

# RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

*Accepted Manuscripts* are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This *Accepted Manuscript* will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

## Comparative study of dry-mixing and wet-mixing activated carbons prepared from waste printed circuit boards by NaOH activation

Yujiao Kan, Qinyan Yue\*, Baoyu Gao, Qian Li

Shandong Provincial Key Laboratory of Water Pollution Control and Resource Reuse, School of Environmental Science and Engineering, Shandong University, Jinan 250100, China

\* Corresponding author. Tel: +86 531 88365258; fax: +86 531 88364513

E-mail address: [qyyue58@aliyun.com](mailto:qyyue58@aliyun.com)

**Abstract:** Two activated carbons have been produced from non-metallic fraction (NMF) of waste printed circuit boards (WPCB) by sodium hydroxide activation in two methods, dry-mixing and wet-mixing. Dry-mixing is the waterless way by direct powder maceration, activated carbon prepared through this way is called AC. Wet-mixing is by impregnation within an aqueous solution, activated carbon prepared through this way is called WAC. Activated carbons differed with the physical structure and chemical properties which were derived from N<sub>2</sub> adsorption/desorption isotherms and Fourier-transform infrared spectroscopy (FTIR). Batched sorption studies were performed to compare the ciprofloxacin (CIP) adsorption properties of the two carbons. Experiments proved that the method of mixing has great influence on the preparation of activated carbons, AC showed better characteristics and adsorption properties than WAC. AC had 2304 m<sup>2</sup>/g of surface area, while WAC had 1141 m<sup>2</sup>/g of surface area. Fourier transform infrared spectra indicated two activated carbons had similar functional groups. For both adsorbents, the adsorption kinetics followed the pseudo-second-order model. The adsorption equilibrium data were very well represented by Langmuir equations.

**Keywords:** waste printed circuit boards; activated carbons; dry-mixing; wet-mixing; carbonation; NaOH

## 1. Introduction

With the phenomenal advancement and growth in electronic industries, much demands for electric and electronic equipments (EEE) make the replacement of electronic equipments more frequent, resulting in large amounts of electronic waste (E-waste) to be disposed of<sup>1</sup>. Current estimate shows nearly 45 million tons of E-waste is generated globally per annum and the number is growing at an exponential rate<sup>2</sup>.

Waste printed circuit boards (WPCB) are one of the most complicated constituents of WEEE. WPCB, which contains valuable resources together with some hazardous materials, are thus considered to be an attractive secondary resource and an environmental contaminant<sup>3</sup>. In order to recycle the valuable resources, hydrometallurgical process which includes various steps of leaching, separation and purification is the main route<sup>4,5</sup>. Unfortunately, toxic water would be generated during these procedures. Novel approaches to reuse WPCB are urgently to be proposed. Because of the high content of organic compounds in non-metallic fraction (NMF) of WPCB<sup>6</sup>, it can be used as a low-cost raw material for preparing activated carbons. Researches focused on the preparation of activated carbon from WPCB are few<sup>7,8</sup>.

Activated carbon can be prepared by different activating agents. The use of alkali hydroxides (NaOH, KOH) for the production of microporous activated carbons has attracted great interest due to the valuable properties of the materials produced by this process. Compared with KOH activations, NaOH activation has advantages such as: (I) lower dosage; (II) cheaper; (III) more environmentally; (IV) less corrosive<sup>9</sup>. Another reason is that NaOH occurs carbonation in the presence of water. Different mixing ways

may display different reactions, which has great influence on the preparation of activated carbon. For the reason above, we choose NaOH as the activating agents.

Ciprofloxacin (CIP) is a synthetic antibiotic widely used for the treatment of several bacterial infections that can end up into water courses due to incomplete metabolism in humans or coming from effluents of drug manufacturers. The presence of CIP in water sources can lead to the development of antibiotic resistant bacteria, which is extremely harmful to the health of the human <sup>10</sup>. Thus, removing CIP from water has become an increasingly important subject. Various methods including adsorption <sup>11</sup>, degradation <sup>12</sup> and oxidation <sup>13</sup> had been studied for removing CIP. Adsorption is considered the most suitable treatment because it inhibits the toxic properties and restricts the transportation into water systems <sup>14</sup>.

This study focused on comparison of dry-mixing and wet-mixing to prepare NMF-based activated carbons by NaOH activation. Dry-mixing is the waterless way by direct powder maceration, activated carbon prepared through this way is called AC. Wet-mixing is by impregnation within an aqueous solution, activated carbon prepared through this way is called WAC. The two activated carbons differed with the physical structure and chemical properties which were derived from N<sub>2</sub> adsorption/desorption isotherms and Fourier-transform infrared spectroscopy (FTIR). Batched sorption studies were performed to compare the CIP adsorption properties of AC and WAC. Experiments proved that the method of mixing had great influence on the preparation of activated carbons, and AC showed better characteristics and adsorption properties than WAC.

## **2. Materials and methods**

### *2.1. Materials*

The non-metallic powders were provided by Shandong Zhonglv Eco-recycle Co., Ltd. The properties of the raw materials were represented in Fig.1. All chemical reagents

used in this study were analytical grade. CIP ( $C_{17}H_{18}FN_3O_3$ ) was purchased from Sangon Biotech (Shanghai, China) Co., Ltd.

## 2.2. Preparation of AC and WAC

First, a carbon-rich carbonized sample was prepared from the pyrolysis of the raw materials under  $N_2$  atmosphere at  $600\text{ }^\circ\text{C}$  for 2 h. The carbonized sample was solid powder with size lower than 0.25 mm (60 mesh) diameter. Next, the carbonized sample was mixed with NaOH by two different processes: dry-mixing or wet-mixing. The progress flow charts had been showed in Fig.2.

In the dry-mixing, sodium hydroxide powders are directly mixed with a given amount of the carbonized sample. It should be emphasized that the process is done in absence of water.

In the wet-mixing, the carbonized sample was mixed with sodium hydroxide adding 10mL distilled water. Then stirring often to make sure the sodium hydroxide dissolved completely. After the impregnation process, the mixtures were dried at  $110\text{ }^\circ\text{C}$  for 5 h.

For the two preparation methods, dry-mixing or wet-mixing, the NaOH/carbonized sample weight ratio was kept equal to 3:1. The activation heat-treatments were conducted under  $N_2$  flow at  $800\text{ }^\circ\text{C}$  for 1 h in a cylindrical furnace. After the heat treatment, a washing process was carried out by using a 2 M HCl solution firstly, and afterwards washed with distilled water until the pH value reached to neutral. Then, carbons were dried at  $110\text{ }^\circ\text{C}$  for 4 h, ground and sieved by sieves to 0.147 mm. The carbon prepared by dry-mixing was named as AC. The carbon prepared by wet-mixing was named as WAC.

