

Dechlorination of Polyvinyl Chloride by Hydrothermal Treatment with Cupric Ion

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Highlights

1. Cu^{2+} could significantly reduce the HTT temperature for dramatical dechlorination of PVC
2. FTIR and SEM were performed to reveal the dechlorination mechanism both in physical and chemical
3. Cu^{2+} accelerates the reaction pathways of substitution and elimination for dechlorination of PVC
4. The proportion of different routes for dechlorination was tried to quantified relatively by XPS
5. Cu^{2+} could efficiently avoid PVC agglomeration and promote porous structure in the particle

Abstract

Hydrothermal treatment (HTT) is able to remove chlorine effectively from polyvinyl chloride (PVC), however, the reaction temperature is critical in practical application. Less energy-intensive hydrothermal dechlorination condition with cupric ion (Cu^{2+}) has been proposed in this study. In particular, Cu^{2+} was applied in HTT of PVC at temperature ranging from 200 °C to 240 °C. It has been found that the introduction of Cu^{2+} distinctly accelerated PVC decomposition and dechlorination at 220 °C. When Cu^{2+} concentration was increased from 0.01 mol/L to 0.20 mol/L, the dechlorination efficiency was significantly improved from 15.46% to 67.89%. Dramatic dechlorination occurred as residence time was longer than 15 min during HTT. Besides, both elimination and substitution dominated the HTT dechlorination. The facilitated dechlorination after the addition of Cu^{2+} was mainly due to the enhanced dispersion and formation of micropores in hydrochar. On the whole, HTT could be a promising pretreatment technology for copper-containing PVC in electronic wastes to prepared chlorine free hydrochar for combustion or pyrolysis applications, the optimal HTT condition would be 220°C, 60min with 0.1mol/L Cu^{2+} .

Key words: hydrothermal treatment; polyvinyl chloride; dechlorination; catalytic effect; cupric ion

1. Introduction

Polyvinyl chloride (PVC) is made of vinyl chloride by free radical addition polymerization, which is one of the most widely used chlorinated plastics (Özsin and Pütün, 2018). In 2016, the global production of PVC have reached 58.5 million tons and it is expected to grow at an annual rate of 3.2% by 2021 (Yu et al., 2016), The disposal of used PVC resulting in a large amount of PVC wastes.

At present, PVC wastes is mainly treated by landfill, incineration or pyrolysis (Buekens and Cen, 2011; Sadat-Shojai and Bakhshandeh, 2011; Yu et al., 2016). However, these disposal methods exist obvious shortcomings and high risk due to the Cl in PVC. For example, PVC is difficult to decompose by landfill and the degradation products (e.g., microplastic or chlorinated organic compounds in leachate) can lead to soil and groundwater contamination (Qi et al., 2020; Takeshita et al., 2004; Wowkonowicz and Kijenska, 2017). Even though pyrolysis is an likely suitable method to convert PVC wastes into energy, one noteworthy problem in PVC pyrolysis is that the obtained liquid product normally contains quite amount of Cl. Combustion of PVC or chlorinated liquid fuels will exhaust sorts of harmful substance polychlorinated dibenzo-p-dioxins (dioxins) and polychlorinated dibenzofurans (furans) (Liu et al., 2012; Suresh et al., 2017). Therefore, it is necessary to find effective methods to remove Cl from PVC before burning or pyrolysis.

Previous studies have proved that PVC could be decomposed and effectively dechlorinated by hydrothermal treatment (HTT) to prepare chlorine free solid fuel (Lu et al., 2020; Ma et al., 2019; Poerschmann et al., 2015; Shen, 2016; Soler et al., 2018, Yu et al., 2016; Zhao et al., 2020). Chlorine in PVC can be mostly removed by HTT while temperature higher than 300 °C which is

still too energy intensive to be feasible for industrial application (Yu et al., 2016). For lower dechlorination temperature, many studies found that pine wood (Huang et al., 2019), bamboo (Lu et al., 2020), corncob (Yao and Ma, 2018) and cellulosic materials (Ma et al., 2019) etc. showed positive synergistic effect on the dechlorination of PVC. However, the defects of biomass additives were that the optimal synergistic temperature was higher than 250 °C, and the residence time was even up to 4 hours.

Except for biomass additives, Zhao found that adding Ni²⁺ in PVC hydrothermal process can increase the dechlorination efficiency by 6 times at 220°C for 30 min (Zhao et al., 2017). In the past two decades, employing Cu²⁺ as a catalyst to participate in organic chemical reaction has been widely investigated (Kolb et al., 2001; Rostovtsev et al., 2002). However, the effect of Cu²⁺ on the PVC dechlorination by HTT was not focused and well discussed in the previous studies. As copper is easily available, a win-win effect could be expected during the treatment of copper-containing wastes and PVC wastes by co-HTT. For the dechlorination mechanism, the previous studies normally assisted by FT-IR characterization combining with SEM. It is limited to quantitatively identify the dechlorination routes of elimination and substitution. XPS is considered to be a powerful tool give information of the relative amount of different functional groups on the surface of the solid hydrochar.

This work proposes to enhance hydrothermal dechlorination of PVC by Cu²⁺, intending to reduce the hydrothermal dechlorination temperature. Further information on hydrochar was obtained by utilizing the FT-IR, XPS, SEM analysis. It is expected to provide insights about how Cu²⁺ catalyzes PVC degradation and Cl removal as well as to study the possible pathways and dechlorination mechanism of PVC HTT with Cu²⁺. The results indicate that Cu²⁺ can be utilized as

promising catalyst for hydrothermal dechlorination of PVC.

2 Materials and methods

2.1 Materials

PVC powder (CAS: 9002-86-2) without modifier with particle size of 0.1-0.2 mm is purchased from Aladdin Industrial Corporation, used for reaction to exclude the influence of other elements in the reaction process. The ultimate analysis of PVC is shown in supplementary material. The content of carbon, hydrogen and oxygen is closed to the theoretical value according to the chemical formula, saying the PVC powder is rational for this research. The oxygen content might be due to the error of the ultimate analyzer or the adsorption of oxygen on the surface of PVC powder. Cu^{2+} was provided by copper nitrate solution prepared from $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (CAS:10031-43-3) purchased from Guangdong Guanghua Sci-Tech Co., Ltd..

2.2 Hydrothermal treatment process

As Fig. 1 shown, the PVC powder was firstly loaded into the autoclave with 100 ml deionized water or 100 ml $\text{Cu}(\text{NO}_3)_2$ solution. Nitrogen gas was used to sweep out the air in the kettle to prevent the effect of oxygen on the reaction. The time counting started after the temperature in the kettle rise to the set value. Autoclave was cooled to about 50 °C by cooling water to stop the reaction as the holding time achieved. All the reaction condition was list in Table 1. The remaining solid and liquid was processed separation by a vacuum filter. The solid was washed by deionized water while filtration. The obtained solid product (hydrochar) was then dried in the oven for later analysis.

