

Effects of process parameters on the degradation of high salinity industrial wastewater

Zhishen Li, Xiaolei Gao, Dongtian Miao, Wanlin Yang, Yuanquan Xie, Li Ma and Qiuping Wei

ABSTRACT

High salinity wastewater is characterized by high salt content, a large number of organic pollutants and difficulty in biochemical degradation, which has become a major problem in industrial wastewater treatment. In this article, the electrochemical oxidation technology was used to treat high salinity wastewater. The effects of temperature, current density, pH and additives on the removal effect of high salinity wastewater were investigated to optimize the process parameters. The results show that the best degradation effect is when the current density is 21.43 mA cm^{-2} , $\text{pH} = 2$, the temperature is 60°C , and electric field activates additional persulfate. After purification of high salt wastewater, the evaporated salt can be utilized as a resource. The industrial cost of degradation was estimated, and its economic benefits were calculated. This work will provide a theoretical and experimental basis for treating high salt wastewater by boron-doped diamond (BDD) electrochemical degradation technology.

Key words | boron-doped diamond electrode, electrochemical oxidation, high salinity industrial wastewater

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HIGHLIGHTS

- BDD + PS System can efficiently degrade organic matter with low energy consumption but high cost.
- After purification of high salt wastewater, the evaporated salt can be utilized as resources.
- The industrial cost of degradation was estimated and its economic benefits were calculated.

GRAPHICAL ABSTRACT



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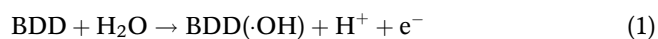
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INTRODUCTION

High salinity wastewater refers to the wastewater with a total salt content of more than 1%, containing a large amount of organic matter, organic heavy metals and radioactive substances (Lefebvre & Moletta 2006). In the chemical industry, many pharmaceuticals and pesticide intermediates (such as chloramphenicol, ciprofloxacin, etc.) are produced, which result in a large amount of wastewater. High salinity organic wastewater will not only corrode buildings and industrial equipment but also inhibit or poison microorganisms. Untreated wastewater will pollute our living environment (Lefebvre & Moletta 2006; Ismail *et al.* 2008). The removal of organic pollutants from high salinity industrial wastewater is of vital importance to the ecological environment, and the purification of high salinity industrial wastewater will also facilitate the recycling of resources.

It is difficult to achieve the degradation of high concentrated organic wastewater with high salinity by traditional treatment technology. For example, a biological method is adopted for treatment, which mainly decomposes organic matter by cultivating salt-tolerant bacteria (Camarillo & Stringfellow 2018; Joshiba *et al.* 2019). Plenty of salt will lead to the increase of osmotic pressure of microbial cells, thus dehydrating and crushing microbial cells, inhibiting microbial growth and enzymatic action, and finally reducing the effect of wastewater treatment (Lefebvre & Moletta 2006; Castillo-Carvajal *et al.* 2014). It is difficult to achieve the desired purification effect using physical and chemical treatment with extensive investment and high operating costs (Dou *et al.* 2003; Holler *et al.* 2005). In contrast, electrochemical oxidation technology is widely used as an efficient, economical and environmentally friendly new treatment technology (Chen 2004). Electrochemical oxidation technology refers to the formation of hydroxyl radicals ($\cdot\text{OH}$) and a series of strongly oxidized substances through electrochemical reactions. The oxidized substances will oxidize organic pollutants and turn them into nontoxic intermediates or even completely mineralized into water and carbon dioxide (Poyatos *et al.* 2010). The anode material is crucial in the electrochemical oxidation method and determines the degradation efficiency (Garcia-Segura *et al.* 2018). Compared

with other materials, boron-doped diamond (BDD) electrode has excellent electrochemical properties, such as strong corrosion resistance, stable chemical properties, high oxygen evolution potential and wide electrochemical window, and has been widely used in industrial wastewater research in recent years (Heikki *et al.* 2015; Qi *et al.* 2016; Natsui *et al.* 2019; Wei *et al.* 2020). The electrochemical oxidation reaction mechanism is shown in Equations (1) and (2) (Enache *et al.* 2009; Zhou *et al.* 2016). Inorganic salts such as NaCl and Na_2SO_4 in salt-containing wastewater can be used as supporting electrolytes so that no additional additives are needed in the electrochemical oxidation process, which is conducive to resource-saving.



At present, some researchers have researched the oxidative degradation of organic substances by BDD electrodes. For instance, Mei *et al.* (2018) studied the effects of degradation parameters and BDD electrode preparation parameters on the degradation effect of reactive orange simulated dye wastewater. Persulfate has been used to assist or promote the degradation of simulate wastewater (Miao *et al.* 2020a), but its degradation effect has not been reported in actual industrial wastewater. There have been many reports on the energy consumption of electrochemical oxidation degradation, but they are all limited to laboratory conditions. The total cost and economic benefits of actual industrial production are not estimated.