## 2.3. Characterization methods

SDT Q600 equipment was used to obtain thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC) diagram. Scanning electron microscope (SEM, Hitachi S-520) was used to study the changes in surface morphology. The BET surface area ( $S_{BET}$ ) and porous properties of AC and WAC were determined by  $N_2$  adsorption/desorption isotherms at 77 K using a surface area analyzer (Quantachrome Corporation, USA). The  $S_{BET}$  and the total pore volume ( $V_{tot}$ ) were obtained by the manufacturer's software. The  $S_{BET}$  was derived from the Brunauer–Emmett–Teller (BET) theory. The micropore surface area ( $S_{mic}$ ), external surface area ( $S_{ext}$ ) and the micropore volume ( $V_{mic}$ ) were evaluated by the t-plot method. The pore size distribution was obtained by the Density Functional Theory (DFT) method. The mean pore diameter ( $D_p$ ) was obtained from  $D_p = 4V_{tot}/S_{BET}$ . The surface functional groups of AC and WAC were recorded by the KBr technique using a Fourier transform infrared (FTIR) spectrometer (Fourier-380FT-IR, USA), and the spectra were recorded in the spectral range 4000–400  $cm^{-1}$ .

#### 2.4. Adsorption procedure

Parallel series of batch adsorption tests were carried out in conical flask with cap containing AC or WAC. In both of them, 0.05 g of solid adsorbent was introduced to 50 mL solution containing a specific amount of CIP (200-800 mg/L). All pH measurements were carried out using a pH meter (Model PHS-3C, Shanghai, China). The initial pH levels of the experimental solutions were adjusted to constant values by adding various concentrated HCl or NaOH solutions. The flasks were then transferred to a water-bath thermostatic shaker (SHA-B, Shanghai, China) at determined temperature and shook at

170 rpm for 24 h to ensure that the adsorption process reached equilibrium. One conical flask containing 50 mL CIP solution sample was taken off at various time intervals to determine adsorption kinetics. Samples were filtered using a 0.45  $\mu\text{m}$  membrane filter, and the CIP concentration of the filtrate was analyzed using UV/Vis spectrophotometer (UV-754, Shanghai) at the maximum wavelength of 275 nm.

### 2.5. Adsorption isotherm and kinetic models

In order to explain the adsorption mechanism, the kinetic data were analyzed with pseudo-first-order<sup>15</sup>, pseudo-second-order<sup>16</sup>, Elovich<sup>17</sup> and intra-particle diffusion models<sup>18</sup>. Similarly, the isothermal data were analyzed with Langmuir<sup>17</sup>, Freundlich<sup>19</sup> and Temkin models<sup>20</sup>. The kinetic and isotherm models were listed in Table 1. The determination coefficient ( $R^2$ ) and normalized standard deviation ( $\Delta q_e$ ) were evaluated to define which models best describes the experimental data.  $\Delta q_e$  was calculated using the following equation<sup>20</sup>:

$$\Delta q_e (\%) = 100 \times \sqrt{\frac{\sum [(q_{e,\text{exp}} - q_{e,\text{cal}}) / q_{e,\text{exp}}]^2}{N - 1}} \quad (1)$$

Where  $N$  is the number of experimental data points.

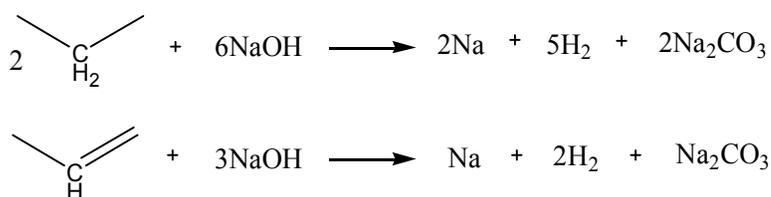
## 3. Results and discussion

### 3.1. Thermal analysis

The two samples were prepared by dry-mixing or wet-mixing, respectively. Both of them were heated between 20 and 800 °C under N<sub>2</sub> atmosphere. The thermal analyses are illustrated in Fig.3. The pyrolysis process can be divided into three steps: an initial weight loss due to the evaporation of moisture (a: 5.19%; b: 12.58%), a significant mass loss in 200-500 °C, which was the main weightlessness area for the precursors (a: 27.86%; b:

22.31%), benzene reacted with NaOH to form new structures resulting in the loss of organic compounds. A slow mass loss at the last stage between 500 and 800 °C (a: 8.43%; b: 6.49%), confirming the stable structure of the resultant char was formed in this temperature range. Because of the different mixing method, the thermal analyses of two samples in the three mass loss stages have significant differences, especially in the first stage, since the precursor of WAC have higher moisture content than the precursor of AC.

The carbon-rich carbonized sample was prepared from the pyrolysis of the non-metallic powders under N<sub>2</sub> atmosphere at 600 °C for 2 h. The main reaction process was showed in Fig.4. The first step of the decomposition process is the release of water and the formation of unsaturated structure. For the structure I, when C-O and C-Br were broken, bisphenol A (BPA) would be generated. For the structure II, the extraction of H resulted in the formation of phenol. Structure II reacted with NaOH under different conditions. The main reactions were showed as follows <sup>21</sup>:



### 3.2 SEM analysis

The SEM profiles of AC and WAC were presented in Fig. 5. Both the samples had a significant difference in appearance. The fragmentation degree of AC was higher than that of WAC. The activating agents-NaOH played a bigger role in the dry-mixing than in the wet-mixing. During the wet-mixing, part of NaOH occurred carbonation, which prevent the development of porosity. The porosity of two samples was related to the volatile matter and gas generated in the activation progress.

### 3.3 Textural structure

The N<sub>2</sub> adsorption/desorption isotherms at 77 K has been determined in AC and WAC to assess their porous texture, which conclude pore volume, pore area and average pore diameter. Fig. 6 and Fig. 7 show the N<sub>2</sub> adsorption/desorption isotherms and pore size distributions, respectively. The structural parameters of AC and WAC were summarized in Table 2.

According to the classification of International Union of Pure and Applied Chemistry<sup>22</sup>, the majority of physisorption isotherms can be grouped into the six types corresponding to six different types of pore structure. From Fig. 6, it can be seen that the N<sub>2</sub> adsorption/desorption isotherms for both adsorbents belongs to types I, corroborating that AC and WAC are microporous carbons. Additionally, the plateau showed nearly parallel to the axis of  $P/P_0$ , confirming the presence of micropores with no or few mesopores<sup>23</sup>. Compared with WAC, the pronounced increase in the volume of N<sub>2</sub> adsorbed and desorbed amount at the low pressure region of AC demonstrates the development of microporosity. In addition, the pore size distribution (Fig.7) of AC and WAC showed that a vast majority of the pores fall into the range of microspore.

As shown in Table 2, WAC showed a low  $S_{BET}$  in comparison to AC, probably because the amount of NaOH was not sufficient react with chars. When the materials containing NaOH and water are in air, thus, in a CO<sub>2</sub> atmosphere, the carbonation of the NaOH occurs (R.1), resulting in the reduction of NaOH. In the conditions of activation experiments (activation temperature of 800 °C), the Na<sub>2</sub>CO<sub>3</sub> is stable, is does not turn to any other sodium compound active for the activation, and therefore the carbonation of the

NaOH prevent the development of porosity. In another indication that the yield of WAC is higher than that of AC <sup>24</sup>.

The results above showed that AC has better porous characteristic than WAC. The drying stage during the preparation of WAC is negative, lowering the development of porosity <sup>25</sup>.