Table 1. Experimental parameters

Parameters	Values
Temperature (°C)	200, 220, 240
Holding time(min)	0, 15, 30, 45, 60
Cu ²⁺ concentration(mol/L)	0, 0.01, 0.05, 0.1, 0.2

2.3 Characterization of products

The Cl content in the hydrochar was measured combining oxygen flask combustion and selective chloride ion electrode. The liquid product from filtrate, washing process and absorption solution were collected to measure by the selective chloride ion electrode. Fourier transform infrared spectrometer (FT-IR, Bruker TENSOR 27) was applied to characterize the surface functional groups of PVC and hydrochar. Scanning electron microscope (SEM, s-3400n) was applied to analyze the morphological properties of solid samples. X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific ESCALAB 250XI+) was used to analyze the surface of PVC and hydrochar to quantitatively measure the different species of Cl and carbon.

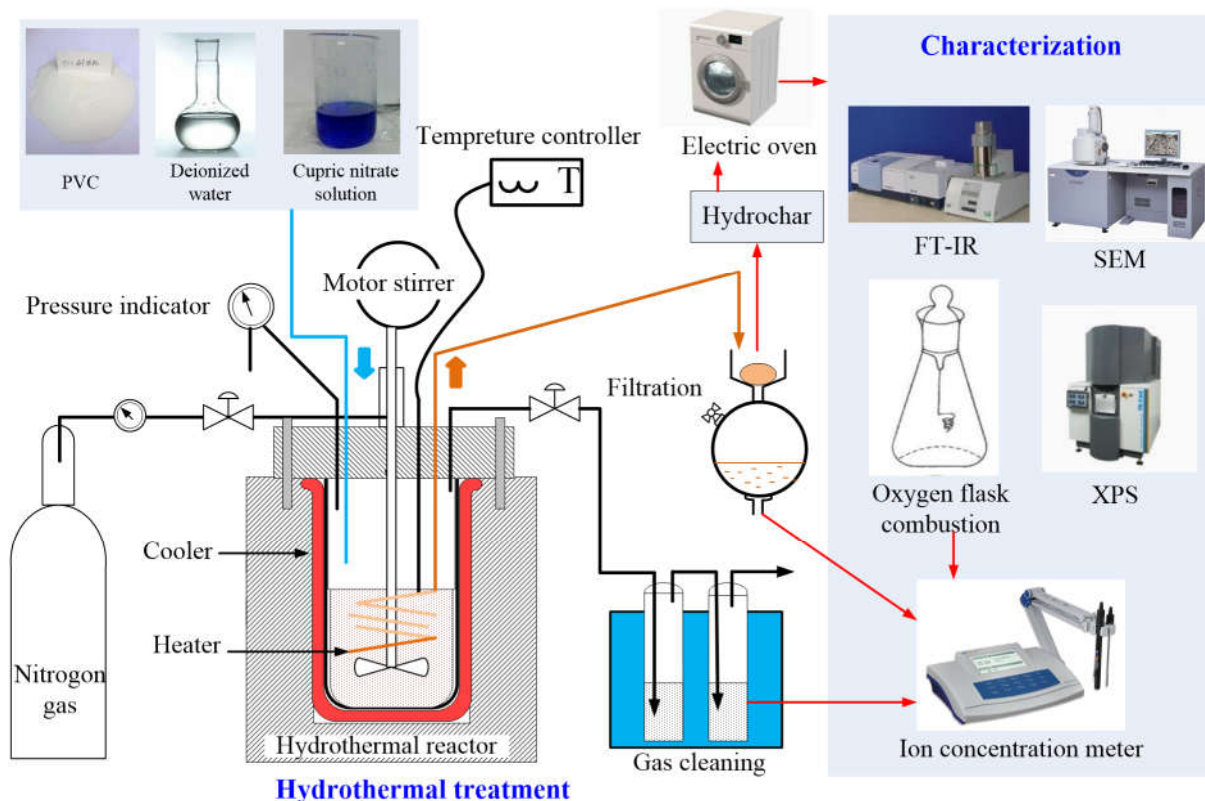


Fig. 1 The schematic diagram of hydrothermal treatment and characterization.

2.4 The solid recovery and dechlorination efficiency of PVC

The solid recovery was calculated as follow:

$$\text{Solid recovery} = M_1/M_0 \times 100\%$$

where M_1 represents the mass of HTT residue solid after drying, M_0 represents the mass of the PVC input. The lower the solid recovery is, the higher the degradation efficiency.

The dechlorination efficiency of PVC is expressed by the removal of Cl, reflected by the Cl content in solid and liquid products as follow:

$$\text{Dechlorination} = (\text{Cl in the liquids}) / (\text{Total Cl in the PVC}) \times 100\%$$

where Cl in liquid represents the Cl mass in the liquid from the reactor, washing process and impingers. Total Cl in the PVC represents the Cl mass in PVC powder.

3 Results and discussion

3.1 Effect of Cu^{2+} on the solid recovery of PVC

Fig. 2 shows the effect of Cu^{2+} on the solid recovery as hydrochar at different hydrothermal temperature of PVC for 30 min. When the temperature was at 200 °C, the solid recovery of PVC HTT without and with Cu^{2+} was above 98 wt.%, showing inconspicuous difference. When the temperature rose to 220 °C, the solid recovery of PVC HTT with 0.1 mol/L Cu^{2+} was 58.1 wt.%, significantly lower than that of PVC HTT without Cu^{2+} (98.71 wt.%), indicating the Cu^{2+} provide a strong catalyst effect on the degradation of PVC at HTT temperature of 220 °C. Zhao et al. (2018) proposed that the addition of NaHCO_3 and Na_2CO_3 had a significant influence on the solid recovery at HTT temperature of 220 °C, which is consistent with the present study. While, as temperature increased to 240 °C, the solid recovery of PVC without and with Cu^{2+} fell sharply to 54.4 wt.% and 50.8 wt.%, respectively. The synergistic effect of cupric ion on the degradation of PVC was clearly weakened at a higher temperature. One possible reason is that the heat and mass transfer is so fast at 240 °C that the effect of Cu^{2+} was not apparently. Existing researches pointed out that severe thermal degradation of PVC started to take place from 250 °C (Gandon-Ros et al., 2020; Kosuda et al., 2012; Xiao et al., 2014), while in this study, the temperature at which PVC largely decomposed was 240 °C. This phenomenon indicates that the temperature of hydrothermal is the dominant factor affecting the solid recovery of PVC. Still, Cu^{2+} is an effective catalyst for PVC degradation at mild temperature around 220 °C.

