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Chemical dechlorination of hexachlorobenzene with polyethylene glycol and hydroxide: Dominant effect of temperature and ionic potential

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Persistent organic pollutants (POPs) originating from POP waste are playing an increasingly important role in the elevation of regional POP levels. In this study we realized the complete dechlorination of high concentration hexachlorobenzene (HCB) waste in the presence of polyethylene glycol and hydroxide, rather than using conventional high temperature incineration. Here, we demonstrate the dominant effect of temperature and hydroxide on HCB dechlorination in this process. Complete dechlorination of HCB was only observed at temperature about 200 °C or above within 4 h reaction, and the apparent activation energy of this process was 43.1 kJ/mol. The alkalinity of hydroxides had notable effects on HCB dechlorination, and there was a considerable linear relationship between the natural logarithm of the HCB dechlorination rate constant and square root of the ionic potential of metal cation ($R^2 = 0.9997$, $p = 0.0081$, $n = 3$). This study highlights a promising technology to realize complete dechlorination of POP waste, especially at high concentrations, in the presence of PEG in conjunction with hydroxide.

Despite restrictions on the use and production of persistent organic pollutants (POPs) in recent decades, there is evidence that some POPs concentration in atmosphere have leveled off much over 20 years or even are still elevated especially in urban and industrial areas^{1–3}. The primary emissions originating from high concentration POP wastes, such as obsolete pesticides, transformer oil containing PCBs, furniture or electrical devices incorporating fire retardants, and wastes from remediation site, are playing an increasingly important role in regional POPs levels^{4,5}. Those POP wastes are found throughout all around the world, for example, the estimated volumes of POP pesticides stockpiled in the European Union and China were >5370 t and 4059–6093 t, respectively^{6,7}. Therefore, appropriate technologies urgently need to be developed for the environmentally sustainable treatment of POP waste, in particular for wastes of high POP concentrations.

In the last decade, numerous studies have been reported, which have focused on the degradation of low concentration of POPs through hydrodechlorination pathway with Pd-based catalysts, nanoscale iron particles or bimetal catalysts^{8,9}. Due to self-inhibition by the chlorine ion derived from the hydrodechlorination reaction⁹, a solid Pd-based catalyst was not effective for the degradation of waste containing high concentrations of POPs. As a consequence, the treatment of POP waste at high concentration still mainly relies on high temperature incineration technology, which possesses high environmental risk due to the potential generation of dioxins^{10,11}. Thus, non-incineration technologies in the absence of noble metal catalyst are desired.

In our previous research¹², several different systems, including paraffin oil with hydroxide¹³, glycerol with carbonate¹⁴, and alkali polyethylene glycol (APEG) were investigated, among which the APEG process was the most efficient technology for the treatment of hexachlorobenzene (HCB). Polyethylene glycol (PEG) was once used as a phase-transfer catalyst in liquid-liquid two-phase dehydrohalogenation and was then introduced for the decomposition of polychlorinated biphenyls (PCBs) in transformer oil^{15,16}. However, most of these investigations focused on the removal of target pollutants rather than the dechlorination efficiency. Consequently, the reaction temperature of these experiments was mainly set below 150 °C, under which the removal efficiency was sufficient but the POPs were only partly dechlorinated. The incomplete dechlorination products of this process were hydroxylated PCBs¹⁶, which are also of great concern regarding their environmental and metabolic impact^{17,18}.



In addition, except investigations on the influence of temperature, PEG molecular weight and the reagent ratio^{16,19–21}, few researches have been conducted to determine the effect of alkali in the APEG process. The alkalinity of a hydroxide can be influenced by the corresponding metal ion²². The ionic potential and Lewis acidity of the metal ion have been used to quantify effect of metal ion on the properties of corresponding substances^{23,24}. However, since the hydroxyl ion is the functional substance in the APEG process, the importance of cation in hydroxide on the dechlorination process has been rarely investigated, which has only been preliminarily noticed and discussed in our previous research¹². Meanwhile, though nucleophilic substitution pathway¹⁶ and hydrodechlorination²⁵ pathway were separately proposed to interpret the dechlorination mechanism in the APEG process, the relationship between these two pathways has been rarely discussed.

