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Indirect electrochemical oxidation of pentachlorophenol in the presence of different halides: behavior and mechanism

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ABSTRACT

Indirect electrochemical oxidation (EO) of pentachlorophenol (PCP) wastewater was carried out in the presence of different halides through the electrogeneration of active halide (AH). The EO effect and electrochemical behaviors of PCP under different conditions are present in this paper. The cyclic voltammetry (CV) curves indicated higher electrogeneration efficiency of active halogen in NaBr solution. Chronoamperometric response proved the formation of passivating polymer on anode surface. The conversion rate of PCP was distinctly different for different halides following the order $Br^- > Cl^- > F^- > I^-$. The proper oxidation potential of Br^- to active bromine led to the optimal electrooxidation effect of Br^-. With the rise of temperature the reaction rate decreased at first from 30 to 45 °C and then increased from 45 to 60 °C. The complicated variation of PCP conversion on rising temperature was depicted by the electrochemical measurements and a mathematic model.

Keywords: Indirect electrooxidation; Pentachlorophenol; Dechlorination efficiency; Temperature; Halide

1. Introduction

Pentachlorophenol (PCP) as one of the persistent organic pollutants has aroused great environmental concern recently. According to IUPAC, PCP was extensively used as preservative or herbicide in agricultural and industrial domains because of its acute toxicity [1]. Apart from this, it is also chemically inactive and biorefractory. PCP has been defined as one of the priority pollutants by the US Environmental Protection Agency (EPA) [2]. Therefore, the effluents containing PCP needed to be treated prudentially. Numerous sewage disposal processes including adsorption [3,4], biodegradation [5], photocatalysis [6], microwave-assisted catalytic oxidation [7], catalytic hydrogen peroxide oxidation [8], and electrochemical oxidation (EO) [9–13] have been employed to degrade PCP from environment.

EO is an efficient technique to remove organic pollutants. In the process, there are two modes of electrolysis, (1) direct electrolysis or (2) indirect electrolysis [14]. For indirect electrolysis, the addition of chloride ion as a mediator is a very promising method [15,16].

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The Cl^- could be oxidized at the anode surface to form *in situ* active chlorines which are powerful oxidants (Eqs. (1)–(3)), e.g. hypochlorite acid or sodium hypochlorite. These substances can oxidize the organics near the anode surface or/and in the bulk of the solution (Eq. (4)) [17].

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{1}$$

$$Cl_2 + H_2O \rightarrow HClO + H^+ + Cl^- \tag{2}$$

$$Cl_2 + 2OH^- \rightarrow ClO^- + Cl^- + H_2O \tag{3}$$

$$ClO^-/HClO + \text{organics} \rightarrow \text{Intermediates} \rightarrow CO_2 + H_2O + Cl^- \tag{4}$$

Compared with the direct anodic oxidation, higher current efficiency and pollutant degradation rate could be achieved in the indirect electrolysis processes in the presence of Cl^-. The method has been utilized to remove organics in many academic papers [17–25]. Buso et al. proved that higher COD removal could be attained in chloride-mediated medium at Pt anode with respect to the one in chloride-free solution [21]. Panizza et al. found that with the rise of Cl^- dosage, the rate of COD removal was dramatically improved [22]. The comparison of electrooxidation effects between boron-doped diamond (BDD) anode and active electrodes (DSA anodes) in the presence of Cl^- carried out by researchers has proved that the performance of active electrodes was surprisingly higher than that of inert electrodes [17,23]. The process was particularly suitable for the effluents containing Cl^- themselves and high COD as well as NH_3-N removal with low energy cost have been achieved without additional Cl^- [26–28].

It has been reported that potentially harmful byproducts might be electrogenerated in the Cl^- indirect electrooxidation processes and then the toxicity of effluent might be increased [29]. But further investigations have proved that these products could be completely degraded in the end [30] and were not identified by GC-Mass [31].

Hitherto, few papers have been published on the degradation of PCP by EO mediated by Cl^- [11,31]. Wu et al. contrasted the decomposition of PCP at oxidative and reductive potentials in the presence of Cl^- employing a Pt electrode as working electrode [11]. Patel et al. investigated the disposal of PCP in simulated wastewater and pulp bleaching effluent [31]. Though high efficiency of PCP degradation has been obtained, both papers paid less attention on the electrochemical behaviors of PCP in Cl^--mediated electrochemical system. As a result, electrochemical measurements of PCP in medium containing different halides need to be critically studied.

Not only is the chloride a promising homogeneous catalyst, but fluoride and bromide ions could also be employed to remove organics as redox reagents according to Martinez-Huitle et al. [20]. Moreover, the introduction of other halides (F^-, Br^-, and I^-) might be of great help to clarify the dechlorination effect of PCP in indirect EO processes. Since the toxicity of chlorophenols increases with the rising number of Cl atoms [32], the dechlorination capacity of this system was important to be identified with the help of other halides.