### 3.3 Surface chemistry analysis

The adsorption abilities had much to do with the surface chemistry characteristic. In order to understand the surface chemistry differences of AC and WAC, Table 3 summarizes the  $\text{pH}_{\text{pzc}}$  and number of surface functional group. The two adsorbents have different values of surface acidity and basicity, which is represented as the amount of acidic groups and basic groups, respectively. AC has higher  $\text{pH}_{\text{pzc}}$  value, smaller amount of acidic functional group and larger amount of acidic functional group than WAC.

The FTIR spectrums of AC and WAC revealed different functional groups (Fig. 8). The broad band at  $3402 \text{ cm}^{-1}$ , which could be attributed to the O–H stretching vibration from  $\text{OH}^-$  groups (characteristic of NaOH) <sup>23</sup>. The peak at  $1565 \text{ cm}^{-1}$  is attributed to the formation of oxygen functional groups such as C=O stretching in quinone structure <sup>26</sup>. The bands at  $1402 \text{ cm}^{-1}$  are assigned to C–H bending in alkyl groups. The broad band between 1200 and  $1000 \text{ cm}^{-1}$  has been assigned to C–O stretching in alcohols and phenols <sup>26</sup>. This part represented various configurations of C, O, H and N bonds in the carbon structures <sup>27</sup>.

Seen from Fig.8, AC and WAC had very similar spectra, which confirmed that the two samples had the similar functional groups on the surface. It indicated that the

activation mechanism of the two preparation methods were the same. Compared with AC, the intensity of the peaks at  $3402\text{ cm}^{-1}$  in WAC reduced. In the initial reaction period for preparing WAC, the carbonation of the NaOH occurs, NaOH reacted with  $\text{CO}_2$  to form  $\text{Na}_2\text{CO}_3$ , which weakened the intensity of the characteristic band of NaOH at  $3402\text{ cm}^{-1}$  <sup>25, 28</sup>.

### 3.4 Adsorption experiments

#### 3.4.1 The effect of contact time and adsorption kinetics of CIP onto AC and WAC

The time required to reach the equilibrium in the adsorption study has been considered as a significant parameter. Fig. 9 illustrated the effects of contact time on the adsorption of CIP onto AC and WAC at  $25\text{ }^\circ\text{C}$ . The CIP concentration decreased rapidly in the first 4 h, and then the equilibrium was gradually obtained within 13 h. AC exhibit much better sorption and stronger adsorption affinity to CIP due to the larger surface area and total volume compared to WAC. This phenomenon implied that although adsorbent surface area and porous properties were the main affecting factors that affect the adsorption of CIP, other factor like the surface chemistry of adsorbents also may affect the adsorption.

The kinetic parameters were listed in Table 4. It can be seen the models of pseudo-first-order and Elovich were not suitable to describe the experimental data, presenting the lower  $R^2$  (0.92-0.98) and the higher  $\Delta q_e$  values (3.05-10.29%). Instead, the pseudo-second-order model was well fitted to the experimental data with a higher  $R^2$  ( $>0.99$ ) and lower  $\Delta q_e$  value ( $<1.5\%$ ). The pseudo-second-order model assumed that the adsorption progress was affected by chemical interactions which lead to binding of the

adsorbate to the adsorbent surface as strong as covalent bonding, which was consistent with the cation exchange and electrostatic attraction mechanism<sup>18</sup>.

The intra-particle diffusion model assumed the adsorption mechanism occurred through the diffusion of the adsorbate molecules into the pores of adsorbent material<sup>16</sup>. The plots obtained for  $q_t$  versus  $t^{1/2}$  were shown in Fig. 10. The parameters ( $k_{pi}$ ,  $C_i$  and  $R^2$ ) were listed in Table 4. As can be seen in Fig. 10, all the adsorption data exhibit multi-linear plots, illustrating that two or more steps influenced the adsorption process. The first linear sections did not pass through the origin, which meant the intra-particle diffusion was not the only rate-controlling step<sup>29</sup>. The first stage indicated external mass transfer or external film resistance controlled the CIP adsorption. The second stage described the gradual adsorption, where the intra-particle diffusion was the rate-limiting step. The third stage was assigned to the equilibrium, where the intra-particle diffusion started to slow down due to the extremely low concentration of CIP remaining in solution, resulting in lower  $k_{pi}$  values for both stages<sup>30</sup>.

#### 3.4.2 Effect of pH

The adsorption of CIP onto AC and WAC as a function of pH had been shown in Fig. 11. The adsorption of CIP onto AC and WAC was pH-dependent. The main reason for the change of adsorption capacity is the electrostatic interactions between adsorbent and adsorbate<sup>31</sup>. The molecular structure of CIP is also an important factor to affect the adsorption. CIP has three species ( $CIP^-$ ,  $CIP^0$ ,  $CIP^+$ ) under different pH condition.  $CIP^+$  is the cationic form existing in the solution pH < 6.1, which is due to the protonation of the amine group.  $CIP^0$  is the zwitterionic form existing in the solution pH between 6.1 ( $pK_{a1}$ )

and 8.7 ( $pK_{a2}$ ), which contributes to balance the charge in the solution. CIP<sup>-</sup> is the anionic form existing in the solution  $pH > 8.7$ , which is due to a proton loss from the carboxylic group<sup>32</sup>. The adsorption behavior should also be combined with the surface charge characteristics of AC and WAC. The  $pH_{pzc}$  value of the two adsorbents were shown in Table 3. The positively charged adsorbents gradually become negatively charged as the pH value increases<sup>33</sup>. At solution  $pH < pK_{a1}$  ( $pK_{a1}=6.1$ ), the CIP molecules and adsorbents surface have opposite charges, thus adsorption is expected to be enhanced. When  $pH > pK_{a2}$  ( $pK_{a2}=8.7$ ), the amounts of CIP adsorbed onto adsorbents are expected to be depressed, which was because CIP and adsorbents surfaces were negatively charged and repelled each other<sup>34</sup>. The electrostatic effect for the sorption of CIP was shown in Fig.12.

#### 3.4.3 Adsorption isotherm

Adsorption isotherms reflect the capacity of the adsorbents and the interaction between adsorbents and adsorbates. The parameters of isotherm models for Langmuir, Freundlich and Temkin were shown in Table 5. The Langmuir model described an adsorption process that occurred upon a homogeneous surface where the adsorbate is distributed in monolayers. According to the Table 5, Langmuir model showed higher determination coefficient and lower normalized standard deviation than Freundlich and Temkin models, which indicating this adsorption process was monolayer coverage.