In the present study, we investigated the effect of temperature, alkali and PEG on the dechlorination efficiency with the utilization of hexachlorobenzene (HCB) as a model compound. Based on the results, the role that alkali and PEG played and the dominant factors in the APEG process have been discussed.

Results

Temperature. The HCB removal efficiency (HRE) and dechlorination efficiency (HDE), which were calculated based on the remaining HCB and the chloride yield by equation (1) and (2), were measured to investigate the influence of temperature on the HCB dechlorination process.

$$\text{HRE} = \left(1 - \frac{m_{\text{HCB},t}}{m_{\text{HCB},0}} \right) \times 100\% \quad (1)$$

$$\text{HDE} = \frac{m_{\text{Cl}^- ,t}}{m_{\text{HCB},0} \times \eta} \times 100\% \quad (2)$$

Where $m_{\text{HCB},0}$ represents the initial addition of HCB, g; $m_{\text{HCB},t}$ and $m_{\text{Cl}^- ,t}$ represent the residual HCB and the chloride ion produced after reaction, g; η is the weight percentage of chlorine in HCB, which is 74.74%.

As shown in Figure 1a, in the presence of 18 equivalents (relative to HCB) of sodium hydroxide (NaOH) and 9 equivalents of PEG200 (polyethylene glycol with average molecular weight of 200 g/mol), more than 99.99% of the HCB was removed after 3 h at 150 °C. The HCB concentration reduced from initial 9.7% to as low as 0.6 ppm after 2 h reaction at 200 °C. Compared to the previous researches with lower initial PCBs concentration¹⁹, this suggests that HCB at

high concentrations can be also successfully removed in the presence of PEG and NaOH at relatively low temperatures (150–250 °C).

In addition, with the increasing of temperature from 150 to 250 °C, the reaction time required for 99.99% removal of HCB decreased from 3 h to 0.5 h. According to Filipis's research²¹, the kinetics of the PCB removal in the presence of KPEG reagent was first-order for PCB. So we used the first order kinetic model to calculate the HCB removal rate constant. By increasing the reaction temperature from 150 to 250 °C, an order of magnitude increase in the removal rate constant were achieved, from 0.0303 min⁻¹ to 0.306 min⁻¹. The apparent activation energy of HCB removal in the presence of PEG200 and NaOH was 43.1 kJ/mol, which was calculated according to the Arrhenius formula. This value was only about one half of the activation energy of 78–101 kJ/mol for PCB removal from contaminated dielectric oil, in which the additional energy for the dissolution KPEG in oil phase may account for the increasing activation energy²¹. And it is higher than the activation energy of 16.6 kJ/mol for HCB reduction with nanoscale zero-valent iron and 37.9 kJ/mol for HCB dechlorination with lead-iron bimetallic particles^{26,27}, indicating that reaction temperature had a more significant influence on the dechlorination in this study than it has in other technologies, which involve mainly heterogeneous catalytic hydrodechlorination.

Although the results of removal efficiency indicated that HCB at high concentration can be sufficiently removed after 4 h at 150 °C in the presence of PEG200 and NaOH, the dechlorination efficiency of HCB was only 54.5% at this condition. Even by increasing the reaction time to 10 hrs, the complete dechlorination of HCB was not achieved. In addition, as shown in Figure 1b, almost complete dechlorination of HCB within 4 h reaction was only observed at 225 and 250 °C. By comparing Figure 1a and Figure 1b, the results show that the HRE was much higher than the corresponding HDE in the dechlorination process, especially at the beginning of the reaction. This indicated that complete chlorine mineralization lagged far behind the removal of HCB in this process.