Among various operative parameters, the influence of temperature on the mineralization of pollutant has been focused on by some researchers. In general, the EO rate will be increased with the rise of temperature following Arrhenius behavior [33,34]. But strangely in the Cl^--mediated EO process, negative impact of temperature on the incineration rate was reported by Bonfatti et al. and Zheng et al. [19,35]. So the influence of temperature on the decay of pollutants should be carefully considered when employing halides as mediators in indirect electrolysis process.

Hence, this paper mainly studies the degradation effect and electrochemical behaviors of PCP in the presence of different halides at active anode (Ti/RuO_2) through experimental and theoretical method. At the same time, EO dechlorination effect of PCP was also discussed. To fulfill the objectives several operative parameters, particularly the types of halides and reaction temperatures, were investigated through bulk electrolysis and electrochemical measurements. It should be noted that for the first time the CV and chronoamperometry measurements were performed at different temperatures.

2. Experimental

2.1. Chemicals

$Ti/RuO_2 + TiO_2$ anode was purchased from Hangzhou Cell Company, Hangzhou Zhejiang, China. The cathode was made of Ti. Both electrodes have the same sizes: $50 \times 40 \times 2$ mm PCP, chemical grade, was obtained from Sinopharm Chemical Reagent Company, Shanghai, China. NaF, NaBr, NaCl, and NaI from Kermel Chemical Reagent Company, Tianjin, China were all analytically pure. All other chemical reagents used here were of analytical grade and were used as received. The concentration of PCP was $50\,mg\,L^{-1}$ with $10\,g\,L^{-1}$ Na_2SO_4 and certain amount of sodium halide. Initial pH of the solution was 8.0, adjusted by 5% NaOH or 3 mol L^{-1} H_2SO_4.

2.2. Electrolysis experiment

Experimental setup is exhibited in Fig. 1. The EO mediated by different halides was carried out at continuous processes in a single compartment cell under galvanostatic condition. The gap between anode and cathode was 10 mm. The PCP solution (200 ml) was circulated constantly around the electrochemical cell by a peristaltic pump. The flow rate was 50 ml min^{-1}. The temperature of the solution was controlled by water bath. Different parameters, concentration of Cl^-, current density, kinds of halides, and reaction temperatures were systematically experimented. The duration of reaction was 60 min and 1 ml solution was carefully extracted from the reactor at 0, 10, 20, 40, and 60 min. Open circuit experiment has proved that reactor and tubing showed no effect on reaction results. To avoid the influence of anode passivation on the mineralization of PCP, 30 min electrolysis in 1 mol L^{-1} NaCl solution without PCP at the current density of 50.0 mA cm^{-2} was conducted prior to PCP indirect EO.

2.3. Electrochemical measurements

Electrochemical measurements were carried out in a standard three-electrode cell using a computer-controlled CHI630D electrochemical analyzer (Chenhua Instrumental Corporation, Shanghai, China). Two $Ti/RuO_2 + TiO_2$ electrodes with the area of 4 cm^2 were used as the working electrode and counter electrode. The reference electrode was a saturated calomel electrode (SCE). The three-electrode system was surrounded by a heating jacket so that temperature could be controlled. Then the electrochemical behaviors at different temperatures (30, 45, and 60 °C) could be studied.

2.4. Analysis

The concentration of PCP in aqueous solution was measured by Elite 1201 HPLC system, Elite Company, China. The aliquots of 10 μl were injected into the chromatograph. The mobile phase was methanol–2‰ ammonium acetate aqueous solution (85/15, V/V) at a flow rate of 1.0 ml min^{-1}. PCP was separated by a reversed phase column of ultimate XB-C18 (Welch Materials Inc. China) and was detected by a UV-vis detector at 320 nm wavelength. The concentration of F^-, Cl^-, and Br^- was determined by ion chromatography, Shimazu Corporation, Japan.

3. Results and discussion

3.1. The electrochemical behaviors in different solutions

The CVs of $Ti/RuO_2 + TiO_2$ electrode in different solutions were shown in Fig. 2. There was no obvious difference between the CV curves representing NaCl and blank solutions (10 g L^{-1} Na_2SO_4) in the potential region of water stability ($E < 1.103$ V vs. SCE). Only when the potential exceeded 1.103 V (vs. SCE), could higher current density be observed in the system containing NaCl compared with that in blank solution. Then the oxidation of Cl^- to active chlorine had to be taken place simultaneously with oxygen evolution. However, as for the CV curve of NaBr solution,

