol.39(17) (2005) 6851-6859.

[13] Kebing Li, Houyang Liu, Yushao Bu, et al. New pressure swing adsorption technology for recovering effective components from methanol tail gas and its application . Natural gas chemical industry. 29 (3) (2004) 31-35.

[14] Xincheng Lu, Jianchun Jiang. Treatment of volatile organic compounds and application of activated carbon . Biochemical engineering of biomass. 43 (1) (2009) 45-51.

[15] Nan Ma,Yaojin Tian , Guangping Yang , et al. Study on the performance of modified activated carbon fiber electro Fenton reactor. Environmental science.35 (7) (2014) 2627-2632.

[16] Shim J W,Park S J,Ryu S K．Effect of modification with HNO3 and NaOH on metal adsorption by pitch-based activated carbon fibers.Carbon.39(11）(2001) 1635-1642．

[17] Li L,Liu S Q, Liu J X．Surface modification of coconut shell based activated carbon for the improvement of hydrophobic VOC removal . Journal of Hazardous Materials.192（2）(2011) 683-690．

[18] Wen H C,Yang K,Ou K L,et al．Effects of ammonia plasma treatment on the surface characteristics of carbon fibers .Surface and Coatings Technology.10 (2006) 3166-3169．

[19] Mart ínez F,Pariente I,Brebou C,et al.Chemical surface modified-activated carbon cloth for catalytic wet peroxide oxidation of phenol. Journal of Chemical Technology and Biotechnology.89(8) (2014) 1182-1188．

[20] Lidan Zhang, Xiaopeng Zhao , Qun Ma, et al. Study on adsorption performance of modified activated carbon for benzene waste gas . New carbon materials. 02 (2002) 41-44.

[21] Hanbing Liu , Bing Yang, Nandong Xue . Acid base modified activated carbon and its effect on toluene adsorption. Environmental science.37 (9) (2006)3670-3678.

[22] Fulong LAN . Study on adsorption capacity of modified activated carbon for VOCs. Southwest Jiaotong University, 2017.