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The study of nickel effect on the hydrothermal dechlorination of PVC

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ABSTRACT

The nickel might have involved in the hydrothermal (HT) treatment of poly(vinyl chloride) (PVC) containing wastes because of the corrosion of Ni-containing reactors, which was caused by the HCl generated in this process. This work has been conducted to investigate if the nickel has a positive effect on the HT dechlorination of PVC, which was usually neglected in previous research. The HT dechlorination of two kinds of PVC was performed in subcritical nickel-containing water with various Ni^{2+} concentrations under several HT operating conditions in order to investigate the effect of the nickel on the dechlorination efficiency (DE). The FTIR, ^{13}C NMR and SEM techniques were utilized to characterize the hydrochars and the ICP-OES was used to measure the nickel content in the separated liquid (SL) to explore the possibility of reuse the nickel-containing water. The chlorine in the SLs was measured by potentiometric titration to solve the DE. The results show that the Ni^{2+} could significantly accelerate the HT dechlorination of PVC at a relative mild condition. The DE was about 76% at a HT temperature of 220 °C for 30 min in 0.1 M Ni^{2+}-containing water, 6 times higher than that without Ni^{2+}. The HT temperature has a dominant effect on the DE which reached up to 87% at a HT temperature of 260 °C. At higher HT temperature, the acceleration of Ni^{2+} was not obvious because of the aggravation of the corrosion and also the higher heat and mass transfer. Besides, the DE could not reach 100% at some circumstances because of the cyclization and cross-linking, which would be also weakened under higher temperature. According to the FTIR and ^{13}C NMR spectrum, both elimination and substitution happened during the HT dechlorination with Ni^{2+}. The Ni^{2+} could promote the evolution of the pores in PVCs and strengthen the substitution of −Cl with −OH, which was responsible for the acceleration of dechlorination at mild Ni^{2+}-containing system. The ICP-OES result verified that the Ni^{2+} worked as catalyst and the Ni^{2+}-containing water could be reused. This result was beneficial for both the treatment of the nickel-containing wastewater and also the HT treatment of organic wastes.

1. Introduction

PVC has been widely used to produce commodities such as packing bags, scavenging materials, infusion vessel, armarium, plastic pipes, toys etc., in many aspects of life because of its low price and good performance (Braun, 2002; Wang et al., 2016). As a result, large amount of PVC-containing/organic-chlorinated wastes were generated causing many environmental and social problems (Bidoki and Wittlinger, 2010). Typically, the chlorine content was around 0.2–0.8% for municipal solid wastes (MSW), ~11% for unused cables, 1.1–2.1% (Wang et al., 2003) or even higher as 37% (Ma et al., 2006) for medical wastes, and 0.2–0.3% for landfill mined plastic wastes (Zhou et al., 2014). Normally, the PVC was stable. However, after the temperature was higher than 200 °C, the chlorine in PVC will be released to form HCl causing corrosion (Liu et al., 2015; Slapak et al., 1999), or to form extremely toxic substance such as Dioxin (Bidoki and Wittlinger, 2010; Braun, 2002; Liu et al., 2012). Several methods have been proposed to recycle waste PVC or PVC-containing wastes (Braun, 2002; Sadat-Shojai and Bakhshandeh, 2011; Yu et al., 2016a) and the incineration was widely adopted in many nations (Braun, 2002; Liu et al., 2015; Sadat-Shojai and Bakhshandeh, 2011). Nevertheless, PVC is rather resistant to

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incineration because of its high chlorine content (around 56.8%). The incineration would also suffer from toxic emission and generate a lot of hydrochloric acid (HCl), which could cause corrosion in the furnace and release trace amounts of further harmful gases such as organohalogen compounds, leading to severe environmental problems (Braun, 2002; Liu et al., 2012, 2015; Slapak et al., 1999). One feasible solution is to remove the chlorine from these PVC-containing wastes before its utilization.

Hydrothermal (HT) treatment refers to treatment of materials in water at a certain temperature and pressure to keep the water in either subcritical or supercritical state to degrade the organic matters (Bermejo and Cocero, 2006; Kritzer and Dinjus, 2001; Lavric et al., 2005). It is a homogeneous reaction with advantages of fast reaction rates (Yu et al., 2016a), which has been effectively applied in resources recovery and harmful waste treatment (Benavente et al., 2017; Yu et al., 2016b). Endo and Emori (2001) studied on the HT decomposition of PVC under high pressure and reported that the dechlorination efficiency (DE) could reach 100% at 300 °C under 19.3 MPa. Lu et al. (2002) found the DE was 95% at a temperature of 240 °C for 2 h in an alkaline system. It would be 100% after the holding time was 15 h (Poerschmann et al., 2015). Takeshita et al. (2004) stated that the chlorine in PVC was mainly released in the form of HCl and dissolved in water during HT dechlorination of waste PVC. Lv et al. (2009) studied that the catalytic HT oxidation of waste PVC over Pd/AC (activated carbon) catalyst and reported the DE was increased with the H_2O_2 concentration, reaching up to 90% at a H_2O_2 concentration of 1.76 M.

