Experimental and Theoretical Analysis of By-product Formation Process in EAOP for High Salinity Wastewater Treatment

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Electrochemical advanced oxidation process (EAOP) as the novel treatment of chemical industrial wastewater is widespread concerned in China. PNP (P-nitrophenol) as the typical organic pollutant can be degraded totally in diluted effluents in previous studies, however, the process performed badly in the conditions with high salinity, and the toxic by-products formation aggravate pollution as well. In this paper, the transformation of electrolytes including Cl$^-$ and SO$_4^{2-}$ in EAOP have been studied, confirming the suitable concentration range for PNP degradation in a high level of salinity by considering the degradation rate of target organic and by-products formation. it was concluded that the suitable electrolytic concentration range is 500-5000 mM, and the organics treatment system should be set after nanofiltration section to make conditions with high salinity of NaCl. Finally, the breakup order of bond for PNP simulated in DFT method was hydroxyl group>nitro group>benzene ring, and the bond of benzene ring closest to hydroxyl group was prior attacked.

1. Introduction

With the shortage of water resource, wastewater treatment to achieve 'zero liquid discharge' is mentioned for industries with huge water usage, especially coal-chemical industry which is contributed in remote area far away from water source (Rihua Xiong et al., 2017; Carlos Alberto Martinez-Huitle et al., 2014; Xiaojuan Li et al., 2018). Mostly, effluents are pre-treated by biochemical system, membranes for concentration, and diluted effluents will be used cyclically with the concentrated effluents containing high salinity and complex organics being sent to incineration and landfill systems (Guiyu Yang et al., 2015; Wei Jiang et al., 2017). This traditional method causes secondary pollution and expensive energy consumption for treatment of concentrated effluents (Shenyong Jia et al., 2016). By now, advanced oxidation process (AOP) is more and more attractive for refractory wastewater treatment, especially electrochemical advanced oxidation process (EAOP) taking advantage of electrical energy to generate free radicals is payed attention because of the controllable operating conditions and acceptable cost (Feng Y J et al., 2003; Ying Zhu et al., 2018).

PNP is a typical organic pollutant of coal-chemical wastewater which consists of benzene ring, hydroxyl group and nitro group (Ling Wang et al., 2017). In previous studies, it was found that PNP can be degraded totally in diluted electrolyte (about 0.3~0.5 mM); however, the electro-oxidation process performed badly in concentrated wastewater where the salinity is higher thousands time due to formation of by-products (Ling Wang et al., 2017). Worse more, the contains of by-products are more complex causes potential toxicity and degradation difficulties (Yang yang et al., 2016; Justin T Jasper et al., 2017). The aim of this research is to study transformations of different types of electrolytes in EAOP and formation by-products, thereby confirming the suitable concentration range of electrolytes for PNP degradation in a high salinity level of effluents and simulate the breakup order of bonds for target organic to provide the theoretical basis for pollutant degradation and by-production formation.

The pathways of organics can be simulated by DFT (density functional theory) method, and the breakup order of bonds according to calculations of distribution of charges provide the theoretical basis for pathways of by-products formation (Sibel Barisci et al., 2018; Miao He,2018).

2. Materials and methods

2.1 Materials

All solutions were prepared from reagent-grade chemicals and deionized water (≥18.2 MΩ). Sodium sulfate (Na_2SO_4), sodium chloride (NaCl) were all obtained from Sinopharm Chemical Reagent Beijing Co., Ltd. The PNP stock solution (150 mM) was prepared weekly.

2.2 Electrochemical advanced oxidation process (EAOP)

All experiments were carried out in the 100 mL uncovered rectangular homemade reactor. A Ti/RuO_2 anode plate with double active surfaces and a stainless steel plate were used in electro advanced oxidation system which are separated in 5~6 mm, and the size of them are both 4.5 cm×5.5 cm. Electrochemical oxidation cell is undivided with 80 mL PNP solution, and the current was held constant at 7.5 A L^{-1} (24.24 mA cm^{-2}) using a DC power supply, the changeable cell voltage is observed in different electrolyte conditions. Solutions were stirred at 1000 rpm in open environment to eliminate the influence of mass transfer and accumulation of hydrogen gas. All tests were conducted in environmental temperature (283-288 K). These conditions were defined as baseline condition.

Different dosages of electrolytes including Na_2SO_4 and NaCl commonly containing in chemical wastewater with high salinity were added into 150 mg/L PNP solution to simulate practice work sections in different conditions of electrolyte concentration ranged 5 mM to 50000 mM in order to confirm the optimal work section for organics treatment.