Alkali. The effect of four alkalis on HCB dechlorination efficiency at 200 °C is presented in Figure 2a. HCB was almost totally dechlorinated in the presence of KOH after 2 h at 200 °C. However, only 87.6%, 32.1%, and 10.9% HDE was achieved at the same conditions in the presence of NaOH, LiOH, and Ca(OH)₂, respectively, comparing with HRE of >99.99%, >99.99%, and 83.5% (Figure S1). At 200 °C, the chloride ion yield increased slowly after 2 h when Ca(OH)₂ and LiOH were used as the alkali in the reaction, and the HDE only reached 30.8% and 67.4% even after 10 h reaction, respectively. These results indicated that different base had a

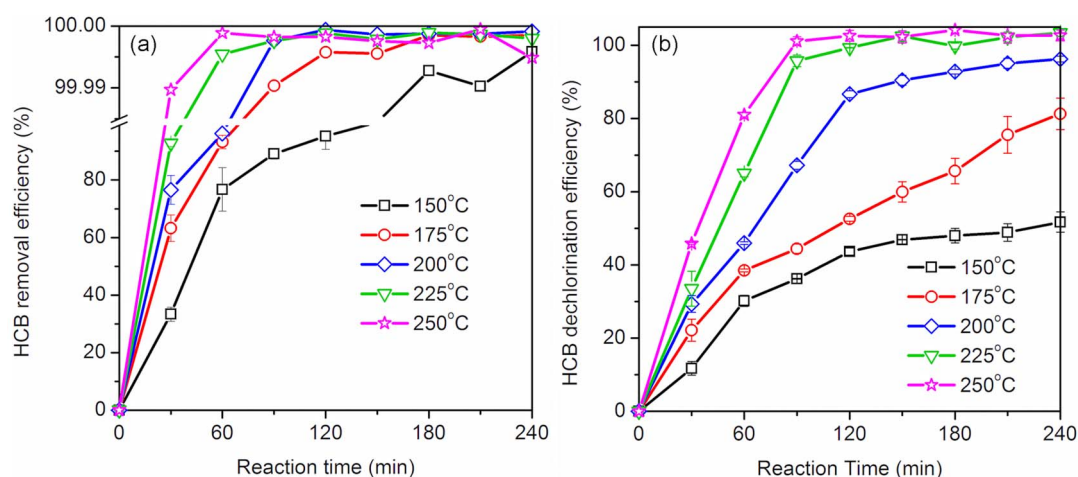


Figure 1 | Time course of HCB decomposition at various temperatures. (a) Removal efficiency; (b) dechlorination efficiency. 0.1 g HCB, 0.6 mL PEG200, and 0.253 g NaOH were added into the reactor.

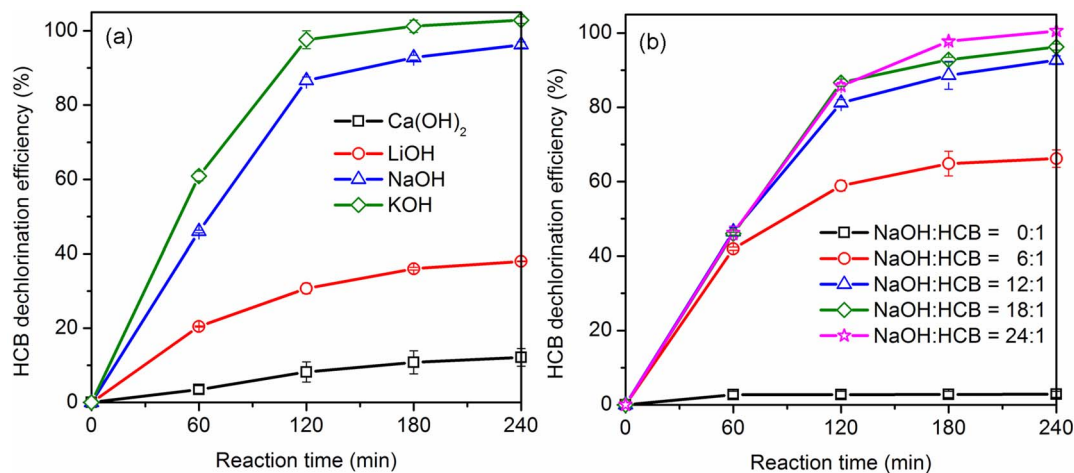


Figure 2 | Effect of alkali type (a) and NaOH dose (b) on HCB dechlorination efficiency. Reaction conditions: (a) 200°C, HCB/PEG200/alkali = 1/9/18 (molar ratio); (b) 200°C, HCB/PEG200 = 1/9.