In view of its successful application, the HT is quite effective to remove chlorine from PVC-containing wastes. The effect of HT operating conditions, such as the HT temperature, residence time, the additives and reaction medium etc., on the chlorine behavior during HT dechlorination of waste PVC or PVC-containing wastes has been widely investigated in the literatures. However, the corrosion of the stainless steel reactor caused by the released HCl could have some influence on the dechlorination behavior, which has not attracted attention from researchers. Fig. 1 presents an evidence of agitator blades corrosion observed in our work. The corrosion produced nickel and chromium, and it became more and more serious (judging from the nickel and chromium content in the liquid) with increasing the HT temperature. At a HT temperature of 260 °C, the nickel and chromium content in the liquid separated from the HT dechlorination of PVC were about 0.036 M and 0.004 M, respectively. As we may know, the nickel is usually worked as catalyst in some chemical conversion process. It could also affect the chlorine behavior during the HT dechlorination of PVC-containing wastes. In light of that, this work intends to investigate on the effect of corrosion on the HT dechlorination of PVC. To realize the objective, the HT dechlorination of two kinds of PVC was performed in subcritical nickel-containing water with various Ni^{2+} concentrations. A HT temperature ranging from 220 °C to 260 °C and a residence time of 0–60 min were adopted to conduct the experiments. Further information on hydrochar was obtained by employing the FTIR, SEM and ^{13}C NMR techniques. The nickel content in the separated liquid (SL) was also measured by the ICP-OS to investigate the possibility of recycling the Ni^{2+}-containing water and reuse the nickel containing wastewater in the HT treatment of chlorinated organic wastes.

2. Materials and methods

2.1. Materials

Two kinds of PVC were adopted in this work. One is purchased from Shanghai Yangli Electromechanical Technology Co., Ltd with an average molecular weight of ~90 000 Da and a chlorine content of 61.5%, noted as “CPVC” hereinafter. The other one is the waste PVC resin powder with a chlorine content of 56.5%, which was provided by a local plastic company, referred as “RPVC” hereinafter. All the chemical reagents were of analytical reagent and purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China).

2.2. HT dechlorination of PVC in subcritical Ni^{2+}-containing water

The HT dechlorination experiments were performed with a 500 mL autoclave. The nickel nitrate solution with Ni^{2+} concentrations of 0 M, 0.01 M, 0.05 M, 0.1 M, and 0.2 M respectively was prepared by dissolving a certain amount of $Ni(NO_3)_2 \cdot 6H_2O$ in deionized water. Before the experiment, 7 g of PVC powder, 0.35 g of NaOH (5%DS of PVC) and 105 mL (15 times of PVC) Ni^{2+} solution were mixed in a 400 mL quartz tube, which was placed in the autoclave subsequently. After sealing the autoclave, the argon with a purity of 99.999% supplied from argon cylinder was imported to the reactor to replace the air. And then, the electric heater was triggered to heat the reactor to a pre-determined temperature which was kept for a certain time. When this process was finished, the reactor was taken out from the heater to cool down. After the pressure was reduced to atmosphere and the temperature was below 100 °C, the gas outlet valve was opened up to release the gaseous products which firstly passed through an ice-water condenser and was then collected by a gas-sampling bag. Finally, the autoclave was opened up and the quartz tube was taken out to gather the slurry samples, which was divided into two parts as

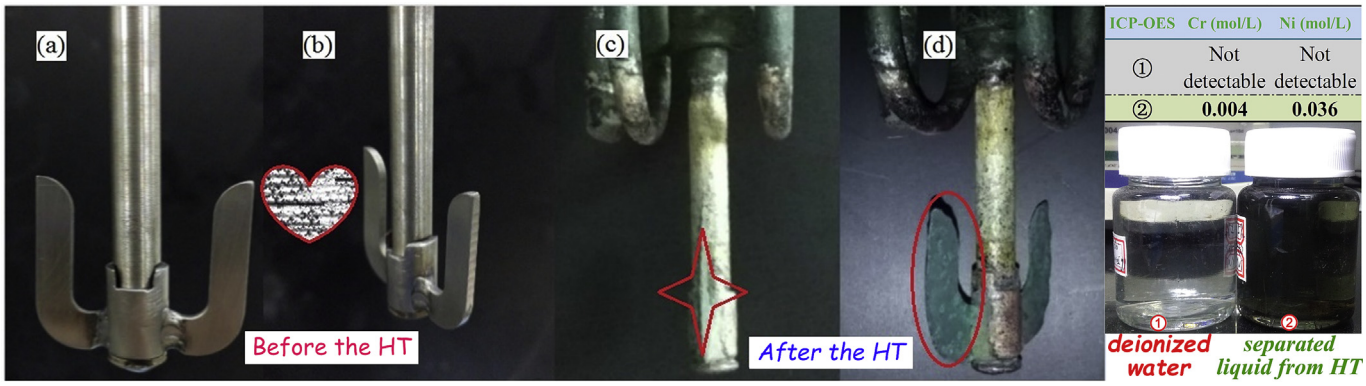

Fig. 1. The corrosion of stainless steel agitator blade during the HT process. (The left two pictures (a) and (b) are blades ready for use, the right two (c) and (d) are blades after several HT dechlorination experiments).