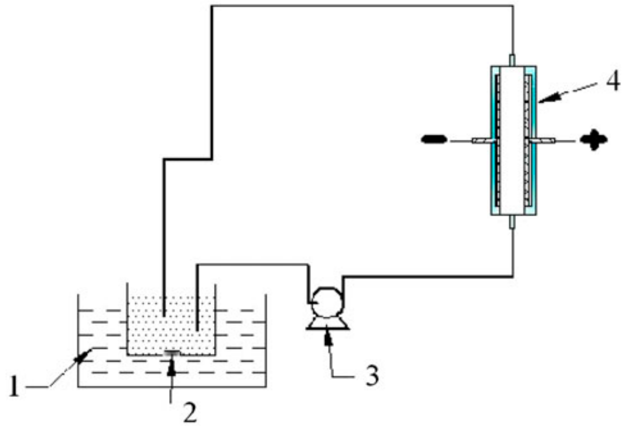

Fig. 1. Setup of the electrolysis system, (1) water bath, (2) magnetic bar stirrer, (3) peristaltic pump, and (4) electrochemical cell.

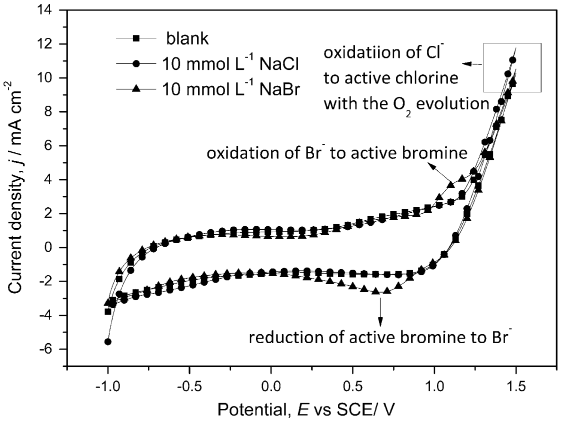

Fig. 2. The CV curves of blank, NaCl and NaBr solutions without PCP at a $Ti/RuO_2 + TiO_2$ electrode, scan rate: 50 mv s^{-1}, Na_2SO_4: 10 g L^{-1}, pH 8.0, and temperature: 30 °C.

there was a clear oxidation peak at 1.051 V (vs. SCE) and a reduction peak at 0.682 V (vs. SCE) which might correspond to the oxidation of Br^- and reduction of active bromine. The oxidation potential of Br^- to active bromine demonstrated that Br^- could be oxidized in the potential region of water stability. Thus, higher anodic current efficiency for the electrogeneration of active halogen (AH) could be realized in NaBr solution.

The influence of temperature (30, 45, and 60 °C) on current density was investigated by the chronoamperometric response in Fig. 3. It should be noted that according to [36], the calomel electrode as a reference electrode for work is well recognized in the temperature range from 25 to 60 °C. So the results in Fig. 3 were authentic and reliable. A positive effect of elevated temperature towards the amplification of chronoamperometric current density could be observed just like the CV variation at different temperatures in Fig. S1. According to the Cottrell equation (Eq. (5)) [37], the current density–time relationship can be expressed as follow:

$$j(t) = \frac{nFD_R^{1/2}C_R^*}{\pi^{1/2}t^{1/2}A} \tag{5}$$

where C_R^* and D_R are the concentration in bulk medium and diffusion coefficient of PCP, respectively, and F Faraday constant (96,500 C mol^{-1}). The current density (j) was proportional to the half power of solute diffusion coefficient which was promoted by the boosted temperature. As the lift of temperature might give rise to the magnification of diffusion coefficient, the current density was then enhanced. However, the current density difference value ($j_{v,T} = j_{NaCl,T} - j_{blank,T}$) between solution containing NaCl and blank solution at 30 °C (0.85–0.90 mA cm^{-2}) was larger than that at 45 °C (−0.16 to −0.18 mA cm^{-2}) and 60 °C (0.75–0.80 mA cm^{-2}). Since the $j_{v,T}$ might reflect the rate of active chlorine electrogenerated, it can be inferred that the elevated temperature was not beneficial for electrogeneration of active chlorine. The chronoamperometric curve at 1.0 V (vs. SCE) demonstrated that anodic oxidation did not happen at this potential.

The chronoamperometric response of the $Ti/RuO_2 + TiO_2$ electrode in 10 mmol L^{-1} NaCl solution with or without PCP at different temperatures was also investigated. As shown in Fig. 4, both the chronoamperometric current density in the absence and in the presence of PCP increased with the elevated temperature. But the current density in the solution without PCP was much higher than that in PCP medium at the same temperature. Just like the results acquired by Santos et al., CV current density also decreased with the addition of phenol [30]. It was asserted that the decline might be the result of the formation of a polymeric film by the phenol oxidation on the anode surface [38]. And according to literature [39–41], the passivating film generated through PCP electrooxidation could also be found on Pt or BDD anode surface. As a result, the reason why chronoamperometric current density decreased with the addition of PCP in this paper was the formation of polymer on anode surface. Moreover, $j_{v,T}$ was expanding with the rising temperature. This is owing to the fact that the hoist of temperature could accelerate the generation of passivation film on electrode surface, indicating negative effect of rising temperature on reaction rate.