#### 3.4.4 Adsorption thermodynamics

Thermodynamic parameters including changes in the standard Gibbs free energy ( $\Delta G$ ), enthalpy ( $\Delta H$ ), entropy ( $\Delta S$ ), were determined by the following equations<sup>35</sup>:

$$\Delta G = -RT \ln K \quad (2)$$

$$\Delta G = \Delta H - T\Delta S \quad (3)$$

where  $R$  ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ) is the gas constant;  $T$  (K) is the absolute temperature;  $K$  ( $\text{L mg}^{-1}$ ) is the Langmuir constant obtained from the plot of  $c_e/q_e$  vs.  $c_e$ . The values of  $\Delta H$  and  $\Delta S$  can be calculated from the slope and intercept of the plot of  $\Delta G$  vs.  $T$ . From Table 6, the  $\Delta G$  values for AC and WAC changed from  $-23.97$  to  $-26.12$  kJ/mol,  $-16.65$  to  $-18.65$  kJ/mol with the increasing temperature, respectively, indicating the adsorption of CIP onto AC and WAC were spontaneous and favorable process and they were more spontaneous at higher temperature. The positive value of  $\Delta H$  confirms an endothermic nature of the adsorption process. The positive value of  $\Delta S$  suggests the increased randomness at the solid/solution interface.

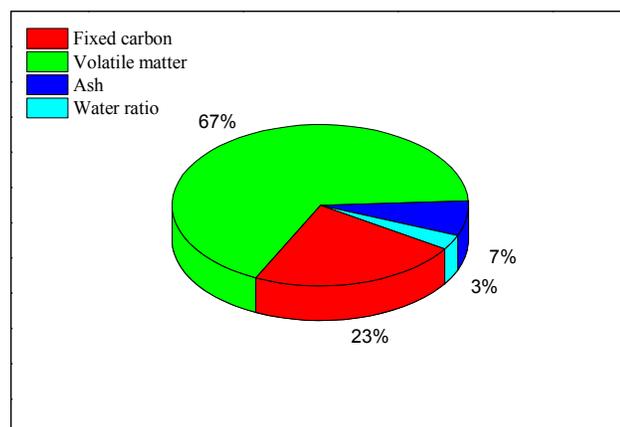
#### 4. Conclusion

Two activated carbons have been produced from NMF of WPCB by sodium hydroxide activation in two methods, dry-mixing and wet-mixing. Dry-mixing is the waterless way by direct powder maceration, activated carbon prepared through way is called AC. Wet-mixing is by impregnation within an aqueous solution, activated carbon prepared through way is called WAC. AC had  $2304 \text{ m}^2/\text{g}$  of surface area and  $1.171 \text{ cm}^3/\text{g}$  of total pore volume, while WAC had  $1141 \text{ m}^2/\text{g}$  of surface area and  $0.576 \text{ cm}^3/\text{g}$  of total pore volume. Fourier transform infrared spectra indicated two activated carbons had similar functional groups. For both adsorbents, the adsorption kinetics followed the pseudo-second-order model. The adsorption equilibrium data were very well represented by Langmuir equations. Experiments proved that the method of mixing has great influence on the preparation of activated carbons, and AC showed better characteristics and adsorption properties than WAC.