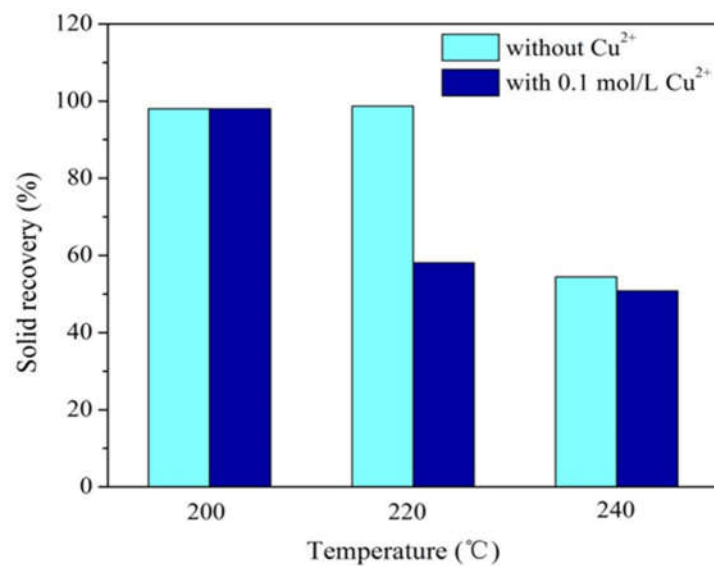


Fig. 2. The variation of solid recovery with HTT temperature for 30 min.

3.2 Effect of Cu²⁺ concentration on dechlorination of PVC

It is known that the organic Cl in PVC can be converted into inorganic Cl by HTT and then mostly migrated into the liquid phase (Shen, 2016). Fig. 3 displays the distribution of Cl in the liquid and hydrochar after HTT with different concentration of Cu²⁺ at 220 °C for 30 min. One can see that the Cl content in the liquid phase product from HTT without Cu²⁺ (Cu²⁺ concentration is 0 mol/L) was 6.24 wt.%. When 0.01 mol/L Cu²⁺ is added, the dechlorination is obviously improved to 15.46 wt.%, indicating that the addition of Cu²⁺ can promote the HTT dechlorination of PVC, which echoes the abovementioned result that Cu²⁺ can accelerate PVC degradation and reduce solid recovery. When the concentration of Cu²⁺ was gradually increased to 0.05 mol/L, 0.1 mol/L and 0.2 mol/L, the corresponding dechlorination were 18.08 wt.%, 57 wt.% and 67.89 wt.%, respectively, implying the Cl removal of PVC increased with the increasing of Cu²⁺ concentration. Xiao et al. (2014) also mentioned that the natural logarithm of PVC dechlorination efficiency constant and the square root of the ion potential of metal cation are a significant linear relationship. However, as the Cu²⁺ concentration is increased from 0.1 mol/L to 0.2 mol/L, the dechlorination

efficiency slowly raised from 57 wt.% to 67.89 wt.% due to the termination reaction of cross-linking and cyclization occurred with the progress of dechlorination and the production of olefins reaction (Starnes, 2002). The influence trend of PVC dechlorination by Cu^{2+} is in accordance with that of Ni^{2+} according by Zhao et al. In a word, in the HTT, concentration of Cu^{2+} as 0.1 mol/L is preferred for enhance the conversion of Cl and dechlorination of PVC.

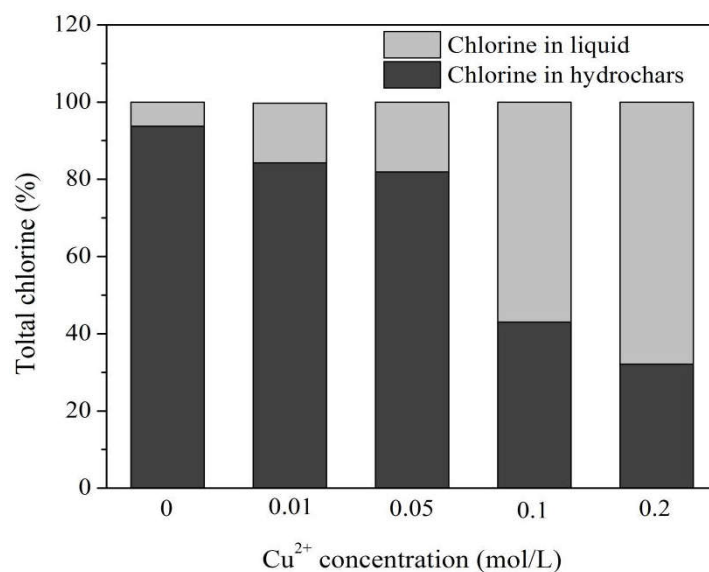


Fig. 3. The Cl distribution in HTT at 220 °C for 30 min with different Cu^{2+} concentration.

3.3 Effect of HTT temperature on dechlorination of PVC

The distribution of Cl in each phase under the HTT temperature from 200 °C to 240 °C for 30 min is shown in Fig. 4. It can be seen that the higher HTT temperature is, the more Cl in the PVC migrate to the liquid. For HTT without Cu^{2+} in Fig. 4(a), when the HTT temperature was increased from 200 °C to 220 °C, the Cl content in the hydrochar dropped slightly from 98% to 93.76%. With temperature further elevated to 240 °C, the Cl content in the hydrochar fallen dramatically to proximately 10 wt.% Previous research also mentioned the dominant dechlorination of PVC during HTT incurred at temperature of 240 °C (Ma et al., 2019). For PVC with 0.1 mol/L Cu^{2+} in Fig. 4(b), the Cl content in the hydrochar reduced from about 93 wt.% to 6 wt.% as the

temperature increased from 200 °C to 240 °C, showing a dramatic downward trend. Above data suggests that the presence of Cu^{2+} obviously boosts the migration of Cl in PVC to the liquid phase. Particularly, in the HTT of 220 °C with 0.1 mol/L Cu^{2+} , Cl content in the liquid phase was high as 58 wt.% which is nine times larger than that of without Cu^{2+} (about 6 wt.%), implying that Cu^{2+} performed a distinct catalytic effect to promote PVC dechlorination at 220 °C. Notably, at 240 °C, The dechlorination of PVC without and with Cu^{2+} showed little difference probably due that the higher temperature accelerated heat and mass transfer controlled by temperature of the reaction system (Poerschmann et al., 2015; Zhao et al., 2017). Poerschmann et al. (2015) has pointed out that the release rate of Cl slowed down when the temperature reached 235 °C, inferring that Cl has been basically transferred to the liquid so as the catalytic dechlorination of PVC by Cu^{2+} became less obvious at 240 °C. The above result can be concluded that Cu^{2+} can promote the hydrothermal dechlorination of PVC, while 220°C would be a suitable temperature.