notable influence on HCB dechlorination at a temperature of 200°C in the presence of PEG200.

By using a first-order kinetics model, the HCB dechlorination rate constants in the presence of different alkalis were calculated. The rate constant of HCB dechlorination decreased in the order $\text{KOH} > \text{NaOH} > \text{LiOH} > \text{Ca(OH)}_2$, which was in agreement with the alkalinity of the alkalis. This indicated that the strength of the alkali used had a strong influence on the HCB dechlorination rate.

The effect of adding different amounts of NaOH on the HDE is shown in Figure 2b. It is clear that virtually no HCB dechlorination (Figure 2b) and removal (Figure S2) occurred in the absence of NaOH. The HDE was almost 100% in the presence of 24 equivalents (relative to HCB) of NaOH after 4 h at 200°C, compared to 97.1% conversion in the presence of 18 equivalents of NaOH. In addition, the HDE was only 63.9% after a 4 h reaction at 200°C, when the molar ratio of NaOH and HCB was 6:1, which is the stoichiometric number of the HCB dechlorination reaction. This indicates that not only the dechlorination of HCB, but other reactions that consume NaOH also occur in the system, which has been proved in previous researches²⁵. The lower dechlorination conversion at low NaOH concentrations suggests that it is necessary to add excessive alkali to the system for the complete dechlorination of HCB.

Although the addition of excess alkali was necessary and beneficial for the dechlorination of HCB, there was plenty amount of alkali remained in the reaction system as shown in Figure 3. The large quantities of residual alkali, regardless of chemical speciation can be recycled with ease because they are water-soluble as indicated by the analysis method. And they can be readily separated from the nonpolar or solid phase, which is the case for most of POP wastes.

PEG. The influence of several kinds of PEG and different PEG dose on the HDE in the presence of NaOH is displayed in Figure 4 (HCB can be nearly completely removed at these conditions, as shown in Figure S3 and Figure S4). As shown in Figure 4a, the final dechlorination efficiency was 96.3%, 91.4%, and 80.7% after a 4 h reaction at 200°C in the presence of PEG200, PEG400, and PEG600, respectively. The HDE decreased with increasing molecular weight of the PEG, which contrasted with the findings of Kimura et al and Brunelle et al.^{15,16,19} In these previous researches, the alkoxide can transfer itself into the non-polar phase via self-complexation to form an “18-crown-6-like” structure, which is soluble in the organic phase, to improve the reaction rate of phase-transfer reaction with the increasing of PEG molecular weight¹⁹. In our study, the transfer of the alkoxide between different phases was not so crucial. However, with the increasing of PEG molecular weight, the steric effect of the

substituent group with a crown-like structure may result in the reduction of HCB dechlorination rate when higher dechlorination efficiency was required. On the other hand, the increasing of viscosity and melting point of PEG due to a higher weight molecular may also result in decreasing in HCB dechlorination rate by lowering the rate for HCB transferring into reaction media.

The effects of using different amounts of PEG200 on the HCB dechlorination efficiency are shown in Figure 4b. It is clear that the HCB dechlorination process followed a similar pattern with a final dechlorination efficiency of 96.3% to almost 100% after 4 h at 200°C when the molar ratio between PEG200 and HCB exceeded 6:1. However, the HDE was reduced in the presence of three equivalents (relative to HCB) of PEG200. The results of our earlier research showed that little dechlorination occurred in the absence of PEG¹². These results indicate that the addition of PEG200 is necessary for the dechlorination of HCB, and six equivalents of PEG200 are sufficient for the complete dechlorination of HCB.