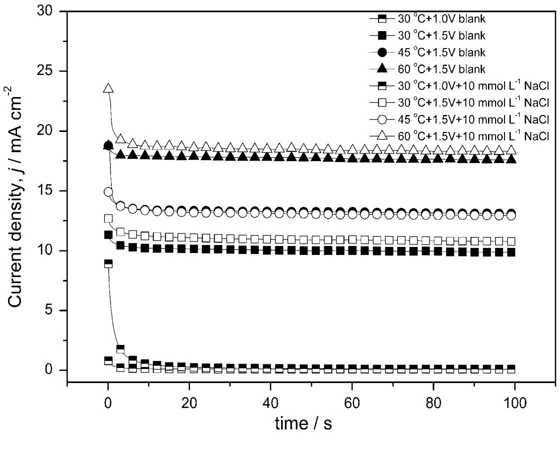

Fig. 3. The chronoamperometric curves at 1.0 V and 1.5 V (vs SCE) with or without NaCl in the absence of PCP at different temperatures (30, 45, and 60 °C), Na_2SO_4: 10 g L^{-1}, and pH 8.0.

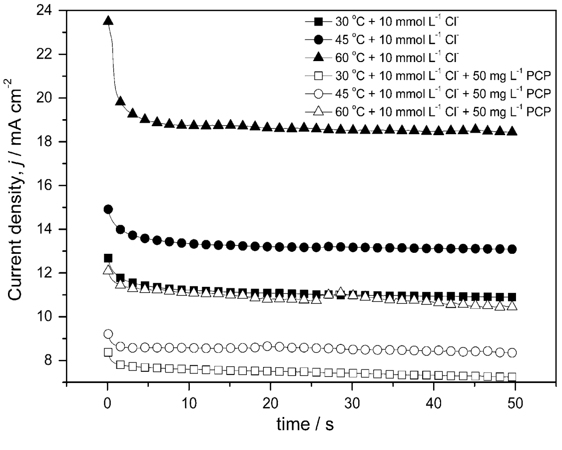

Fig. 4. The chronoamperometric curves at 1.5 V (vs SCE) in 10 mmol L^{-1} NaCl solution with and without PCP at different temperatures (30, 45, and 60 °C), Na_2SO_4: 10 g L^{-1}, and pH 8.0.

3.2. Effect of Cl^- content on the degradation of PCP

Effect of Cl^- dosage (0, 1, 5, and 10 mmol L^{-1}) on the evolution of PCP was experimentally investigated and the results were shown in Fig. 5. The PCP conversion increased from 5.15% to 75.23% accompanied by the raise of Cl^- concentration from 0 to 10 mmol L^{-1}. With the rise of Cl^- concentration, the molar ratio of active chlorine/O_2 electrogenerated was increased according to Eq. (1). Higher PCP mineralization rate was achieved at higher content of Cl^-.

3.3. Effect of current density on the degradation of PCP

As the choice of proper current density is essential for the EO processes, electrolysis was carried out at different current density (2.5, 5.0, and 10.0 mA cm^{-2}) with Cl^- dosage of 10 mmol L^{-1}. Thanks to the rise of current density; PCP conversion increased from 40.25% at 2.5 mA cm^{-2} to 100% at 10.0 mA cm^{-2}. The inset in Fig. 6 manifested that the reaction coincided with pseudo-first-order kinetic model very well (Eq. (6)). The reaction rate constants were 0.010, 0.023, and 0.057 min^{-1} at current density of 2.5, 5.0, and 10.0 mA cm^{-2}, respectively.

$$r_{PCP} = -k[PCP] \tag{6}$$

3.4. Effect of halide varieties on the degradation of PCP

The results in Figs. 5 and 6 demonstrated that Cl^- was an efficient homogenous electrocatalyst. It is interesting to look into the performances of other halides (F^-, Br^-, and I^-) on the abatement of PCP and look into the dechlorination effect of PCP and intermediates in solutions with the help of F^- and Br^-. As shown in Fig. 7, the EO capacity was $Br^- > Cl^- > F^- > I^-$. Unlike other three halides, F^- cannot be oxidized directly to active fluorine (F_2, HFO) in aqueous mediums, so the conversion of PCP in NaF solution was quite low. In spite of higher concentration of active iodine produced, the oxidation potential of I_2 ($I_2 + 2e^- \rightarrow 2I^-$, 0.2905 V vs. SCE, 25 °C) was extraordinarily low. So PCP could not be degraded by active iodine. In the case of Br^-, since the oxidation potential of Br_2 ($Br_2 + 2e^- \rightarrow 2Br^-$, 0.8425 V vs. SCE, 25 °C) was higher than that of I_2 and lower than that of Cl_2 ($Cl_2 + 2e^- \rightarrow 2Cl^-$, 1.1133 V vs. SCE, 25 °C), it makes Br^- the optimal choice to degrade pollutants: higher concentration of active bromine with proper oxidation capacity. Therefore, excellent EO effect in NaBr solution was observed. The higher electrogeneration efficiency of active halogen (AH) in Br^--mediated electrolysis system was also verified by CVs in Fig. 2. According to literature [20], the order of electrooxidation capacity was $F^- >/= Br^- > Cl^-$, which is different from the results in Fig. 5 in this paper. This might be the diversity of anode materials utilized, as the Pt electrode was employed as anode in [20] while in this paper it is $Ti/RuO_2 + TiO_2$ electrode.

