



# Adsorption separation of vinyl chloride and acetylene on activated carbon modified by metal ions



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## ABSTRACT

This work mainly involved the adsorption separation of vinyl chloride and acetylene on modified activated carbons. Six metal ions with different hardness were loaded on activated carbon respectively. The effect of metal ions on the adsorption separation performance of vinyl chloride and acetylene was investigated. The experimental results shown that the separation factor of  $C_2H_3Cl$  to  $C_2H_2$  over modified activated carbon followed the order:  $Al(III)/AC > Mg(II)/AC > Fe(III)/AC > AC > Zn(II)/AC \approx Cu(II)/AC > Ag(I)/AC$ . The effect of the hardness of metal ions on the adsorption capacity of  $C_2H_2$  was more remarkable than that of  $C_2H_3Cl$ , thus the separation factor of  $C_2H_3Cl$  to  $C_2H_2$  increased with the rising of absolute hardness of the metal ions.

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## 1. Introduction

In the last decade, with the sustained development of construction industry, the demand of polyvinyl chloride (PVC) increased rapidly which accounted for about 20% of plastic material usage [1]. Vinyl chloride ( $C_2H_3Cl$ ), as the monomer during the polymerization process, was mainly obtained by hydrochlorination of acetylene ( $C_2H_2$ ), which named by calcium carbide route [2,3]. However, the tail gas of calcium carbide route contained abundant  $C_2H_3Cl$  and  $C_2H_2$ , if it directly discharged into the atmosphere without any treatment, not only it polluted the environment, but also caused an enormous waste of resources [4,5].

At present, adsorption separation technique was widely used to treat the PVC tail gas [6,7]. As the core of adsorption separation, adsorbents with high selectivity of  $C_2H_3Cl$  to  $C_2H_2$  was still needed, which made  $C_2H_3Cl$  return to the polymerization process,  $C_2H_2$  return to the process of hydrochlorination [8,9]. The reported adsorbents included silica gel, activated alumina, zeolite-based materials and carbon-based materials [10]. As porous materials with high specific surface areas and large pore volume, activated carbon (AC) was one of the most important adsorbents, which has been studied for the tail gas treatment [11].

In this paper, six metal ions,  $Al^{3+}$ ,  $Mg^{2+}$ ,  $Fe^{3+}$ ,  $Zn^{2+}$ ,  $Cu^{2+}$  and  $Ag^+$  were separately loaded on the AC to obtain the modified activated carbons. The effect of metal ions on the adsorption separation of  $C_2H_3Cl$  and  $C_2H_2$  were investigated, and the influence of the hardness of metal ions on the separation factor of  $C_2H_3Cl$  to  $C_2H_2$  was discussed.

## 2. Experimental

### 2.1. Materials

The adsorbate (10% vinyl chloride, 10%  $C_2H_2$  and balance with helium) was purchased from Southwest Research Institute of Chemical Industry. The composition simulated the tail gas of the PVC factory.

The AC (40–50 mesh) based on coconut shell, which supplied by Ningxia Activated Carbon Company, China. The other reagents,  $Mg(NO_3)_2$ ,  $Al(NO_3)_3$ ,  $Fe(NO_3)_3$ ,  $Cu(NO_3)_2$ ,  $Zn(NO_3)_2$  and  $AgNO_3$ , were all analytical.

### 2.2. Preparation of adsorbents

$Al(III)/AC$ ,  $Mg(II)/AC$ ,  $Fe(III)/AC$ ,  $Zn(II)/AC$ ,  $Cu(II)/AC$  and  $Ag(I)/AC$  were prepared by impregnating ACs with corresponding metal nitrates separately. 10 g ACs was respectively added to 100 ml 0.1 M  $Al(NO_3)_3$ ,  $Mg(NO_3)_2$ ,  $Fe(NO_3)_3$ ,  $Zn(NO_3)_2$ ,  $Cu(NO_3)_2$  and  $AgNO_3$  aqueous solution respectively at room temperature for 24 h, subsequently filtered and dried at 393 K for 12 h. The loading of metal ions on ACs was measured by combustion experiments

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[12]. The corresponding loading of metal elements on the ACs is 0.5 mmol/g.