2.3 Theoretical research on PNP degradation by the EAOP

The distribution of charges for PNP was calculated in DFT (density functional theory) method by Gaussian 09 software, the pathway simulation of target organics as the basic theoretical analysis of EAOP was carried out.

2.4 Analysis method

The concentration of PNP was measured by UV-Vis spectrophotometry at 400 λm where 1 mL test solution was diluted into 10 times by NaOH buffer where the pH is 10. Dosages of Na_2SO_4 and NaCl were confirmed by auto-titrator (Metrohm, 888 Titrando). Chlorate in samples was quantified by ion chromatography (Metrohm 845), with active chlorine and total chlorine being measured by DPD method. Samples for TOC analysis was conducted using a TOC analyzer. TOC removal rate and PNP concentration were treated as characterizations of EAOP performance and the electrolyte loss and byproduct formation were also other aspects which cannot be ignored.

3. Results and discussion

3.1 Electrolysis of salts in wastewater

In electrochemical oxidation process, electrolytes play roles of not only conductions but also reactants which may result in toxic by-products especially in NaCl solution. The transformations of different electrolytes including Na_2SO_4 and NaCl in EAOP were studied with low or high concentration. Figure 1 showed the SO_4^{2-} concentration change in 5 mM and 50 mM Na_2SO_4 solution. It suggested that losses of SO_4^{2-} was neglected in EAOP where the deviation was due to water electrolysis, and the main effect of Na_2SO_4 was electric conduction.
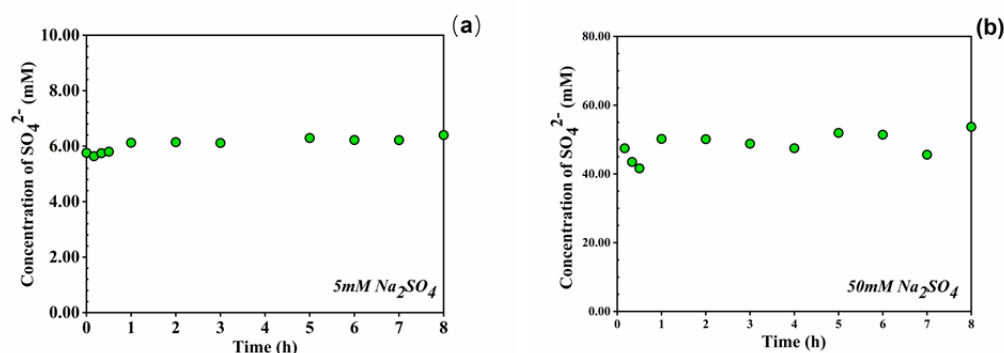

Figure 1: SO_4^{2-} concentration vs. time of electrolysis in 5 mM (a) and 50 mM (b) Na_2SO_4 solution in 8-hour discontinuous experiments.

And experiments about different dosages electrolytes of NaCl were carried out with the results showing in figure 2-3. Cl^- is more active in EAOP than SO_4^{2-} where the valence states of Cl changed from -1 to +5 in operating conditions resulted in potential complex transformation with target organics or self. 74.2% Cl^- was consumed in electrolysis of 5 mM NaCl solution transferred into active chlorine components and chlorate, and related reactive chlorine species contained chloride, active chlorine (mainly ClO^- which played the important role in organic pollutant oxidation), chlorate. What is more, the concentration of total chlorine was basically equal to active chlorine due to trace of amine in deionized water and reagent shown in figure 2. And active chlorine and total chlorine were quantified during electrolysis of 5-500 mM NaCl solution shown in figure 3. it showed the tendency rising up at the beginning and declining in late in electrolysis of 5 mM NaCl solution, same as that where concentration of electrolyte was 50 mM. the results were confirmed by M.E. Herry Bergmann (2017). It was deserved to note that the concentration of active chlorine in electrolysis of 500 mM NaCl solution is about 40 mM and kept a stable state in 8-hour electrolysis process which was equal to the peak value of the experiment with 500 mM NaCl solution. Therefore, active chlorine species were limitedly formed, and the loss of chloride in highly concentrated solutions was minimum based the comparison of chloride content in electrolysis experiment with different dosages of NaCl shown in figure 4.
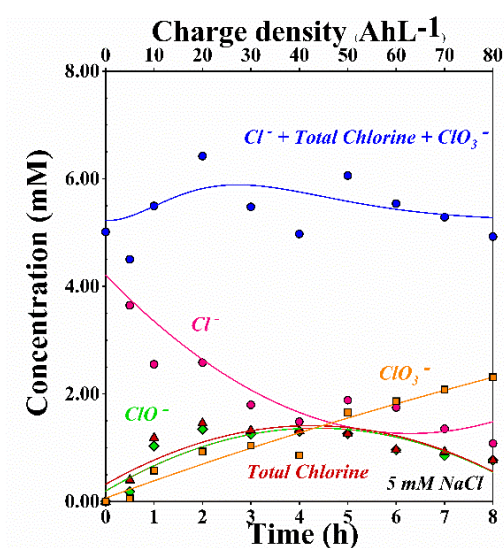