The variation of Cl^- concentration in F^- and Br^- was exhibited in Figs. 7 and 8. As the Cl^- concentration released from the PCP EO process was quite low in F^- or Br^- medium, it is assumed that the deprived Cl from PCP was fully transfromed into Cl^- and the Cl^- was not electrooxidized at the anode. In order to preferably depict the Cl^- variation curves, one concept was put forward: assumed Cl^- concentration which is calculated according to PCP conversion

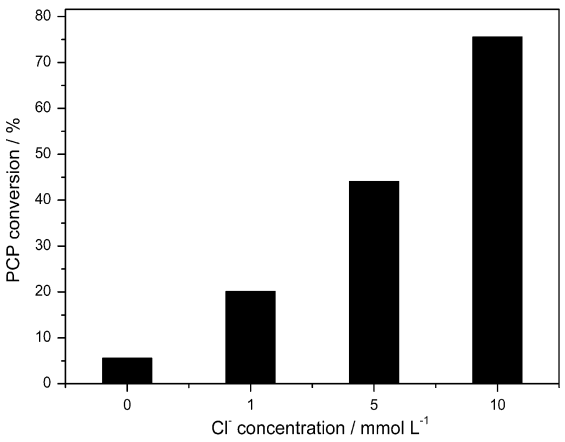

Fig. 5. Effect of Cl^- concentration on the evolution of PCP, current density: 5.0 mA cm^{-2}, initial concentration of PCP: 50 mg L^{-1}, pH 8.0, and temperature: 30°C.

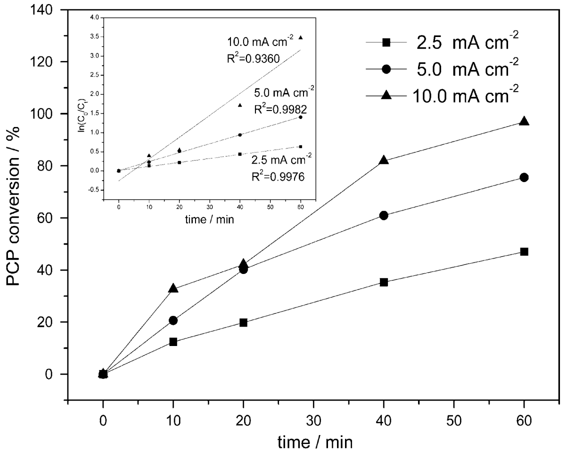

Fig. 6. Effect of current density on PCP conversion, Cl^- concentration: 10 mmol L^{-1}, initial concentration of PCP: 50 mg L^{-1}, pH 8.0, and temperature: 30°C. Inset shows linear regression for PCP conversion plotted with time at different current density.

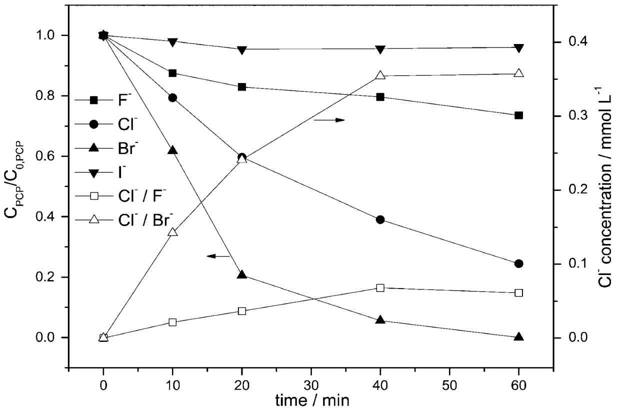

Fig. 7. Effect of halide varieties on the decomposition of PCP, concentration of halide: 10 mmol L^{-1}, current density 5.0 mA cm^{-2}, initial concentration of PCP: 50 mg L^{-1}, pH = 8.0, and temperature: 30°C.