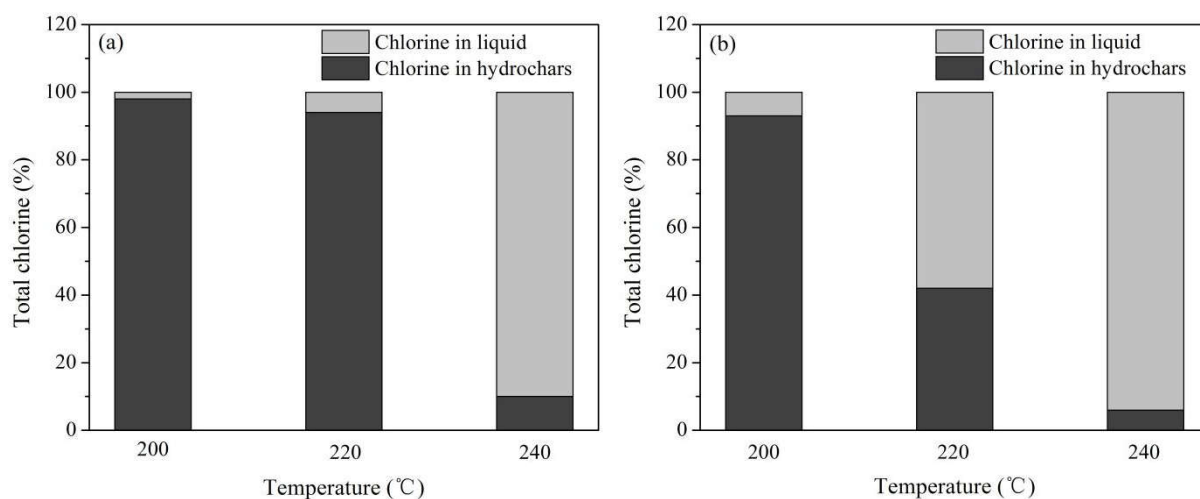


Fig. 4. The variation of Cl distribution with HTT temperature for 30 min without Cu^{2+} (a) and with 0.1 mol/L Cu^{2+} (b).

3.4 Effect of residence time on dechlorination of PVC

Fig. 5 (a) and Fig. 5 (b) shows the variation of Cl in hydrochar and liquid product with

reaction time without Cu^{2+} and with $0.1 \text{ mol/L Cu}^{2+}$ respectively at $220 \text{ }^\circ\text{C}$. One can see in Fig. 5 (a) that the dechlorination was slightly raised from $2.99 \text{ wt.}\%$ to $8.89 \text{ wt.}\%$ when the residence time increased from 0 to 60 min. Prolonging the hydrothermal residence time does not apparently affect the dechlorination without Cu^{2+} . In contrast, for PVC HTT with $0.1 \text{ mol/L Cu}^{2+}$, the amount of Cl in liquid were significantly increased from $11.7 \text{ wt.}\%$ to $86.5 \text{ wt.}\%$ when the residence time was raised from 0 to 60 min. The dechlorination in Fig. 5 (b) at all the reaction time were remarkably increased compared with Fig. 5 (a), proving again the significant catalytic influence of Cu^{2+} at $220 \text{ }^\circ\text{C}$. According to the viewpoints reported by Hashimoto et al. (2007), the residence time of 0 min and 15 min showed in Fig. 5 (b) probably owing to the initial incubation period where the rates were slightly influenced by temperature and additive concentration. In the study of Gandon-Ros et al. (2020), K_2CO_3 was added into PVC HTT and found that dechlorination of PVC mainly occurred within a residence time of 1-3 hours. While in this study, the residence time of 30-60 min shown in Fig. 5 (b) should be attributed to major dechlorination stage in which the reaction proceeded vigorously and the resident time of 60min would be the optimal in the studied condition.

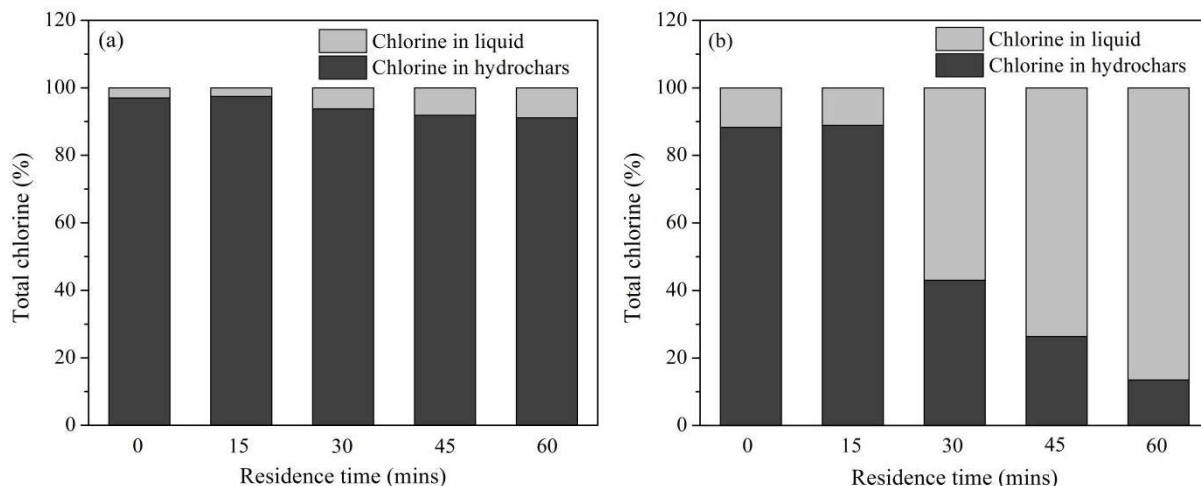


Fig. 5. The variation of Cl distribution with HTT residence time at 220 °C without Cu²⁺ (a) and with 0.1 mol/L Cu²⁺ (b).

3.5 Characterization of hydrochar

3.3.1 Fourier transform infrared spectroscopy

In order to obtain an understanding on the changes of functional groups of PVC in the hydrothermal dechlorination process, the PVC and hydrochar was analyzed by Fourier Transform Infrared (FT-IR). Fig. 6 displays the FTIR spectrums of the PVC (a), the hydrochar from PVC HTT without Cu²⁺ (b) and with Cu²⁺ (c) at 220 °C for 30 min. It can be observed that the absorption peaks mainly changed in the band of 615 cm⁻¹, 695 cm⁻¹, 1095 cm⁻¹, 1615 cm⁻¹ and 3350 cm⁻¹. The absorption band at 615 cm⁻¹, 695 cm⁻¹ were owing to C-Cl stretching vibration (Zhou et al., 2016). The absorption band at 1095 cm⁻¹ could be assigned to the skeletal vibration of PVC chain (Ma et al., 2019). The band at 1615 cm⁻¹ was attributed to C=C groups (Mayer et al., 2012). The absorption band at 3350 cm⁻¹ absorption was due to the existence of -OH groups (Kang et al., 2012). In Fig. 6 (a), strong peaks appeared at 615 cm⁻¹ and 695 cm⁻¹ (C-Cl), meanwhile no absorption peak at 1615 cm⁻¹ (C=C) and 3350 cm⁻¹ (-OH). Comparing with Fig. 6(a), the absorption peak at 615 cm⁻¹ and 695 cm⁻¹ was roughly the same in Fig. 6 (b).