### 2.3. Testing of breakthrough curves

The adsorption apparatus was shown in Fig. 1. A typical adsorption separation process was as following. At first, adsorbent with the ratio of length-to-diameter of 15.0 was added into the mini adsorption column. Then the adsorbent was kept by drying in vacuum for 2 h at 363 K to remove the residual water and impurity from the surface of adsorbents. Subsequently, the adsorbate gas flow through the fixed adsorbent bed at a constant rate of 30 ml/min. The adsorption separation of  $C_2H_2$  and  $C_2H_3Cl$  was conducted at 313 K under 0.1 MPa. The concentration of the feed gas ( $C_0$ ) and outlet gas ( $C$ ) was analyzed by GC online. The breakthrough curve was the variation curve of relative concentration of  $C_2H_2$  and  $C_2H_3Cl$  along with time.

## 3. Results and discussion

### 3.1. Breakthrough curves of $C_2H_2$ and $C_2H_3Cl$

The breakthrough curves of  $C_2H_2$  and  $C_2H_3Cl$  on modified ACs by different metal ions have similar shape with the original AC, therefore the original AC was chosen to illustrate the adsorption separation process, as shown in Fig. 2. In order to describe the adsorption process in detailed, the breakthrough curves of  $C_2H_2$  and  $C_2H_3Cl$  were discussed, which marked as the curve “a-b-c-d-e-f” and “a-g-h-f” separately.  $C/C_0 = 0.05$  (b, g), was generally defined as “breakthrough point”, which meant  $C_2H_2$  or  $C_2H_3Cl$  has began detected in outlet gas.  $C/C_0 = 0.95$  (c, h), could be used to calculate the adsorption capacity of  $C_2H_2$  and  $C_2H_3Cl$ , which meant the adsorption capacity of the adsorbate was near to saturated.

After  $C_2H_2$  reached its adsorption saturation point,  $C/C_0 > 1$  was observed on the breakthrough curve of  $C_2H_2$ , which meant  $C_2H_2$  penetrated through the fixed adsorbent bed totally. The concentration of  $C_2H_2$  in the outlet gas increased could be due to two reasons: (1) in the dynamic method experiment,  $C_2H_3Cl$  was adsorbed constantly, which resulted the total content of the outlet gas decreased, so the concentration of  $C_2H_2$  rise and (2) in the adsorption separation processes,  $C_2H_3Cl$  and  $C_2H_2$  had different interaction with the adsorption sites. Because of the stronger

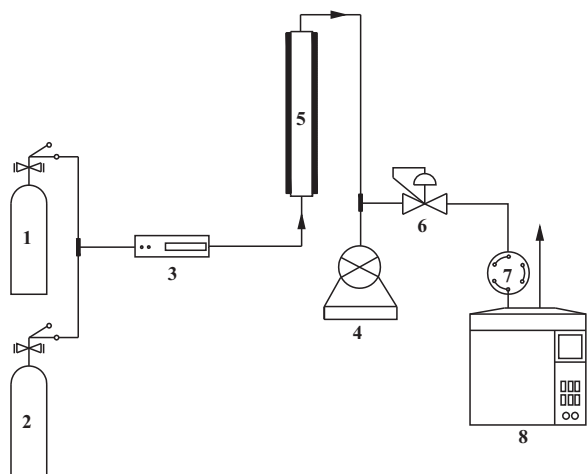


Fig. 1. Schematic diagram of apparatus for gas separation: (1) helium cylinder; (2) the adsorbate gas cylinder; (3) mass flow controller; (4) vacuum pump; (5) mini adsorption column, a stainless steel pipe with 30 cm long and 1.0 cm ID; (6) back pressure valve; (7) six way valve; and (8) gas chromatograph.