provided that Cl on PCP was completely deprived and transformed to Cl^-. Fig. 8 described the relationship between the real and assumed Cl^- concentration in F^-- and Br^--mediated EO systems. The ratio between real and assumed Cl^- concentration manifested that Cl atoms on PCP were not fully deprived from the converted PCP. Compared with the one in F^- medium (about 0.3), higher dechlorination ratio for single PCP molecular converted in Br^- medium (about 0.4) was achieved. This might be due to different reaction mechanism in F^- and Br^- EO systems. As mentioned above, F^- cannot be oxidized to form active fluorine at $Ti/RuO_2 + TiO_2$ anode in aqueous medium. The relatively higher pollutant conversion in F^- medium than that in blank solution might be due to the presence of F^- which can inhibit the oxygen evolution according to [20] by changing the stoichiometry and microstructure on the oxide film. But for Br^-, the pollutant was mainly degraded by the electrogenerated active bromine. Consequently, the diversity of reaction mechanism led to the differences of PCP conversion and dechlorination efficiency. Since the reaction mechanism of Cl^--indirect EO system was analog to that in Br^- medium [20], the dechlorination effect in Cl^--mediated electrolysis system can be speculated.

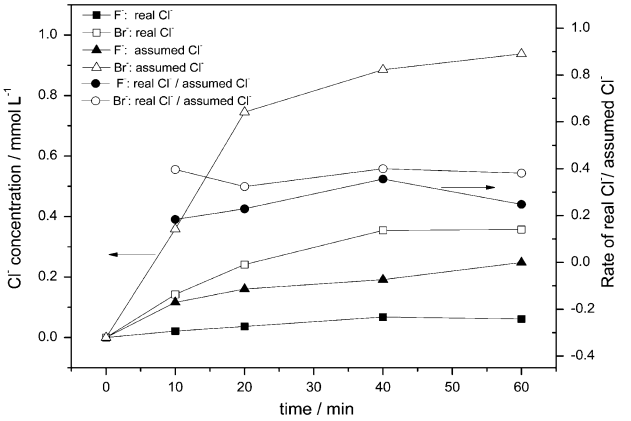

Fig. 8. The relationship between the real Cl^- concentration and assumed Cl^- concentration in F^-- and Br^--mediated EO systems; the reaction condition is the same as Fig. 7.

3.5. Effect of temperature on the degradation of PCP

The decay of PCP at different temperatures (30, 45, and 60 °C) in NaBr and NaCl solutions was exhibited in Fig. 9. Just like the results in literatures [19] and [35], abnormal impact of temperature on PCP conversion was observed. The PCP conversion dropped at first (from 30 to 45 °C) and then increased (from 45 to 60 °C). In NaBr medium, PCP was fully converted at 30 °C while only about 81 and 87% PCP was degraded at 45 °C and 60 °C. In terms of Cl^--mediated system, while PCP conversion was the highest at first 50 min of the reaction at 30 °C, it was surpassed in the end by the reaction performed at 60 °C (about 80%). Table 1 summarizes the rate constants and the regression coefficients in Br^-- and Cl^--mediated electrolysis systems at different reaction temperatures (30, 45, and 60 °C) assuming that the reaction fits pseudo-first-order kinetic model. As shown in Table 1, fairly high regression coefficients were observed. The rate constant at 30 °C was three times more than that at 45 °C in NaBr solution, but it increased from 45 to 60 °C.

Fig. 10 depicts the evolution of real and assumed Cl^- concentration in aqueous mediums at different temperatures. Just like the results in Fig. 9, not all Cl from PCP was deprived and converted to Cl^-. The ratio of real/assumed Cl^- concentration fluctuated between 0.3 and 0.5. The same as the variation of PCP conversion with different temperatures, the final ratio of real/assumed Cl^- concentration under different temperatures in Br^--mediated system also decreased at first (30–45 °C) and then increased (45–60 °C).

As the reaction conformed to pseudo-first-order kinetic model which can be depicted by exponential function, the conversion curve was then matched by Eq. 7. The exponential fit of conversion with time is shown in Fig. 11.

$$R = R_0 + A\exp(-kt) \tag{7}$$

In Eq. (7), R and t represented conversion and reaction time and the theoretical values of R_0, A were 1, −1, k the rate constant (min^{-1}). The fitting results and the regression coefficients are shown in Table 2 which exhibited excellent simulated results.