Simultaneously, weak absorption peaks appeared at 1615 cm^{-1} (C=C) and 3350 cm^{-1} (-OH), likely indicating that a little part of the C-Cl bond in PVC was destroyed during HTT without adding Cu^{2+} . In Fig. 6 (c), the peaks at 615 cm^{-1} and 695 cm^{-1} (C-Cl) diminished obviously while the absorption peaks at 1615 cm^{-1} (C=C), 3350 cm^{-1} (-OH) were remarkably enhanced, implying the promotion of PVC hydrothermal dechlorination by Cu^{2+} is realized by boosting the substitution of hydroxy groups, forming polyenes. Additionally, the peak at 1095 cm^{-1} assigned to the skeletal vibration of PVC chain was diminished, meaning that the PVC carbon skeleton was destroyed to some extent during the HTT with Cu^{2+} . According to the phenomenon above, it can be inferred that hydrothermal dechlorination of PVC is achieved by the cleavage of C-Cl, subsequently transfers Cl element to the liquid product. Since no chlorinated organic compounds were detected in the separation liquid, the essence of PVC hydrothermal dechlorination process should be the organic Cl is converted to inorganic Cl and then immigrated into the liquid phase.

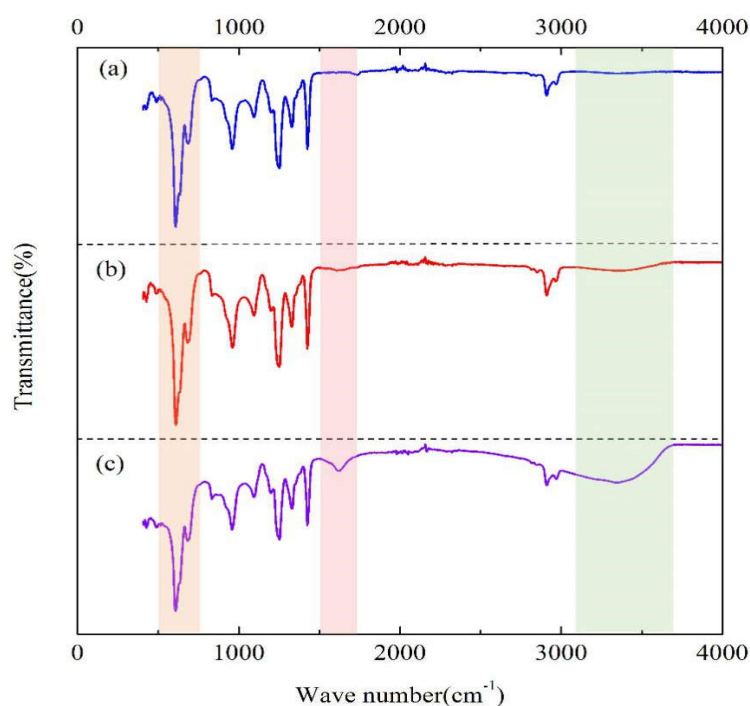


Fig. 6. FT-IR spectra of PVC (a), hydrochar from PVC HTT without Cu^{2+} (b) and with 0.1 mol/L Cu^{2+} (c) at $220\text{ }^{\circ}\text{C}$ for 30 min.

The PVC dechlorination generally followed the free radical mechanism (Starnes, 2012; Takeshita et al., 2004). Firstly, it was triggered by free radicals and structures with poor thermal stability such as allylic chloride (Starnes and Ge, 2004). Then, zipper mechanism drives the dehydrochlorination to remove adjacent -H and -Cl to generate conjugated double bonds (Nagai et al., 2007). Finally, the polymer molecular chain was broken and cross-linked to generate aromatic compounds (Yu et al., 2016). Specifically, the PVC dechlorination can be divided into the following elimination and substitution (Zhao et al., 2017). The substitution would be performed with two routes as shown in Fig. 7. The first route was that a -OH was directly substituted for -Cl, and the other route was that two -OH were substituted for -H and -Cl respectively in a given double carbon segment, and then performed intramolecular dehydration to generate H₂O, HCl and C=C-OH, therefore functional groups including -OH and C=C-OH could be detected in the hydrochar as shown in Fig. 6. In the elimination reaction, -Cl and -H of adjacent carbon atoms remove HCl to form C=C, so the absorption peaks responded for the existing of C=C appeared as showed in Fig. 6 (b) and Fig. 6 (c). According to previous studies, the major dechlorination pathways of PVC were different. In the study of Lu et al. (2002), the substitution of -OH group was not considered as the main way of PVC HTT dechlorination, meanwhile, in the experiment of Li et al. (2017), the way of substitution did not occur, while the elimination was the main dechlorination way. From the analysis of FT-IR spectrum, it can be seen in this study that both the above two dechlorination pathways might occurred. From the weakening of the peak of -Cl and the enhancement of the peak of C=C and -OH after adding 0.1 mol/L Cu²⁺, it is verified that Cu²⁺ played the role of catalytic dechlorination which could promote the Cl removal of PVC. Zhao et al. (2017) reported that the hydrochar from PVC HTT with nickel showed functional group of C=O,

however, it is not observed here, evidencing the possible difference in mechanism of dechlorination.

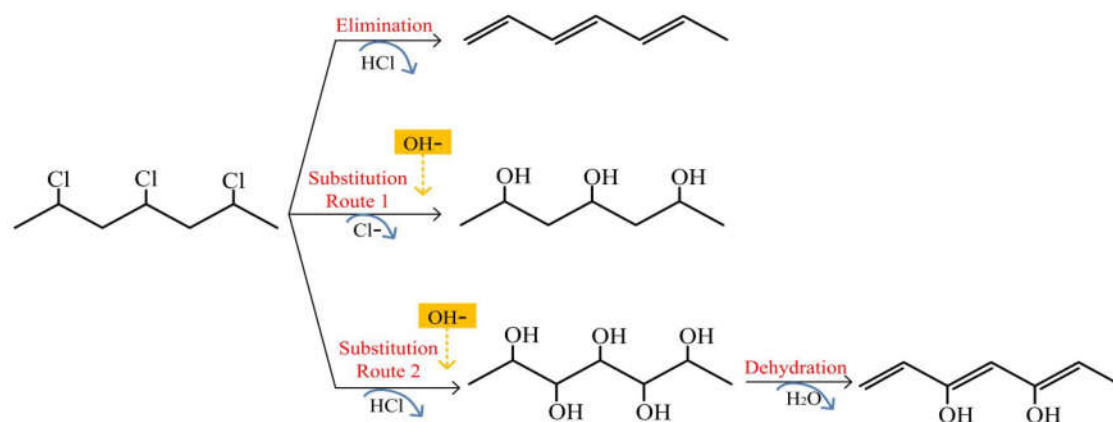


Fig. 7. Chemical pathway for dechlorination of PVC in HTT with Cu²⁺ (Adapted from Nagai et al., 2007; Zhao et al., 2017).