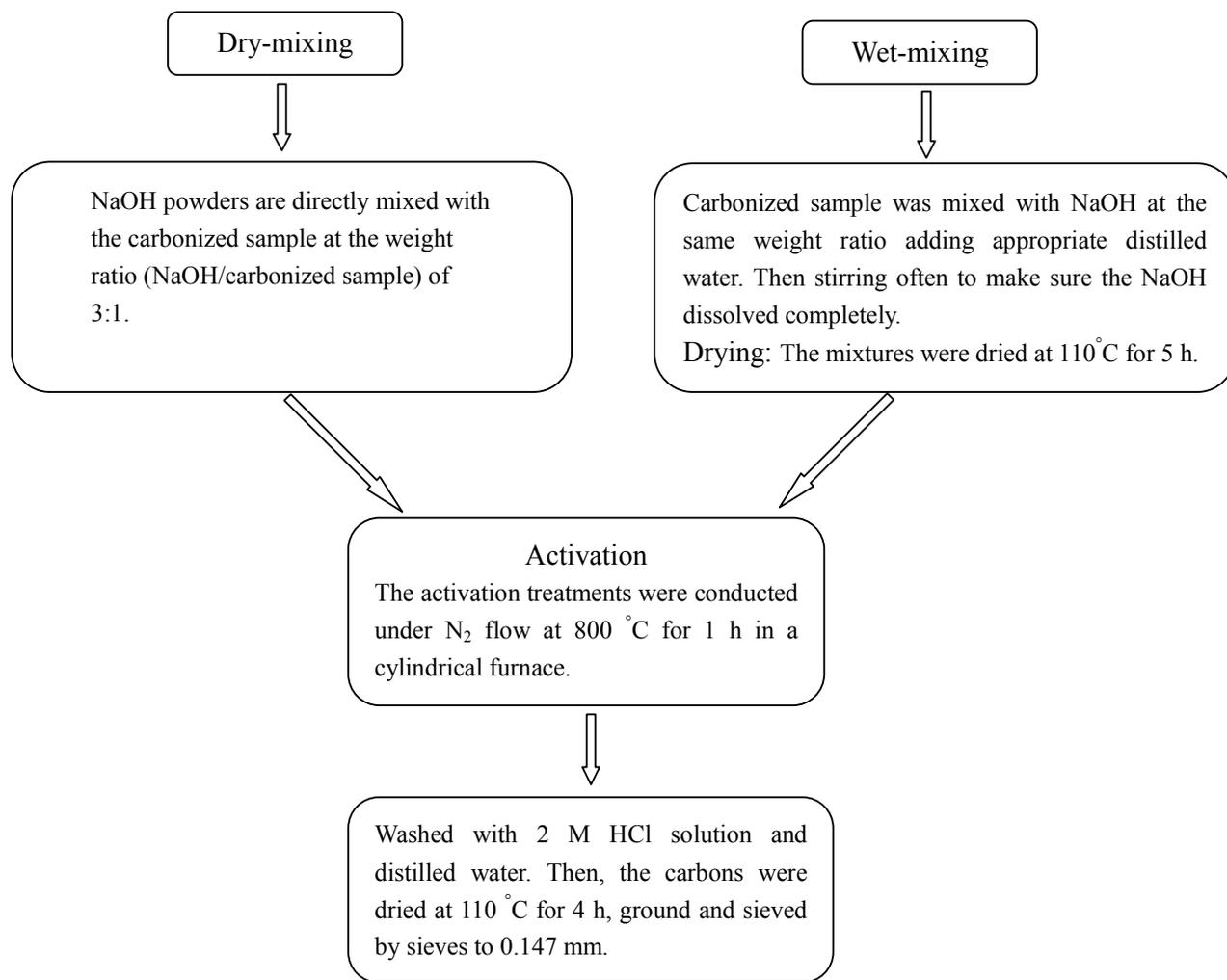
**References:**

1. P. Hadi, C. Ning, W. Ouyang, M. Xu, C. S. K. Lin and G. McKay, *Waste Management*, 2015, **35**, 236-246.
2. B. Ghosh, M. K. Ghosh, P. Parhi, P. S. Mukherjee and B. K. Mishra, *Journal of Cleaner Production*, 2015, **94**, 5-19.
3. T. Hino, R. Agawa, Y. Moriya, M. Nishida, Y. Tsugita and T. Araki, *Journal of Material Cycles and Waste Management*, 2009, **11**, 42-54.
4. Y. Zhang, S. Liu, H. Xie, X. Zeng and J. Li, *Procedia Environmental Sciences*, 2012, **16**, 560-568.
5. I. Birloaga, I. De Michelis, F. Ferella, M. Buzatu and F. Vegliò, *Waste Management*, 2013, **33**, 935-941.
6. Y. Kan, Q. Yue, J. Kong, B. Gao and Q. Li, *Chemical Engineering Journal*, 2015, **260**, 541-549.
7. Y.-H. Ke, E.-T. Yang, X. Liu, C.-L. Liu and W.-S. Dong, *Carbon*, 2013, **60**, 563.
8. J. Q. Zhang, S. H. Liu, J. H. Zu, C. Song and C. B. Yu, *Applied Mechanics and Materials*, 2014, **692**, 396-400.
9. R.-L. Tseng, *Journal of colloid and interface science*, 2006, **303**, 494-502.
10. A. C. Johnson, V. Keller, E. Dumont and J. P. Sumpter, *Science of The Total Environment*, 2015, **511**, 747-755.
11. Y. X. Wang, H. H. Ngo and W. S. Guo, *Science of The Total Environment*, 2015, **533**, 32-39.
12. H. Wang, J. Li, C. Ma, Q. Guan, Z. Lu, P. Huo and Y. Yan, *Applied Surface Science*, 2015, **329**, 17-22.
13. P. Wang, Y.-L. He and C.-H. Huang, *Water Research*, 2010, **44**, 5989-5998.
14. M. Brigante and P. C. Schulz, *Journal of hazardous materials*, 2011, **192**, 1597-1608.
15. Y. X. Wang, H. H. Ngo and W. S. Guo, *The Science of the total environment*, 2015, **533**, 32-39.
16. H. Liu, W. Liu, J. Zhang, C. Zhang, L. Ren and Y. Li, *Journal of hazardous materials*, 2011, **185**, 1528-1535.
17. T. Aysu and M. M. Küçük, *International Journal of Environmental Science and Technology*, 2014, **12**, 2273-2284.
18. B. H. Hameed, *Journal of hazardous materials*, 2009, **161**, 753-759.
19. Y. Sun, Q. Yue, B. Gao, Q. Li, L. Huang, F. Yao and X. Xu, *Journal of colloid and interface science*, 2012, **368**, 521-527.
20. A. C. Martins, O. Pezoti, A. L. Cazetta, K. C. Bedin, D. A. S. Yamazaki, G. F. G. Bandoch, T. Asefa, J. V. Visentainer and V. C. Almeida, *Chemical Engineering Journal*, 2015, **260**, 291-299.
21. M. A. Lillo-Ródenas, J. Juan-Juan, D. Cazorla-Amorós and A. Linares-Solano, *Carbon*, 2004, **42**, 1371-1375.
22. X. Wang, X. Liang, Y. Wang, X. Wang, M. Liu, D. Yin, S. Xia, J. Zhao and Y. Zhang, *Desalination*, 2011, **278**, 231-237.
23. F. Rodriguez-Reinoso, *Pure and Applied Chemistry*, 1989, **61**, 1859-1866.
24. E. Raymundo-Piñero, P. Azañs, T. Cacciaguerra, D. Cazorla-Amorós, A. Linares-Solano and F. Béguin, *Carbon*, 2005, **43**, 786-795.
25. M. A. Lillo-Ródenas, D. Cazorla-Amorós and A. Linares-Solano, *Carbon*, 2003, **41**, 267-275.
26. P. Vinke, M. van der Eijk, M. Verbree, A. F. Voskamp and H. van Bekkum, *Carbon*, 1994, **32**, 675-686.
27. M. M. Rao, D. H. Reddy, P. Venkateswarlu and K. Seshiah, *Journal of environmental*

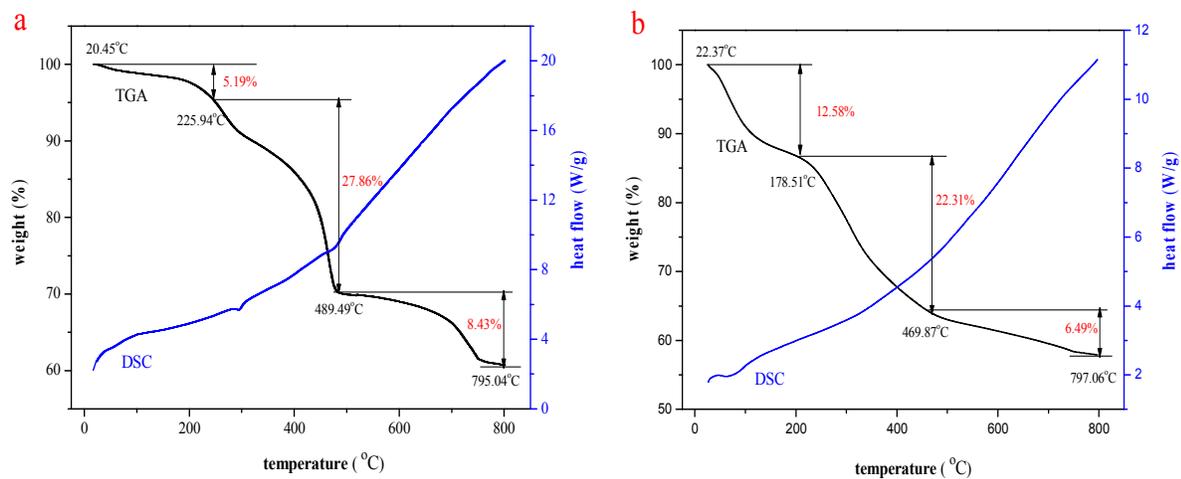
- management*, 2009, **90**, 634-643.
28. P. Zhu, Y. Chen, L. Y. Wang and M. Zhou, *Waste Management*, 2012, **32**, 1914-1918.
  29. S. J. Allen, G. McKay and K. Y. H. Khader, *Environmental Pollution*, 1989, **56**, 39-50.
  30. B. H. Hameed, I. A. W. Tan and A. L. Ahmad, *Chemical Engineering Journal*, 2008, **144**, 235-244.
  31. S. A. C. Carabineiro, T. Thavorn-Amornsri, M. F. R. Pereira and J. L. Figueiredo, *Water Research*, 2011, **45**, 4583-4591.
  32. Q. Wu, Z. Li, H. Hong, K. Yin and L. Tie, *Applied Clay Science*, 2010, **50**, 204-211.
  33. S. A. C. Carabineiro, T. Thavorn-amornsri, M. F. R. Pereira, P. Serp and J. L. Figueiredo, *Catalysis Today*, 2012, **186**, 29-34.
  34. Q. Wu, Z. Li, H. Hong, R. Li and W.-T. Jiang, *Water Research*, 2013, **47**, 259-268.
  35. W. Liu, J. Zhang, C. Zhang, Y. Wang and Y. Li, *Chemical Engineering Journal*, 2010, **162**, 677-684.