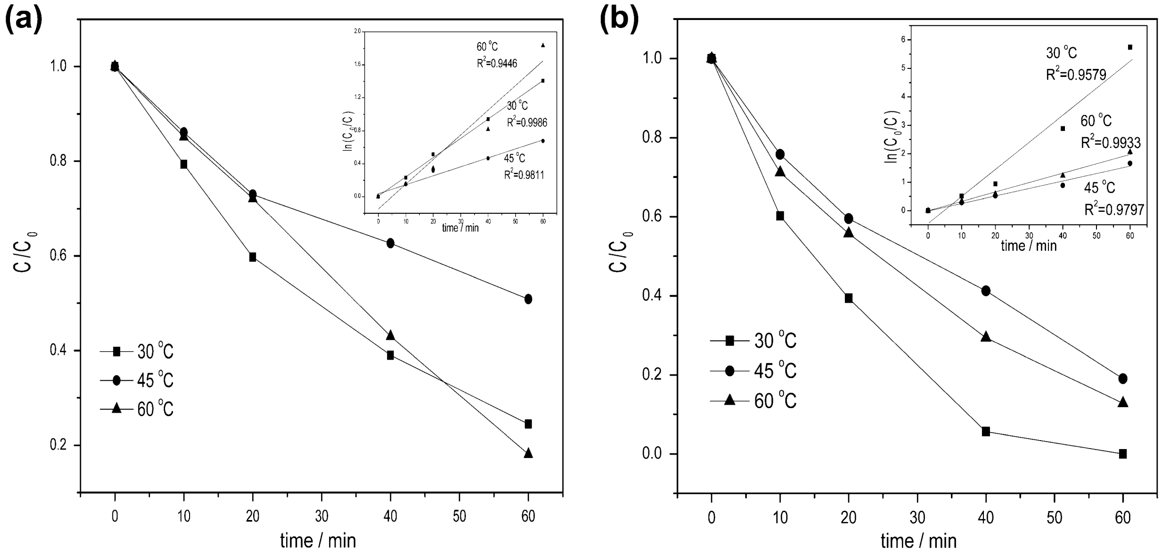

Fig. 9. Effect of reaction temperature on the abatement of PCP in NaBr (a) and NaCl (b) solutions, dosage of Br^- and Cl^-: 10 mmol L^{-1}, current density: 5.0 mA cm^{-2}, initial concentration of PCP: 50 mg L^{-1}, and pH 8.0. Inset shows linear regression for PCP conversion with time at different temperatures.

Table 1
Rate constants of PCP conversion in Br^-- and Cl^--mediated electrolysis systems

Halide variety	Reaction temperatures (°C)	Rate constant (min^{-1})	R^2
Br^-	30	0.0957	0.9579
	45	0.0264	0.9797
	60	0.0337	0.9933
Cl^-	30	0.0234	0.9986
	45	0.0109	0.9811
	60	0.0299	0.9446

Szpyrkowicz et al. [42] and Anglada et al. [28] described the Cl^--mediated EO process with a second-order kinetic constant because of the drop of Cl^- and pollutant concentration. However, the Br^- concentration in this paper was almost the same (results were not shown). This might be due to the differences of anode materials. Then the concentration of active bromine consisting of Br_2, HBrO, and/or BrO^- was fixed for the mass conservation. Likewise, the active chlorine concentration was a constant too. As a result, the electrogeneration rate of active halogen (Eq. (8)) would equal to the consumption rate of active halogen (AH) which comprised the valid reaction rate with pollutants (Eq. (9)) and invalid decomposition rate of AH (Eq. (10)). α which varied with the reaction temperatures and the status of electrode represented the current efficiency for AH evolution. β, the stoichiometric number of the reaction of AH with PCP, was determined by the concentration of PCP and oxidation capacity of AH that related with the temperature and aqueous pH. Thus, the valid reaction rate of AH could be expressed in Eq. (11) and then invalid decomposition rate might be acquired according to Eq. (12) with the help of θ that was affected by the temperature and aqueous pH. Consequently, the model can be put forward and simplified in Eq. (13).

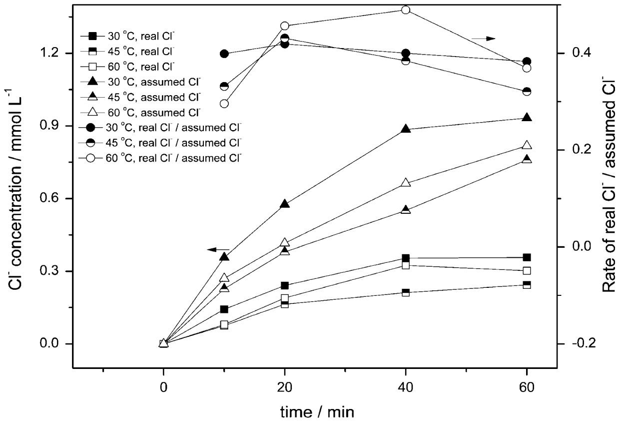

Fig. 10. The relationship between real Cl^- concentration and assumed Cl^- concentration at different temperatures, the reaction condition is the same as Fig. 9.