3.3.2 X-ray photoelectron spectroscopy

The mechanism of hydrothermal dechlorination of PVC was widely discussed by previous studies (Ma et al., 2019; Zhao et al., 2017), mainly inferred from the information of the functional group changes shown in FT-IR. XPS spectrums and the deconvoluted curves enable to deliver the relative XPS intensity of different functional groups on the surface of solid sample. Here, XPS is applied intending to further clarify that the group changes through proper curve fitting of Cl and carbon spectrum. The Cl in PVC is in the form of C-Cl bonds, that is organic Cl. After hydrothermal reaction, the C-Cl bond is broken and the Cl element is released as ionized Cl, namely inorganic Cl. Curves in Fig. 8 display the relative XPS intensity of different types of Cl on the surface of PVC (a) and hydrochar from PVC HTT at 220 °C without Cu²⁺ (b) and with Cu²⁺ (c). The deconvolution of Cl 2p peak method was mentioned previously with a further optimization of the ratio of Lorentzian and Gaussian for the peaks (Levi et al., 2015).

It is showed that PVC contained predominantly organic Cl, accounting for 95.81% of the

peak area. After HTT at 220 °C, the Cl in hydrochar is consisted of 66.14% organic Cl and 33.86% inorganic Cl, manifested that HTT can partly transfer organic Cl into inorganic Cl but still some Cl remained in the hydrochar after washing process. Interestingly, with 0.1 mol/L Cu²⁺, organic Cl accounted for 85.37% and inorganic Cl accounted for 14.63% in the hydrochar which was reduced by more than a half compared with that of without adding Cu²⁺ (33.86%). Whereas, according to results in Figs. 4 and 5, the dechlorination of the former (around 58 wt.%) was obviously higher than that of the latter (about 6 wt.%). The paradoxical observation inferred that one of the ways of Cu²⁺ catalyzing PVC hydrothermal dechlorination might be to promote the migration of inorganic Cl in the hydrochar to the liquid by changing the surface physicochemical properties that needed further characterization.

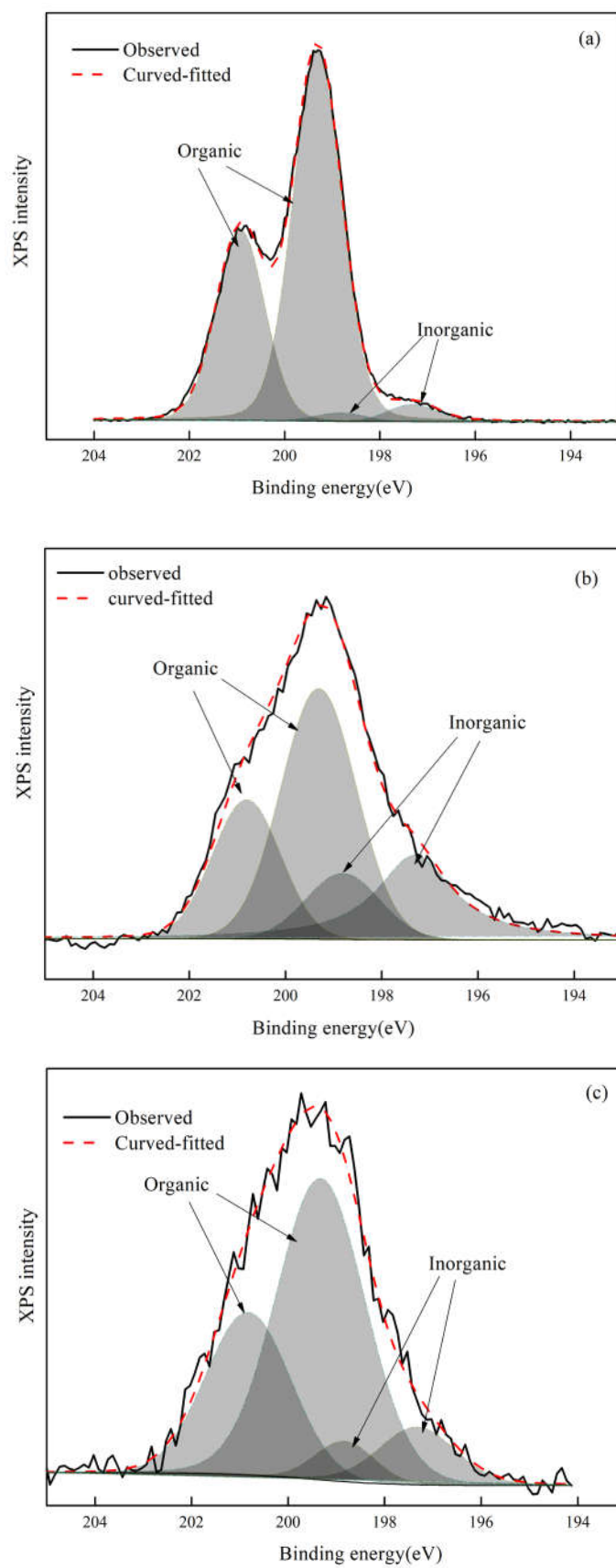


Fig. 8. Cl 2p XPS spectra with curves fitting of PVC (a) and hydrochar from PVC HTT at 220 °C for 30 min without (b) and with 0.1 mol/L Cu²⁺ (c).