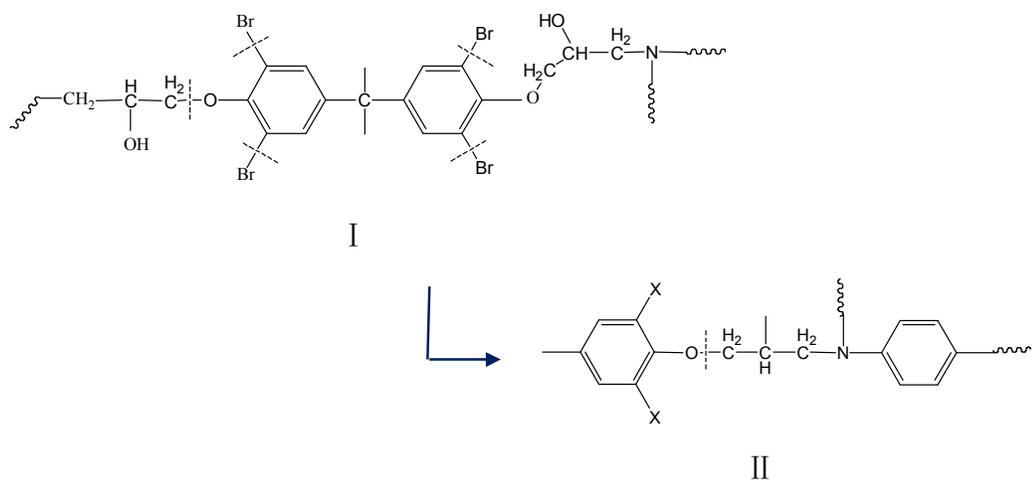
**Fig. 1.** The properties of non-metallic powders.



**Fig. 2.** The progress flow charts of AC and WAC.

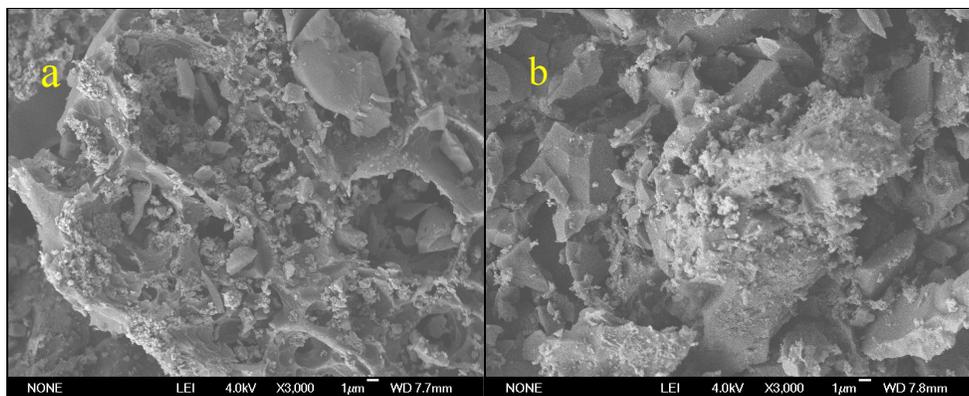


**Fig. 3.** Thermal analysis (DSC/TGA) of dry-mixing (a) and wet-mixing (b)

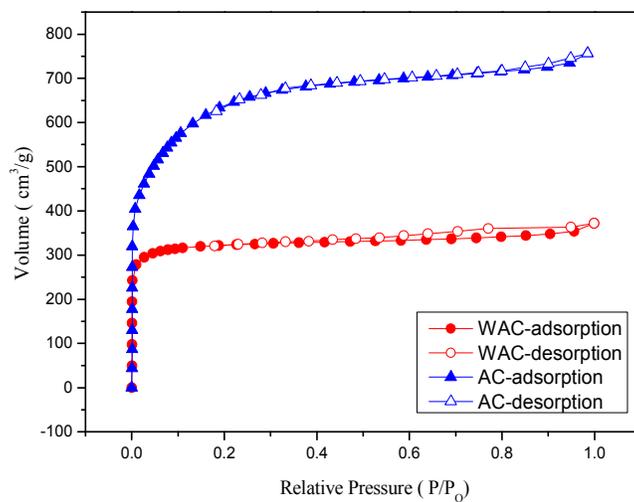


**Fig. 4.** The pyrolysis of epoxy resin monomer ( I :the brominated epoxy resin monomer;

II :X is H or Br)



**Fig. 5.** SEM micrographs of (a) AC and (b) WAC.



**Fig. 6.** The adsorption-desorption isotherms of N<sub>2</sub> at 77 K for AC and WAC.

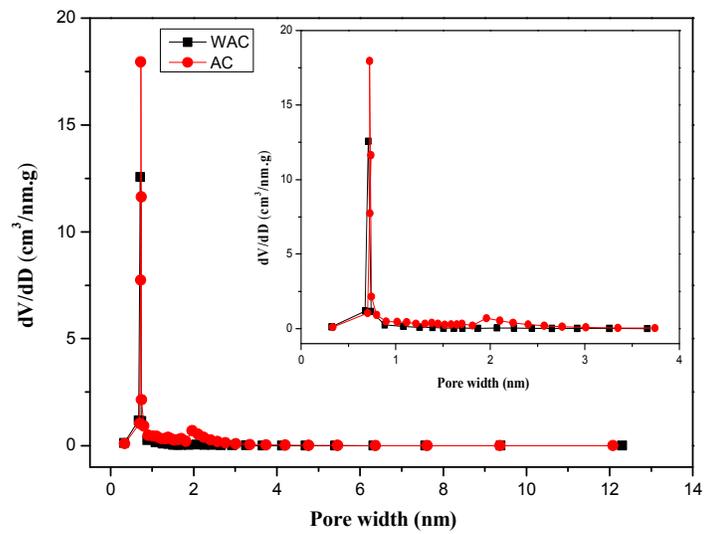
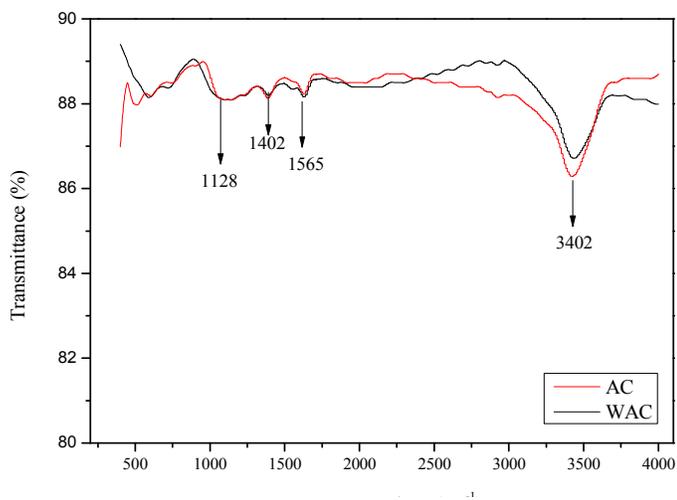
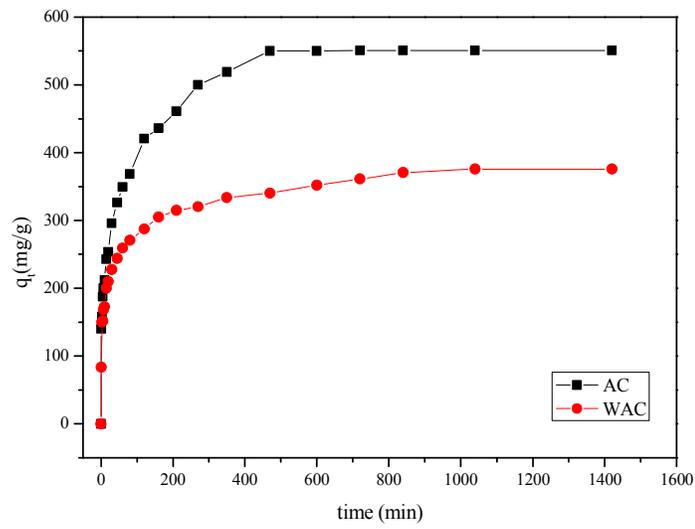