Figure 2: Concentrations of chlorine species in electrolysis with 5 mM NaCl solution in 8-hour discontinuous experiments.
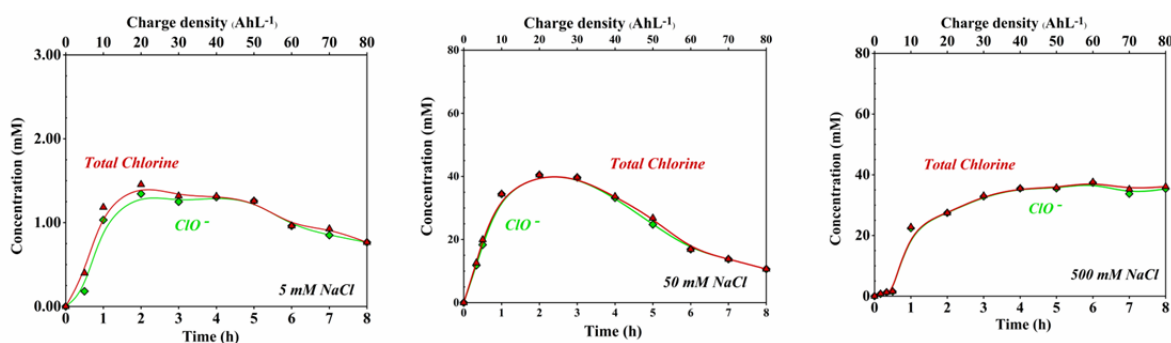

Figure 3: Concentrations of ClO^- and total chlorine in electrolysis with 5-500 mM NaCl solution in 8-hour discontinuous experiments.
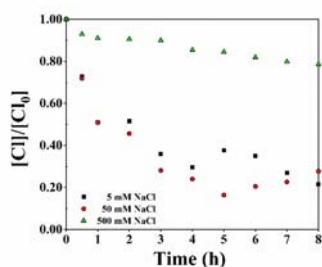
Figure 4: Concentration change of chloride in solution during electrolysis process

In conclusion, the electro advanced oxidation process was suitable for treatment of wastewater containing high concentrated NaCl (~500 mM) because of maximum active chlorine species formation and minimum loss of electrolyte. There were no special requirements of concentration to the solution where electrolyte was Na_2SO_4.

3.2 Degradation of PNP with high salinity in EAOP

Figure 5-8 showed the EAOP performance for PNP as the target organic pollutant in different electrolytic environment. It was concluded that PNP can be degraded both in Na_2SO_4 (aq.) (figure 5-6) and NaCl (aq.) (figure 7-8) following the pseudo first-order kinetics, and the degradation rate increased monotonically with increasing concentration of electrolytes. It should be noted that PNP was totally degraded in 20 min with the concentrated NaCl (aq.) displaying advantages compared with Na_2SO_4 (aq.) due to the selectivity of benzoic organics degradation (Yingying Xiang, 2016).

Although the degradation rate of PNP in NaCl solution was satisfying, the TOC removal rate was not comparable due to byproduct formation. It suggested in figure 8 that the intermediates during PNP degradation process in NaCl contained effluents were formed and not oxidized completely causing potential heavier treatment pressure.
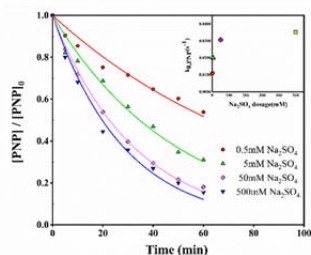

Figure 5: Time-dependent PNP degradation by EAOP with the concentration of Na_2SO_4 ranged from 0.5 mM to 500 mM.
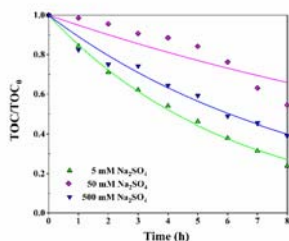