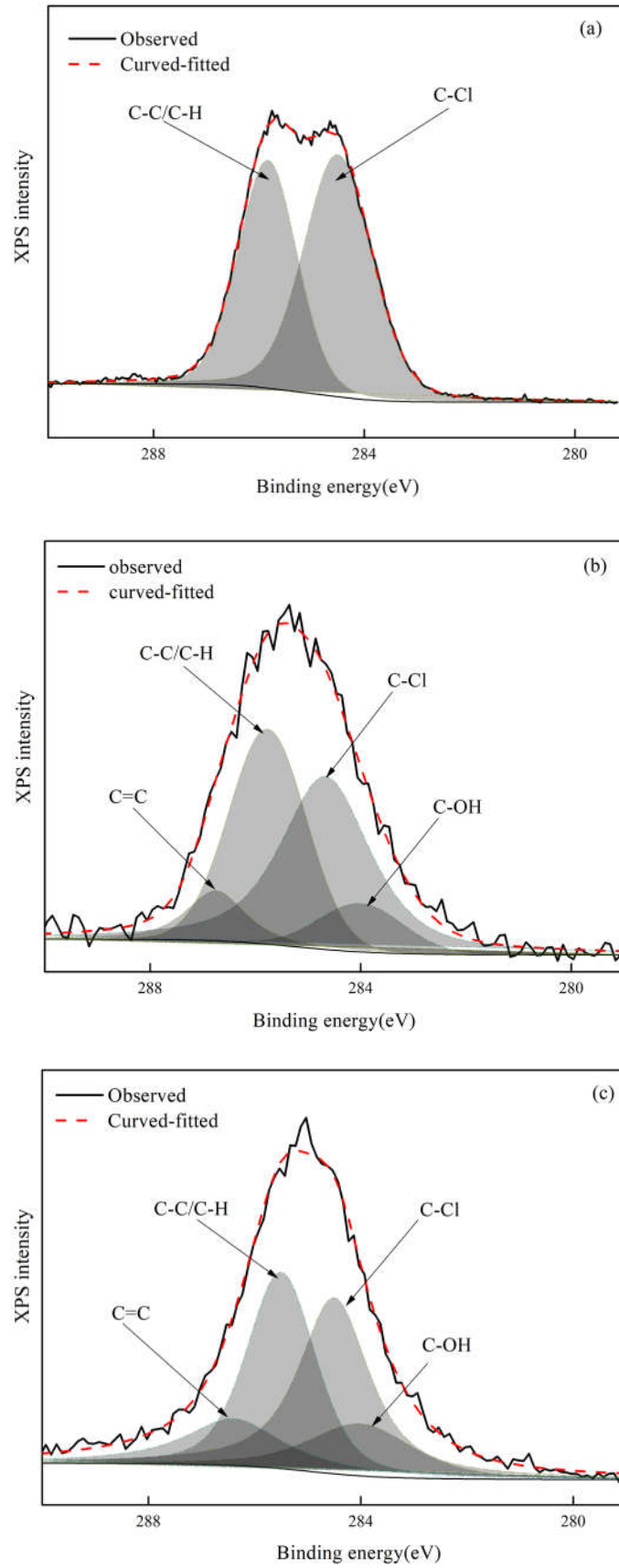


Fig. 9. Cl s XPS spectra with curves fitting of PVC (a) and hydrochar from PVC HTT at 220 °C

for 30 min without (b) and with 0.1 mol/L Cu^{2+} (c).

As for the functional group of carbon, the PVC should contain mainly C-Cl, C-C and C-H, the binding energy of C-C and C-H for carbon is at around 284.5 eV (Levi et al., 2015) and C-Cl for carbon is at around 285.5 eV (Golczak et al., 2008). Based on the FT-IR spectrum in Fig. 6, it can be inferred that carbon functional group of C=C, C-OH is existing in the hydrochar. The binding energy of the two is 284.0 eV (Heeg et al., 2001) and 286.5 eV (Levi et al., 2015) respectively. The deconvolution of the C1 XPS spectrums was conducted by XPSPEAK software firstly with fixed binding energy, FWHM and Lorentzian-Gaussian ratio, optimizing the peak area. Secondly, the optimization of peak area and Lorentzian-Gaussian ratio were done with the fixed binding energy and FWHM. The two steps optimization validate the approximation that the lifetime of the final state and the screening of the electrons do not vary very much with the chemical environment. The fitting curves are shown in Fig. 9 where PVC, hydrochar from PVC HTT without Cu^{2+} and with Cu^{2+} is presented in Figs. 9 (a) (b) and (c), respectively. The deconvoluted peaks area proportion of different samples is listed in Table 2.

The C1 s spectra of PVC clearly show two dominant components of C-C/C-H and C-Cl. The intensity proportion of them is 55.63% to 44.37%, which is different from the theoretical ratio of the bond amount of C-C to C-Cl, indicating that the intensity proportion cannot directly account for the amount of the functional groups. While, the peak area still can relatively give the quantitative information of the functional group changes (Levi et al., 2015). As shown in Fig. 9 (b), after HTT, the C1s peaks of PVC changed dramatically. The dominant functional groups are still C-C/C-H and C-Cl, sharing 44.77% and 37.38%, respectively. While, new components of C=C and C-OH appeared, respectively account for 9.1% and 8.74% of the total peak area, verifying

again slightly dechlorination incurred at this condition. By adding Cu^{2+} , the functional groups sorts are same as HTT without Cu^{2+} , while the new components of C=C and C-OH accounted to 14.28% and 14.70%, respectively, which are much higher than that of without Cu^{2+} . This evidenced that Cu^{2+} catalyze the hydrothermal dechlorination by promote the substitution of -Cl by -OH groups and elimination of HCl to produce C=C.

Table 2 Deconvoluted peaks area proportion of different samples.

Functional groups of carbon	PVC	Hydrochar without Cu^{2+}	Hydrochar with Cu^{2+}
C=C	0	9.10	14.28
C-C/C-H	55.63	44.77	36.85
C-Cl	44.37	37.38	34.17
C-OH	0	8.74	14.70

3.3.2 Morphological properties

The photographs and SEM graphics of the PVC and hydrochar was presented to further discuss how Cu^{2+} promote the conversion of organic Cl and the migration of inorganic Cl. As can be seen in Fig. 10 at left row, pure PVC powder presents irregular white particles with particle size of 0.1-0.2 mm. After HTT at 220 °C for 30 min, the PVC particle agglomerated to form a ball of orange, bond with rough surface, irregular ridges and uneven pores probably due to the release of gas at high temperature. While added Cu^{2+} , the hydrochar changed into black brown porous sheet materials with relatively smooth surface and uniform particle size (about 5-15 microns in diameter). It is estimated that the polyene series with more than seven double bonds are colored, and the average number of about 15 conjugated double bonds can completely absorb visible light

(Yoshioka et al., 2009). Therefore, the gradual deepening of color of hydrochar proved that the increase of conjugated double bonds leads to the formation of polyene structure. In addition, the hydrochar from HTT PVC with Cu^{2+} was brittle to be smashed probably due to the destroying of carbon skeleton.

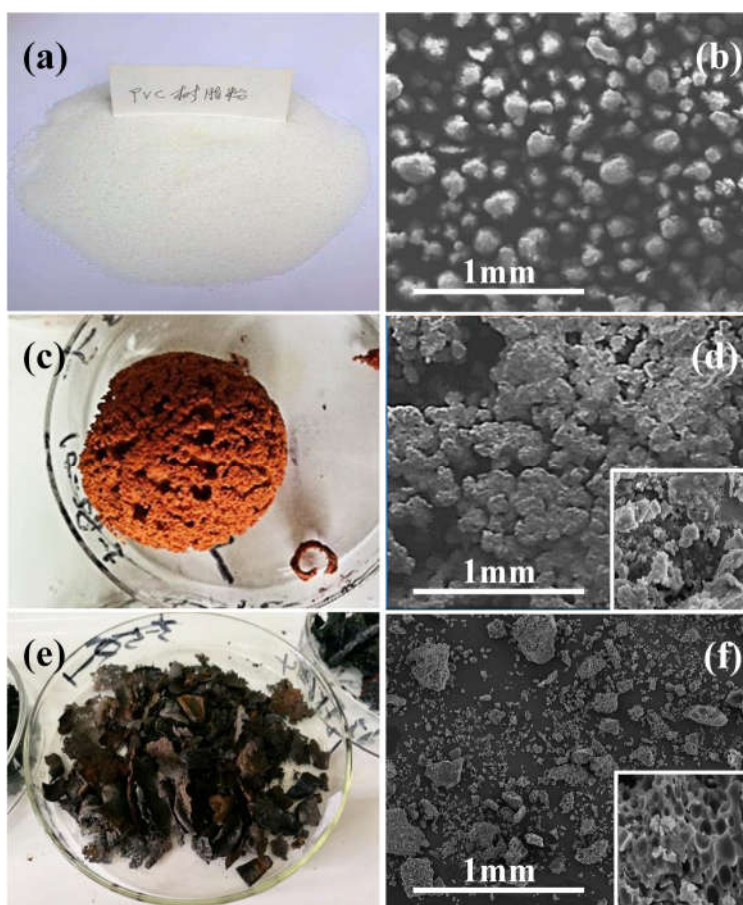


Fig. 10. Pictures and SEM images of PVC (a, b), hydrochar from PVC HTT at 220 °C for 30 min without Cu^{2+} (c, d) and with 0.1 mol/L Cu^{2+} (e, f).