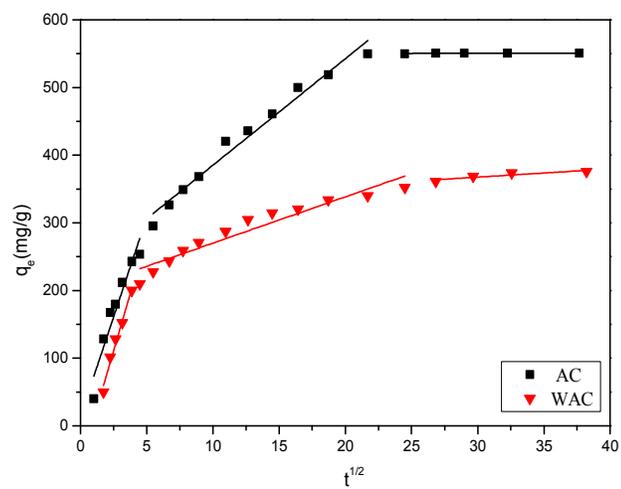
Fig. 7. Pore size distributions for AC and WAC.



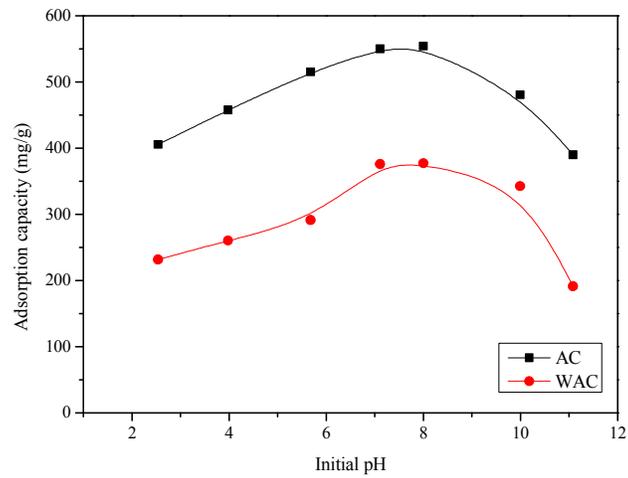
**Fig. 8.** FTIR spectra of AC and WAC.



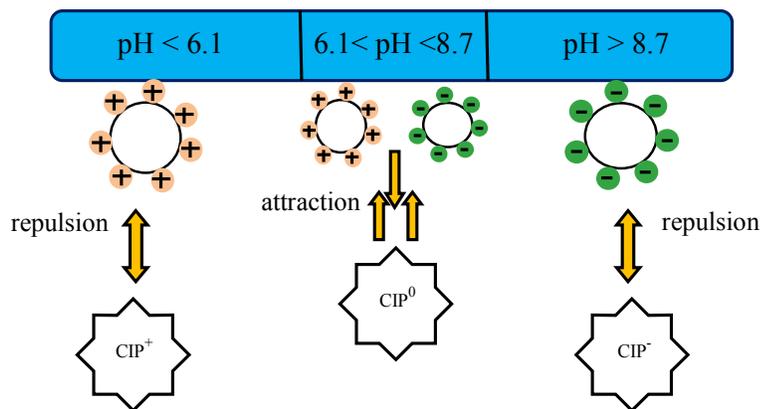
**Fig. 9.** Effect of contact time on CIP adsorption by AC and WAC.



**Fig. 10.** Intra-particle diffusion model for adsorption of CIP onto AC and WAC.



**Fig. 11.** The influence of solution pH on the adsorption of CIP onto AC and WAC.



**Fig. 12.** The electrostatic effect for the sorption of CIP.

**Table 1**

The kinetic models and isothermal models

Kinetic models	Names
$q_t = q_e(1 - e^{-k_1 t})$	Pseudo-first-order
$q_t = \frac{tk_2 q_e^2}{1 + tk_2 q_e}$	Pseudo-second-order
$q_t = \frac{1}{\beta} \ln(1 + \alpha\beta t)$	Elovich
$q_t = k_{pi} t^{1/2} + C_i$	Intra-particle diffusion
Isothermal models	Names
$q_e = \frac{q_m K_L c_e}{1 + c_e K_L}$	Langmuir
$q_e = K_F c_e^{1/n}$	Freundlich
$q_e = B_T \ln(K_T c_e)$	Temkin

$q_t$ —adsorbed amount at any time;  $q_e$ —adsorbed amount at equilibrium;  $k_1$ —rate constant of pseudo-first order model;  $k_2$ —rate constant of pseudo-second order model;  $\alpha$  and  $\beta$ —Elovich constants;  $k_{pi}$  and  $C_i$ —Intra-particle diffusion constant;  $q_m$ —maximum adsorption capacity;  $K_L$ —Langmuir constant;  $K_F$  and  $n$ —Freundlich constants;  $B_T$  and  $K_T$ —Temkin constants.

**Table 2**

Porous structure parameters of AC and WAC

Type	$S_{BET}$	$S_{mic}$	$S_{mic}/S_{BET}$	$S_{ext}$	$S_{ext}/S_{BET}$	$V_{tot}$	$V_{mic}$	$V_{mic}/V_{tot}$	$V_{ext}$	$V_{ext}/V_{tot}$	$D_p$	Yield
	(m <sup>2</sup> /g)	(m <sup>2</sup> /g)	(%)	(m <sup>2</sup> /g)	(%)	(cm <sup>3</sup> /g)	(cm <sup>3</sup> /g)	(%)	(cm <sup>3</sup> /g)	(%)	(nm)	(%)
AC	2304	1938	84.11	366	15.89	1.171	0.847	72.33	0.324	27.67	2.032	34.28
WAC	1141	1073	94.04	68	5.96	0.576	0.474	82.29	0.102	17.71	2.031	38.40

**Table 3**

The surface chemistry of AC and WAC

---

Acidic and basic function group concentration (mmol/g)

---

Samples	pH <sub>pzc</sub>	Basic	Lactone	Carboxyl	Phenolic	Total acidic
AC	6.98	0.971	0.580	0.423	0.969	1.972
WAC	6.25	0.722	0.745	0.311	1.053	2.109