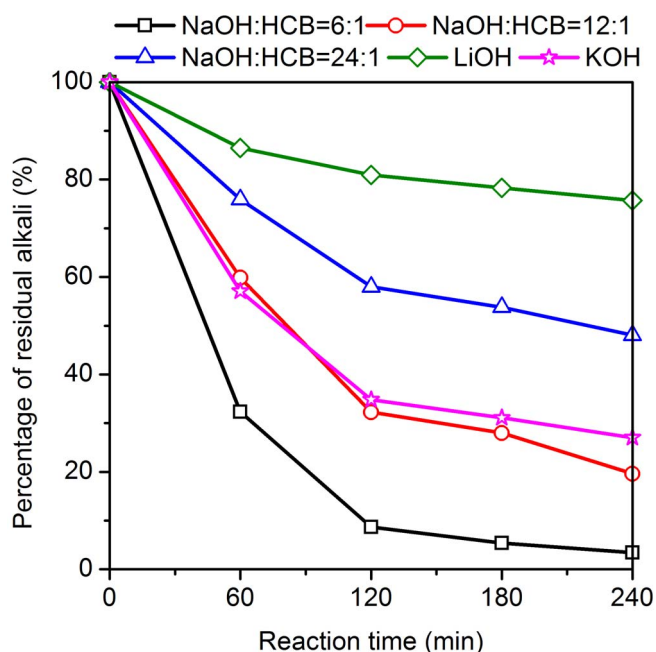


Figure 3 | Percentage of residual alkali after several different treatments. The residual alkali was measured by acid-base titration method and was converted to equivalent of initial alkali.

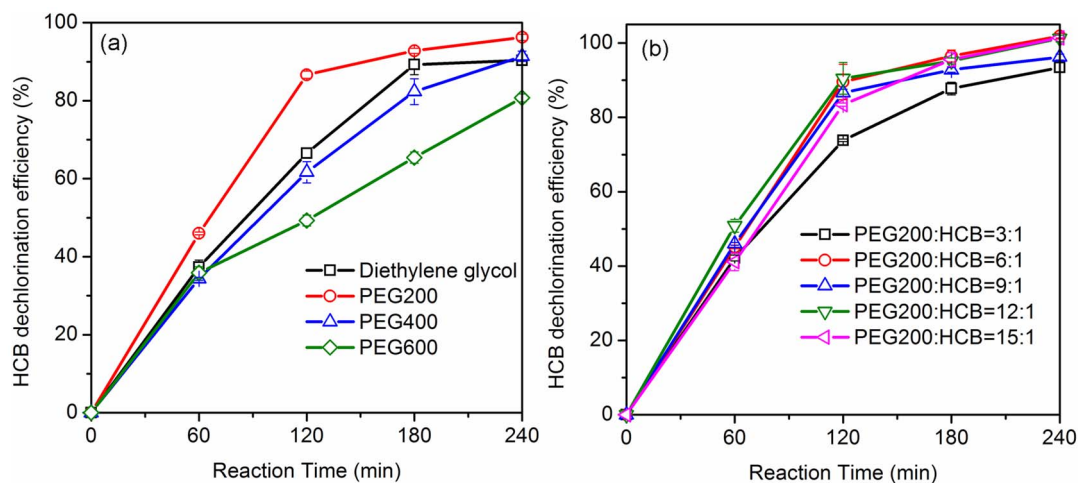


Figure 4 | Effect of alkali species (a) and PEG200 dose (b) on HCB dechlorination efficiency. Reaction conditions: (a) 200°C, HCB/PEG/NaOH = 1/9/18 (molar ratio); (b) 200°C, HCB/NaOH = 1/18.