In Fig. 10 (d), the magnified figures of the pulverized hydrochar of HTT PVC agglomerated by adhering at the edge of particle. While agglomeration phenomenon disappeared after adding Cu^{2+} . The possible reason was proposed as Fig. 11. Firstly, high-price metal cation (such as Ca^{2+} , Mg^{2+} , Cu^{2+} , etc.) has a strong hydration effect. When Cu^{2+} diffuses to the surface of PVC particles, it increases the thickness of hydration film on the surface of particles, thus enhancing the repulsion

force of hydration between particles so as to reduce the agglomeration effect (Al-Hashmi et al., 2012; Pashley, 1981, 1982). Weakened agglomeration will increase the interface between water and PVC particle, boosting the conversion of organic Cl into inorganic Cl. Secondly, the changes of surface chemical composition and microstructure of hydrochar affect the surface wettability (Liu et al., 2004). According to the previous FT-IR analysis results, the addition of Cu^{2+} heightened the hydroxyl substitution, and the presence of a large number of hydroxyl groups makes water molecules form hydrogen bonds with the hydroxyl group (Hu and Michaelides, 2008), thus enhancing the hydrophilicity. Liu et al. (2019) demonstrated that the high agglomeration rate was due to the low wettability, suggesting that the presence of hydroxyl group inhibited the agglomeration effect.

As displayed in Fig. 10 (f), porous structure is significantly formed while PVC HTT with Cu^{2+} . The large number of micropores makes the surface of hydrochar rougher. For the hydrophilic surface, the liquid can easily enter into the grooves on the surface. Subsequently, the conversion of Cl by substitution, as well as the form Cl^- attached on the inner surface of hydrochar are easier to immigrate into the liquid phase, which might be the explanation on why the content of inorganic Cl on the surface of hydrochar reduced (echoing the XPS experiment results). Moreover, reducing Cl^- can eliminate the ‘salt bridge’, consequently preventing the occurrence of hard agglomeration (Zhu et al., 2008). In a word, the reaction involved in the whole process of Cu^{2+} inhibition of agglomeration is mutually reinforcing, influencing and promoting each other.

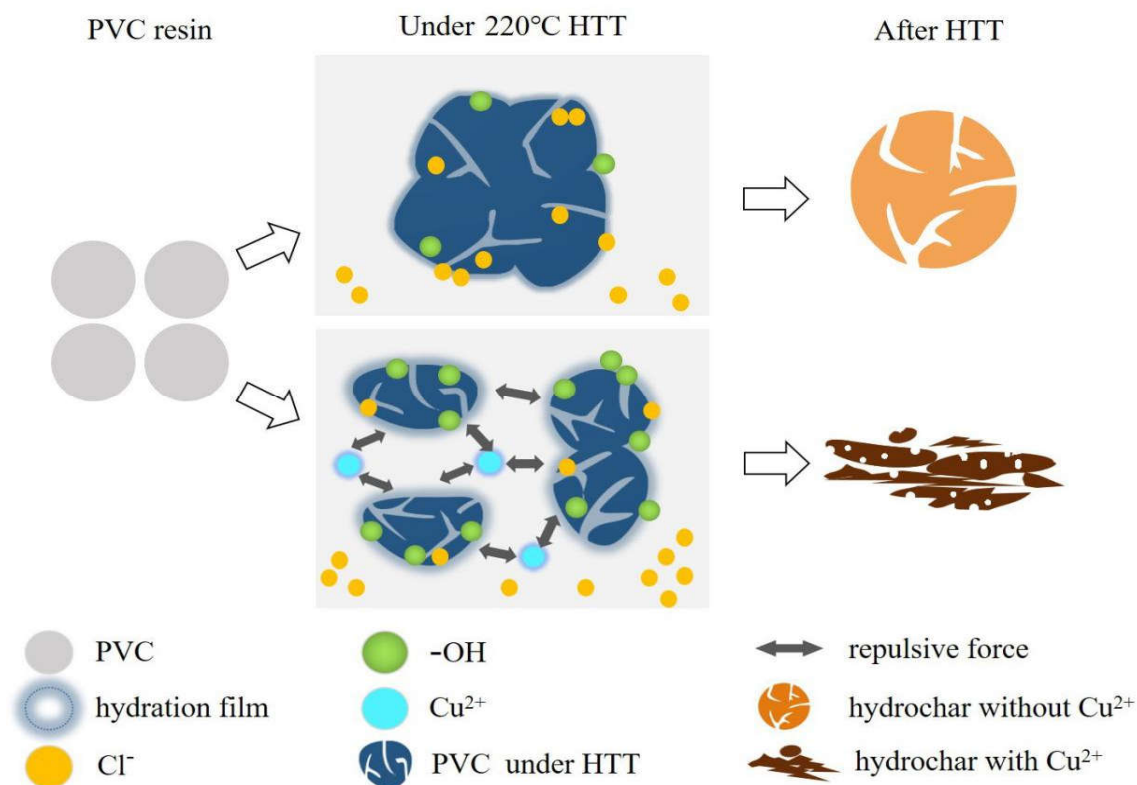


Fig. 11. Possible mechanism of PVC dechlorination with and without Cu²⁺ by HTT at 220 °C.

4 Conclusions

In this study, the effect of Cu²⁺ on dechlorination of PVC in HTT has been investigated. It was confirmed that Cu²⁺ exhibited an extraordinary catalytic effect on the degradation and dechlorination of PVC at 220 °C. After adding 0.1 mol/L Cu²⁺, the solid recovery was significantly reduced to 58.1 wt.% as compared to 98.71 wt.% in the absence of Cu²⁺, while the removal efficiency of Cl was remarkably enhanced from 6 wt.% to 58 wt.%. Both the elimination and substitution acted as important roles in hydrothermal dechlorination of PVC regardless of the addition of Cu²⁺. Introducing Cu²⁺ could mainly enhance substitution effect. HTT of PVC with More specifically, the hydration of Cu²⁺ may promote repulsion force of hydration between PVC particles. The substitution of -Cl with -OH could be strengthened and led to a more hydrophilic surface of hydrochar. The disappearance of hydrochar agglomeration would provide good

structure characteristics for the migration of Cl from the hydrochar surface into the liquid phase as well as the subsequent use of hydrochar as solid fuels. Therefore, HTT of PVC with Cu^{2+} could shed light on low temperature dechlorination pretreatment of PVC wastes before downstream burning or pyrolysis, especially for copper-containing PVC in electronic wastes. the optimal HTT condition would be 220°C, 60min with 0.1mol/L Cu^{2+}

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