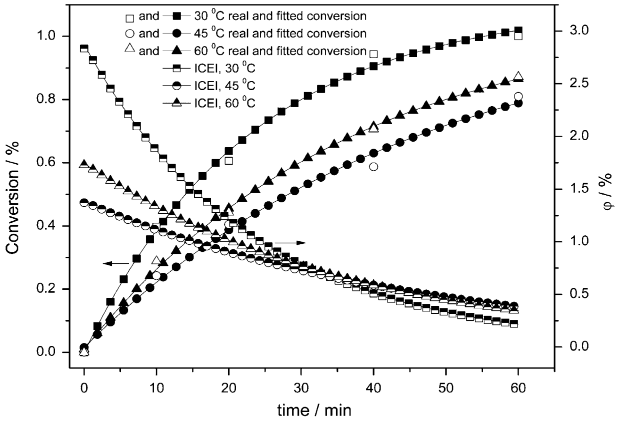

Fig. 11. The exponential fit of conversion on time and the ICEI variation on time in NaBr solutions at different temperatures, the reaction condition is the same as Fig. 9.

Table 2
The parameters of fitted exponential curve in Br^--mediated system

Reaction temperatures (°C)	C_0	A	k (min^{-1})	R^2
30	1.1014	−1.1015	0.04321	0.9914
45	1.0876	−1.0720	0.02131	0.9830
60	1.0742	−1.0642	0.02716	0.9957

$$r_{\mathrm{AH,\ generation}} = \frac{\alpha j A}{nFV} \tag{8}$$

$$\mathrm{AH} + \beta\mathrm{PCP} \rightarrow \mathrm{Intermediates} + \mathrm{CO_2} + \mathrm{H_2O} + \mathrm{Br^-/Cl^-} \tag{9}$$

$$\mathrm{AH} \rightarrow \mathrm{O_2} + \mathrm{HBr/HCl} \tag{10}$$

$$r_{\mathrm{AH},\quad \mathrm{valid}} = \frac{1}{\beta} r_{\mathrm{PCP}} \tag{11}$$

$$\theta = \frac{r_{\mathrm{AH},\quad \mathrm{invalid}}}{r_{\mathrm{AH},\quad \mathrm{valid}}} \tag{12}$$

$$\varphi = \frac{nFV \cdot |r_{\mathrm{PCP}}|}{jA} \tag{13}$$

where $\varphi = \frac{\alpha \cdot \beta}{1+\theta}$, represents the instantaneous current efficiency idex (ICEI) for the degradation of PCP. As the instantaneous degradation rate of PCP could be acquired according to Eqs. (6) and (7), then φ could be calculated by Eq. (13). Then the variation of φ with time for Br^--indirect electrooxidation system at different temperatures is depicted in Fig. 11.

Table 3
The pH variations in Br^--mediated electrolysis system

Time (min)	30°C	45°C	60°C
20	8.0	8.0	8.0
40	7.2	6.5	6.3
60	6.4	5.9	5.2

There are at least three reasons related with the abnormal ICEI variation aroused by temperature. First, the electrogeneration efficiency of AH (α) was decreased with the rise of reaction temperature. Though the rate constant of each reaction was reduced by decreasing temperature, the current efficiency for AH evolution was enhanced with the drop of temperature [19]. This was also proved in Fig. 3. Moreover, as indicated by Fig. 4, the rise of temperature was also beneficial for the formation of polymer on anode surface which could inhibit the generation of AH. Second, the invalid decomposition (θ) of AH might be accelerated by elevating the reaction temperature [35]. Third, as shown in Table 3, higher concentration of H^+ was produced in electrolyte of 60 °C. Since the drop of pH could enhance the oxidation capability of active halogen according to [19,26,35], the stoichiometric number (β) for reaction of active halogen with PCP subsequently increased with the elevated temperature. From this point of view, rising temperature was in favor of the abatement of PCP. Consequently, the joint influence of the positive and negative effects of temperature led to the phenomenon that PCP conversion dropped at first (from 30 to 45 °C) and then increased (from 45 to 60 °C).

4. Conclusions

The electrochemical measurements and bulk electrolysis of PCP with different halides as redox mediators were experimentally and theoretically investigated. With the rise of Cl^- dosage and current density, the pollutant conversion rate was extremely enhanced. Proper oxidation potential of Br^- to active bromine led to the optimal performance of Br^- in the degradation of PCP, which is supported by the experimental results and CVs in Fig. 2. The chronoamperometric curves (Figs. 3 and 4) indicated that the rise of temperature did not favor the eletrogeneration of active halogen and was conductive to the generation of adherent polymer film on the anode surface. Then the PCP conversion decreased first (from 30 to 45 °C). However, due to higher concentration of H^+

at higher temperature (60 °C), the PCP conversion increased afterwards (from 45 to 60 °C). A mathematic model in Eq. (13) was used to interpret the complex reaction mechanism. The higher ratio of real/assumed Cl^- concentration in NaBr medium than that in NaF solution was due to different reaction mechanisms between Br^- and F^- electrolysis systems.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in http://dx.doi.org/10.1080/19443994.2013.785369