In this study, PEG played an important role, which was similar to a catalyst for accelerating the HCB dechlorination process. In the absence of PEG, HCB should react directly with NaOH or OH^- , which is a less reactive nucleophilic substitution reagent. As a result, HCB dechlorination occurred rarely even with molten NaOH in the absence of PEG²⁸. However, in the presence of PEG, NaOH reacted primarily with PEG to form alkoxide, which is a far stronger nucleophilic substitution reagent²⁸. HCB is easily dechlorinated with the substitution of a chlorine atom by PEG alkoxide to form aryl polyglycol and a chlorine ion¹⁹.

Discussion

According to the results, HCB can be efficiently dechlorinated in the presence of PEG and alkali below 250°C. Since there was only HCB, PEG and alkali in the reaction system and virtually no HCB dechlorination occurred when only either PEG or alkali presented, it indicated that the reaction between PEG and alkali is the basis of the HCB degradation. As presented from equation (3)–(5), hydrogen from the hydroxyl in PEG can be dehydrogenized by hydroxyl ions derived from hydroxide to form PEG alkoxide. Alternatively, PEG can react with the hydroxyl ion to form the salt of the corresponding carboxylic acid and large amounts of hydrogen^{25,29}.



The production of PEG alkoxide and hydrogen, from the reaction between PEG and hydroxide, suggests that the two different degradation pathways may occur in the presence of PEG and hydroxide, the nucleophilic substitution and the hydrodechlorination pathways. However, the chromatogram of hexane extraction from the reaction media (Figure 5) shows that the concentration of benzene compounds containing low levels of chlorine was negligible, with only less than 0.02 mol% of initial HCB was detected, throughout the dechlorination process, which indicates that hydrodechlorination is the minor mechanism of HCB degradation and the major mechanism is nucleophilic substitution dechlorination.

For the major nucleophilic substitution pathway, the reaction temperature can influence the HCB dechlorination in two different aspects. First, high temperature was required for the production of PEG alkoxide. As shown in equation (3) and (4), the proton and OH^-

dissociated from the PEG and hydroxide can react to form H_2O , an alkoxide group, and a metal cation. At relatively high temperature, the water can vapor into gas phase, and the PEG dissociation reaction equilibrium is then shifted toward the right side to generate enough PEG alkoxide for the HCB dechlorination. On the other hand, temperature can affect the rate constant of HCB dechlorination by influencing the rate of elementary reactions in this system, including the dissociation of PEG and hydroxide and the nucleophilic substitution between PEG alkoxide and HCB.

Considering the high HCB concentrations used in this study, the volume of the reaction media was extremely low, allowing the system temperature to be increased easily. Due to the low dechlorination efficiency and reaction rate at relatively low temperatures as described in this work, reaction temperatures above 200°C are recommended for the complete dechlorination of HCB with PEG and NaOH.

With regard to the effect of various hydroxides on the HCB dechlorination, we used ionic potential (ϕ) to quantify the influence of an alkali on the HCB dechlorination rate. The ionic potential of the cation in the hydroxide, which is defined by equation (6)²³, has a significant influence on the chemical and physical properties of an

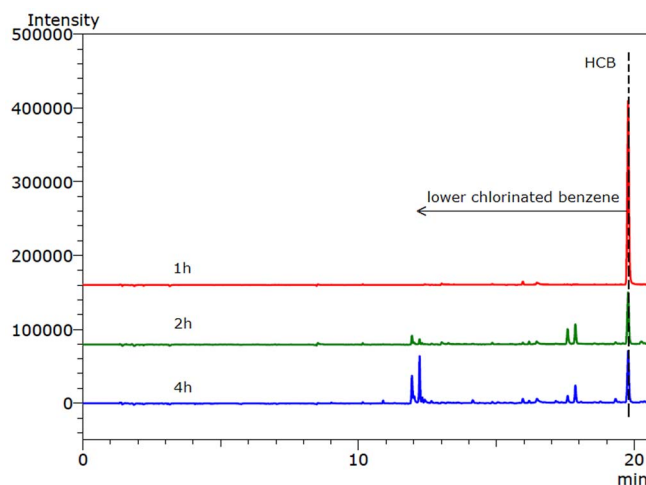


Figure 5 | GC/ECD chromatogram of hexane extraction after HCB dechlorination reaction. Reaction temperature was 200°C, and 0.1 g HCB, 0.6 mL PEG200, and 0.35 g KOH were added into the reactor. The hexane extraction was directly measured by a GC/ECD (GC-2010 Plus, Shimadzu, Japan) without further dilution.