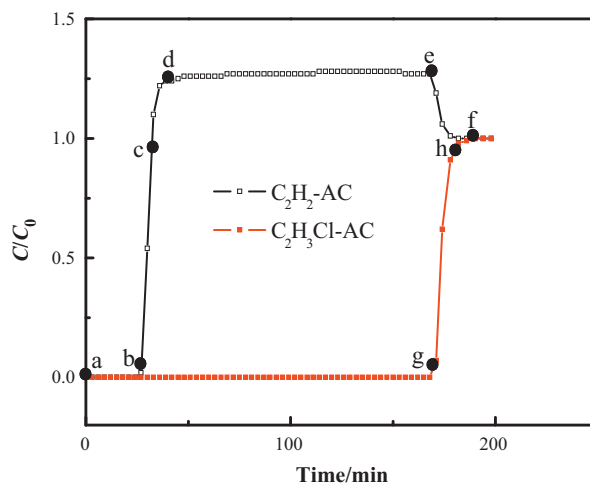


Fig. 2. Breakthrough curves of  $C_2H_2$  and  $C_2H_3Cl$  on the original AC.

competitive adsorption capability of  $C_2H_3Cl$ ,  $C_2H_3Cl$  could replace the adsorbed  $C_2H_2$  continually, made the concentration of  $C_2H_2$  in the outlet gas rise remarkably. If the rise of the concentration of  $C_2H_2$  was only caused by the first reason, the max concentration of  $C_2H_2$  in the outlet gas should be calculated by the following formula,  $C = 10\% / (1 - 10\%) = 11.1\%$ ,  $C_2H_2$  was not adsorbed, helium (80%) as well, whereas  $C_2H_3Cl$  was still completely adsorbed, so  $C/C_0 = 1.11$  should be obtained theoretically. However, the peak value of  $C/C_0$  arrived the maximum of 1.27 at point d. The difference of  $C/C_0$  between the theory and the experiment could be attributed to the competitive adsorption of  $C_2H_3Cl$  and  $C_2H_2$  with AC, as discussed in the second reason. The max peak of  $C/C_0 \approx 1.27$  maintained flat during points d to e, which indicated the replacement of  $C_2H_2$  was conducted step by step. The phenomenon was due to that the ratio of column length-to-diameter was 30.0 ( $> 10.0$ ), which made the mixture adsorbate gas flow with the model of “plug flow” [13]. Between points e and f, the concentration of  $C_2H_2$  in the outlet decreased, whereas the concentration of  $C_2H_3Cl$  increased simultaneously. At point g,  $C_2H_3Cl$  has began penetrate the fixed adsorbent bed. At point h, the adsorption capacity of  $C_2H_3Cl$  was near to saturation. After point f,  $C_2H_3Cl$  penetrated through the fixed adsorbent bed totally, and the composition of the outlet gas was stable, which was identical to that of the raw adsorbate material gas.

In order to illustrate the effect of metal ions, the breakthrough curves of  $C_2H_2$  and  $C_2H_3Cl$  over the modified ACs were split to the curve “a-b-c-d-e-f” and “a-g-h-f” separately as shown in Fig. 3(A) and (B). From Fig. 3(A), the breakthrough time of  $C_2H_2$  (point b) followed the order:  $Al(III)/AC < Mg(II)/AC < Fe(III)/AC < AC < Zn(II)/AC \approx Cu(II)/AC < Ag(I)/AC$ , and the detailed time were listed in Table 1. It could be predicted that the adsorption capacity of  $C_2H_2$  over  $Al(III)/AC$ ,  $Mg(II)/AC$  and  $Fe(III)/AC$  was lower than that of the original AC, however,  $Cu(II)/AC$ ,  $Zn(II)/AC$  and  $Ag(I)/AC$  represented the opposite results. Correspondingly, as shown in Fig. 3(B),  $C_2H_3Cl$  followed the same trends as  $C_2H_2$ , which meant ACs-modified had identical effect with the adsorption capacity of  $C_2H_2$  and  $C_2H_3Cl$ .

### 3.2. Adsorption separation performance of $C_2H_3Cl$ to $C_2H_2$

Generally, the adsorption separation performance was evaluated by separation factor ( $S$ ).  $S = (x_{C_2H_3Cl} / y_{C_2H_3Cl}) / (x_{C_2H_2} / y_{C_2H_2})$ , where  $x_{C_2H_3Cl}$  and  $x_{C_2H_2}$  are the molar fractions in the adsorbed phase, while  $y_{C_2H_3Cl}$  and  $y_{C_2H_2}$  are the molar fractions in the feed gas respectively [14].

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