Figure 6: Time-dependent TOC/TOC_0 (TOC_0 = 80 mgC/L) by EAOP with the concentration of Na_2SO_4 ranged from 5 mM to 500 mM.
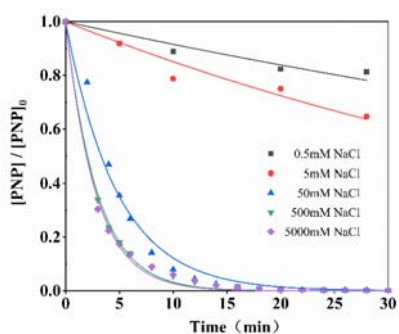
Figure 7: Time-dependent PNP degradation by EAOP with the concentration of NaCl ranged from 0.5 mM to 5000 mM.
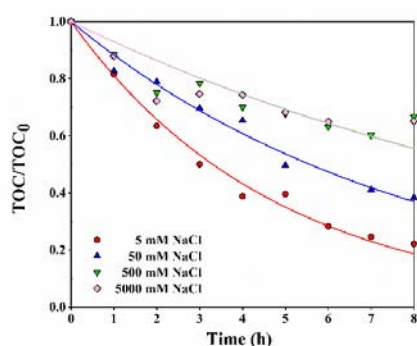

Figure 8: Time-dependent TOC/TOC_0 (TOC_0 = 80 mgC/L) by EAOP with the concentration of NaCl ranged from 5 mM to 5000 mM.

3.3 Density functional theory modeling and theoretical analysis

To explain the mechanism of the PNP degradation, the electron structure calculation for the molecule has been carried out with DFT method in M062X/cc-PVQZ level of theory using the Gaussian 09 software. Analysis of charge distribution on atoms of PNP showed that H_{12}-O_{11} bond (atoms numeration was presented in figure 7) was maximally polarized. On these atoms, maximum positive and negative charges were concentrated (H_{12} = 0.260 ē, O_{11} = -0.329 ē) causing priority attack of free radicals formed by EAOP. The nitro group will be broken by substitution reaction and the breakup of benzene ring then will be occurred in the bond (C_4-C_5 or C_5-C_6) closed to hydroxyl group. The final products will be CO_2 and H_2O in an ideal degradation process, the intermediates and by-products including HAAs (monochloroacetic acid (MCAA), dichloroacetic acid (DCAA),
and trichloroacetic acid (TCAA)) and THMs (chloroform, bromodichloromethane, dichlorobromomethane, and bromoform) will be formed during practical oxidation process.
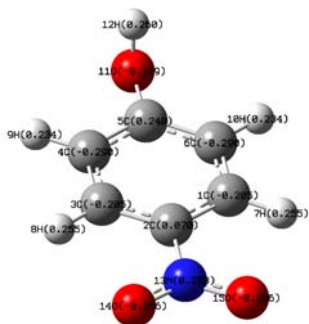

Figure 9: Distribution of charges for PNP.

4. Conclusions

By-products were formed during degradation of PNP wastewater with high salinity in electrochemical advanced oxidation process, especially in the effluents with high concentration of Cl^-. Cl^- was transferred into ClO^-, total chlorine and ClO_3^- in EAOP with the conditions mentioned in this study, the loss of Cl^- cannot be ignored when the concentration ranged 0.5~50 mM. Once the concentration was increased to 500 mM and more, the amount of ClO^- and total chlorine were kept in 40 mM for maximum reaching a stable transformation. But the SO_4^{2-} was not consumed when the electrolyte is Na_2SO_4.

The degradation rate of PNP was higher when electrolyte is NaCl because of the selectivity for benzene ring oxidation, and total degradation was achieved with high salinity in 20 min; however, the TOC removal rate was not 100% due to the by-products formation.

In Na_2SO_4 contained effluents, the PNP cannot be totally degraded in 20 min, the by-products were more toxic as well where it was observed that chroma was higher with deep brown residue compared the NaCl contained effluents. Thus, the degradation of pollutants containing benzene ring should be treated in NaCl contained effluent (effluent from nanofiltration) if the salinity is in a high level. And the further treatment for by-products should be carried out in the future.

For PNP, the breakup order of bond is hydroxyl group>nitro group>benzene ring, and the bond of benzene ring closest to hydroxyl group will be attacked according to the calculation of distribution charges for PNP.

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