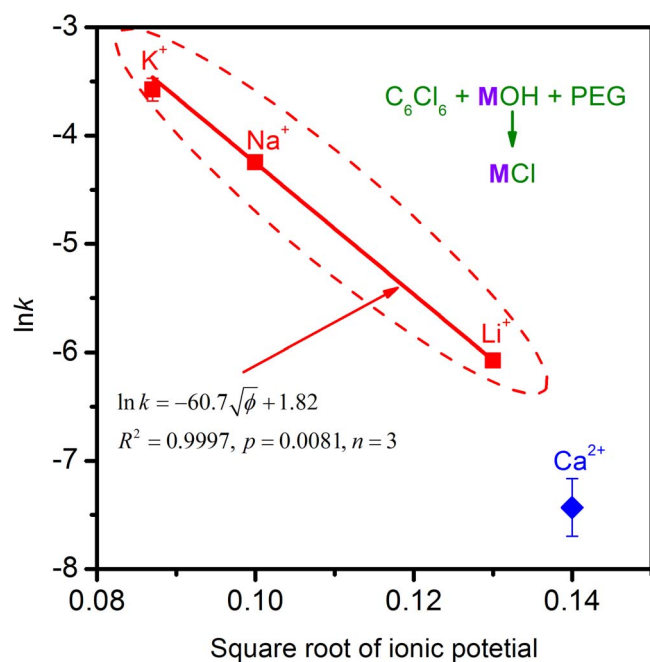


Figure 6 | The relationship between ionic potential and the first-order rate constant of HCB dechlorination. ϕ is the ionic potential of the metal ion in the alkali; k is the first-order kinetics rate constant of HCB dechlorination, min^{-1} . The relationship can be represented by the equation: $\ln k = -60.7\sqrt{\phi} + 1.82$; $R^2 = 0.9997$, $p = 0.0081$, $n = 3$.

alkali. As shown in Figure 6, the natural logarithm of the HCB dechlorination rate constant ($\ln k$) was plotted against the square root of the ionic potential ($\sqrt{\phi}$). As shown in Figure 6, there was a linear relationship between $\ln k$ and $\sqrt{\phi}$ when the alkalis were all hydroxides from group one.

$$\phi = \frac{z}{r} \quad (6)$$

Where ϕ is the ionic potential; z is the charge of the metal ion; r is the radius of the metal ion.

The ionic potential can affect the dissociation of the hydroxide into OH^- and cations (equation 3)²². With decreasing ionic potential, the bond between the metal ion and the oxygen atom is weakened because of the large radius and low charge density. This led to an increase in the OH^- concentration in the media. More alkoxide will be generated to accelerate the HCB dechlorination process. The importance of ionic potential on the HCB dechlorination rate suggests that the generation of alkoxide is one of the most crucial procedures in the dechlorination of HCB in the presence of hydroxide and PEG200.

In our previous research¹², the linear relationship between $\ln k$ and $\sqrt{\phi}$ has also been found when the reaction temperature was 150°C, and the slope of the fitting line was 194.7 with the dechlorination rate constant k measured by min^{-1} . However, in this study, by increasing the temperature to 200°C, the slope decreased by 68.8% to 60.7 which indicated that the dechlorination rate was less dependent on the ionic potential at higher reaction temperature. On the other hand, it also indicated that the difference on the rate constant between 150°C and 200°C decreased with the decreasing of ionic potential, which means that the addition of a stronger alkali in the reaction system can lower the activation energy of the dechlorination process.