---

**Table 4**

Kinetic parameters for the adsorption of CIP onto AC and WAC

Kinetic models	Parameters	Adsorbent	
		AC	WAC
Pseudo-first-order	$q_{e,exp}$	550.72	375.74
	$q_{e,cal}$	394.26	195.02
	$k_1$	0.0043	0.0031
	$R^2$	0.9612	0.9267
	$\Delta q_e$	6.08	10.29
Pseudo-second-order	$q_{e,exp}$	559.91	380.22
	$k_2$	0.0024	0.0003
	$R^2$	0.9948	0.9986
	$\Delta q_e$	1.35	1.08
Elovich	$\alpha$	437.55	286.78
	$\beta$	0.0234	0.0137
	$R^2$	0.9852	0.9790
	$\Delta q_e$	3.05	4.14
Intra-particle diffusion	$k_{p1}$	31.83	19.15
	$C_1$	112.3	117.2
	$R^2$	0.9921	0.9770
	$k_{p2}$	11.79	4.957
	$C_2$	286.3	236
	$R^2$	0.9381	0.9515
	$k_{p3}$	0.002	1.214
	$C_3$	550.6	331.2
$R^2$	0.9592	0.8296	

**Table 5**

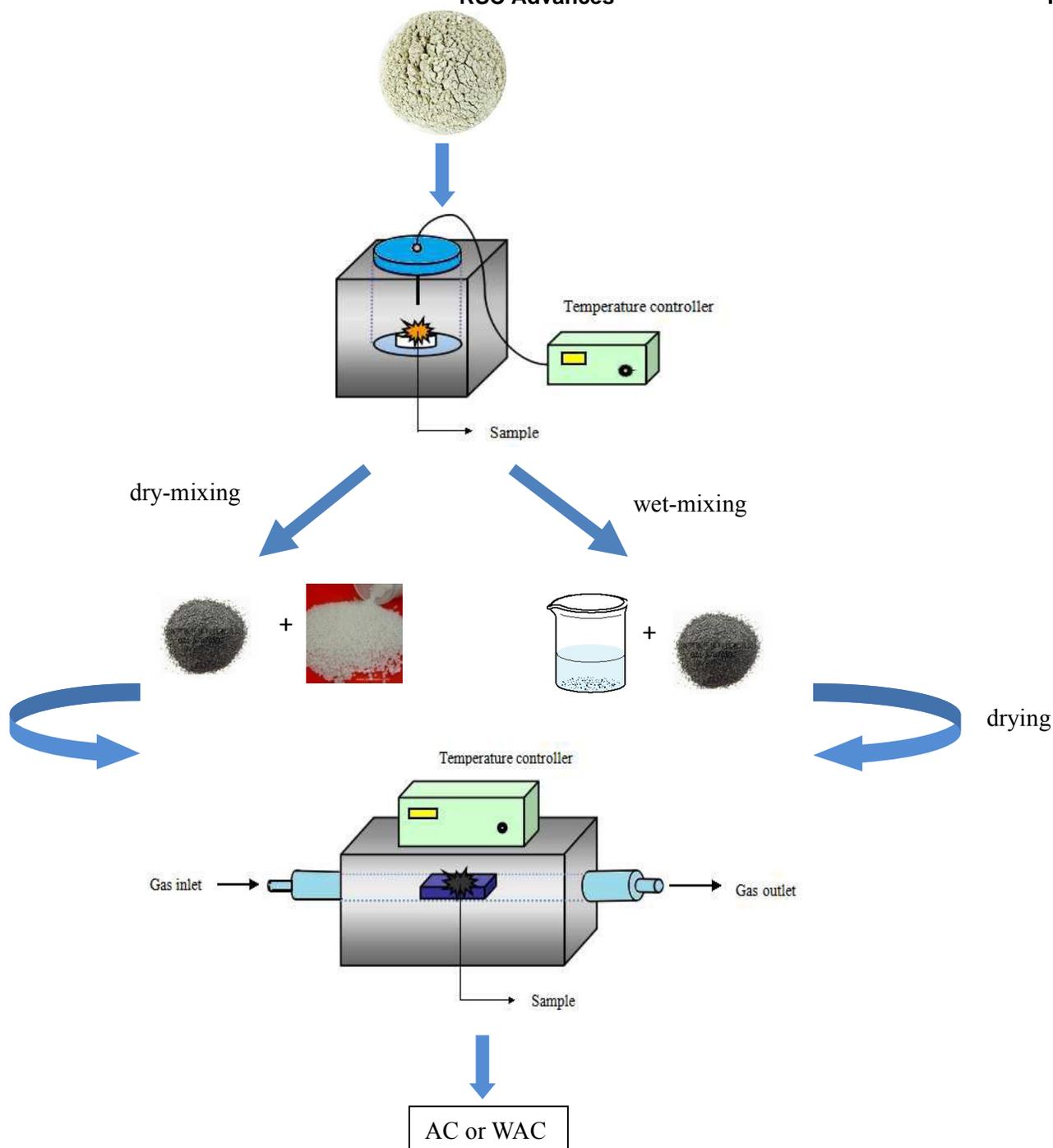
Isotherm parameters for CIP adsorption onto AC and WAC

Isotherm models	Parameters	AC			WAC		
		298K	308K	318K	298K	308K	318K
Langmuir	$q_m$	572.11	586.29	603.84	381.29	406.72	429.65
	$K_L$	0.048	0.051	0.059	0.0025	0.0029	0.0035
	$R^2$	0.9963	0.9903	0.9969	0.9924	0.9942	0.9987
	$\Delta q_e$	0.89	1.17	0.87	1.09	0.93	0.75
Freundlich	$K_L$	297.10	301.72	315.94	176.67	184.99	195.26
	$n$	8.63	7.33	9.04	10.77	11.35	12.07
	$R^2$	0.9814	0.9774	0.9806	0.9733	0.9759	0.9853
	$\Delta q_e$	1.85	2.26	1.90	2.36	2.30	1.54
Temkin	$K_T$	9.874	14.098	21.767	7.176	8.7683	10.0481
	$B_T$	48.21	44.92	41.81	31.64	29.47	25.53
	$R^2$	0.9552	0.9822	0.9370	0.9339	0.9134	0.9005
	$\Delta q_e$	3.92	1.66	5.28	5.45	6.97	8.26

**Table 6**

Thermodynamic parameters for the adsorption of CIP on AC and WAC

Sample	$T$ (K)	$\Delta G$ (kJ/mol)	$\Delta H$ (kJ/mol)	$\Delta S$ (kJ/mol $\cdot$ K)
AC	298	-23.97	8.17	0.11
	308	-24.93		
	318	-26.12		
WAC	298	-16.65	13.27	0.10
	308	-17.59		
	318	-18.65		



Two activated carbons have been produced from non-metallic fraction of waste printed circuit boards by NaOH activation in two methods, dry-mixing and wet-mixing. Dry-mixing is the waterless way by direct powder maceration. Wet-mixing is by impregnation within an aqueous solution, then the mixtures are dried at 110°C for 5 h. The NaOH/carbonized sample weight ratio is kept equal to 3:1. The activation heat-treatments are conducted under N<sub>2</sub> flow at 800 °C for 1 h in a cylindrical furnace. The carbon prepared by dry-mixing is named as AC. The carbon prepared by wet-mixing is named as WAC.