As discussed above, chemical dechlorination with PEG and hydroxide is a promising non-combustion technology for the treatment of HCB. The reaction temperature and alkali species have notable effect on the HCB dechlorination process by influencing

the generation process of alkoxide. In order to realize dechlorination of chlorinated organic compounds quickly and sufficiently, we recommend to increase the reaction temperature and to utilize a stronger alkali. However, further experiments on parameter optimization and investigations on the influence of the physical and chemical properties of the waste are required for the practical application of this technology.

Methods

Materials. Hexachlorobenzene (HCB) was purchased from Beijing HengYe ZhongYuan Chemical Co. Ltd (Beijing, China). Diethylene glycol (C4H10O3) and PEG (polyethylene glycol) with average molecular weights of 200, 400, and 600, respectively, were purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). Lithium hydroxide ($\text{LiOH}\cdot\text{H}_2\text{O}$), sodium hydroxide (NaOH), potassium hydroxide (KOH), and calcium hydroxide ($\text{Ca}(\text{OH})_2$) were obtained from Beijing Chemical Works (Beijing, China). Standard samples of HCB and other chlorobenzenes were purchased from the Chinese National Institute of Metrology (Beijing, China).

Dechlorination process. All experiments were conducted in a 10 mL hydrothermal synthesis reactor (Tianhe Research Collaboration Centre, Yanzhou, China) with an inner cup (inner diameter 2.0 cm, height 3.3 cm) made of polytetrafluoroethylene (PTFE). In a typical experiment, the reactor was charged with approximately 0.1 g HCB, 0.6 mL PEG200 and ~ 0.2526 g NaOH (molar ratio, $\text{HCB}:\text{PEG200}:\text{NaOH} = 1:9:18$). The initial HCB concentration was thus $\sim 10\%$ (mass fraction). The reactor was then sealed with a thread head and calcined in a muffle furnace at preselected temperature. To generate a time curve for the dechlorination process, several reactors were used under identical operating conditions. All the experiments were conducted in duplicate.

Effect of temperature. In these batches, typical mixture of reagents was added into the reactors. The reactors were calcined at 150, 175, 200, 225, and 250°C, separately. The samples were taken at every 30 min.

Effect of reagents components. In these batches, ~ 0.1 g HCB was added into the reactors, different alkali including LiOH , NaOH , KOH , and $\text{Ca}(\text{OH})_2$ with various molar ratio of Alkali:HCB ranging from 0:1 to 24:1, and different PEG including diethylene glycol, PEG200, PEG400, and PEG600 with various molar ratio of PEG:HCB ranging from 3:1 to 15:1 were transferred into the reactors separately to investigate the influence of reagents components on HCB dechlorination. When one influencing factor was being investigated, other factors were fixed as that of in typical experiment (the alkali used was NaOH , the PEG used was PEG200, the molar ratio of $\text{HCB}:\text{PEG}:\text{Alkali}$ was 1:9:18). All the experiments in this section were conducted at 200°C, and the samples were taken at every 1 h.

Sample extraction and analytical methods. The reactors were removed from the furnace at preselected time intervals, and then cooled to ambient temperature with running water. The reaction was quenched immediately by the addition of 5 mL deionized water. In most experiments, the remaining matter could be completely dissolved into the aqueous phase. However, in some cases HCB crystals remained and were not soluble. This portion of remaining HCB was gathered by filtration and quantified using a weighing method. The aqueous phase was completely transferred into a 60 mL separating funnel in which the HCB and other chlorobenzenes were extracted with 15 mL hexane. The remaining aqueous phase was entirely collected in a volumetric flask and diluted to 100 mL with deionized water. The HCB concentration in the hexane was determined using a gas chromatograph equipped with an electron-capture detector (GC-2010 Plus, Shimadzu, Japan). The chloride anion concentration in the aqueous phase was quantified by the silver nitrate titration method.

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Author contributions

Y.X. and J.J. conceived and designed the experiments. Y.X. performed the experiments and wrote the manuscript. J.J. and H.H. reviewed and commented the manuscript.

Additional information

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