In this work, based on previous studies, the effect of the BDD electrode electrochemical oxidation degradation parameters (such as temperature, current density and initial pH) on the degradation of high salinity industrial wastewater is systematically studied. At the same time, the electrochemical oxidation method with BDD was coupled with persulfate activation degradation technology. Electrochemically activated persulfate is proposed. It improves the degradation efficiency and reduces the energy consumption of wastewater treatment. The cost of the degradation

process was estimated, and its cost advantage in practical applications was calculated. The degraded wastewater is evaporated to obtain organic salts without organic matter, which is conducive to recycling. The research of this work will provide a theoretical and experimental basis for the treatment of high salt wastewater by BDD electrochemical degradation technology.

EXPERIMENTAL

Pretreatment of the polycrystalline Si substrate

The silicon substrate of 60×80 mm is etched with alkali before deposition. The etching solution is 10 M KOH solution, the etching time is 30 min and the etching temperature is 80°C .

Preparation of the BDD/Si electrode

The BDD film was deposited on a polycrystalline Si substrate by hot filament chemical vapor deposition with several straight wires of the parallel structure (Li *et al.* 2020, 2021). The reactant gases were methane (CH_4), hydrogen (H_2) and ethyl borane (B_2H_6). The volume ratio of the reactant gases was set at $\text{H}_2 : \text{CH}_4 : \text{B}_2\text{H}_6 = 97:3:1.5$ sccm (standard cubic centimeter per minute), deposition pressure was 3 kPa, deposition time was 12 h and deposition temperature was 850°C .

Reagents

The two kinds of high salinity industrial wastewater used in this work are produced by a pharmaceutical factory in Gan Su province, containing a large number of organic compounds. The main organic compounds in the wastewater are mercaptan and nitrobenzene. In the production wastewater of a pharmaceutical company, nitrobenzene compounds are used as starting materials, and many solvents, mercaptan and other toxic and harmful substances are used as auxiliary materials. In addition to the general solvents, wastewater also contains carbamate, isothiurea, nitrobenzene, aromatic amines and methyl mercaptan, propyl mercaptan compounds. One kind of wastewater contains a great deal of NaCl, and the other contains a great deal of Na_2SO_4 . Analytically pure $\text{Na}_2\text{S}_2\text{O}_8$ (Sinopharm Chemical

Reagent Co., Ltd, China) was used as an active electrolyte. Analytically pure HCl (Xingkong Chemical Glass Co., Ltd, China), H_2SO_4 (Xingkong Chemical Glass Co., Ltd, China) and NaOH (Long Chemical Industry Co., Ltd, China) were used to adjust the initial pH value of wastewater.

Physical and chemical characterization methods of the BDD electrode

Scanning electron microscopy (SEM; Nova NanoSEM 230, FEI, The Netherlands) was used to analyze the surface morphology and grain size of the BDD film. Raman spectroscopy (LabRAM HR800) was used to detect the carbon phase composition and boron doping of the BDD film. An electrochemical workstation (CHI660E, Shanghai) was used to test the electrochemical performance of the BDD film. The oxidation capacity and reversibility of the electrode were characterized by cyclic voltammetry (CV) through a three-electrode system. The working electrode is the BDD electrode, the opposite electrode is a 30×30 mm Pt electrode with a purity of 99.99% and the reference electrode is Ag/AgCl electrode (GaossUnion Co., Ltd, China).

Electrochemical degradation experiments

In the experiment of wastewater degradation, the prepared BDD electrode was used as the anode, and the cathode was the 304 stainless steel sheet with a size of 60×80 mm (it requires ultrasonic vibration in an ethanol solution to remove oil stains). The power supply used in this experiment was the DC stabilized power supply (RD-3020, China). A 500 mL glass beaker was used as the electrolyzer. The beaker was placed on the magnetic agitator (MS7-H550-Pro Dalong Instrument Co., Ltd, Beijing) and the speed was adjusted to 200 rpm.

Analysis of degradation effect

The total organic carbon analyzer (TOC-L, Shimadzu, Japan) was used to test the TOC solution. According to the change of the solution TOC during degradation, the mineralization efficiency of the wastewater was analyzed. The TOC value can evaluate the mineralization efficiency of wastewater. The TOC removal rate can be expressed by

the calculation formula (3) (Martínez-Huitle & Brillas 2009; Mei *et al.* 2019; Miao *et al.* 2020b):

$$\text{TOC removal (\%)} = \frac{(\text{TOC}_0 - \text{TOC}_t)}{\text{TOC}_0} \times 100 \quad (3)$$

where TOC_0 (mg L^{-1}) is the initial TOC value of the wastewater, and TOC_t (mg L^{-1}) is the TOC value when the degradation time of wastewater is t .

The energy consumption of the experimental process is analyzed by the calculation formula (4) (Martínez-Huitle & Brillas 2009):

$$\text{EC} = \frac{EI\Delta t}{V} \quad (4)$$

where E (V) is the average voltage in the degradation process of wastewater; I (A) is the current value in the degradation process; Δt (h) is degradation time and V (L) is the volume of the wastewater.

RESULTS AND DISCUSSION

Physical and chemical characterization of the BDD electrode

The surface SEM and Raman spectra of the BDD electrode are shown in Figure 1(a) and 1(b), and the basic electrochemical properties of the BDD electrode are shown in Figure 1(c) and 1(d). As shown in Figure 1, the grain size of BDD is about 2–3 μm and the film is dense without defects. The rough and uneven surface of the electrode indicates that the etching of the silicon substrate effectively increases the specific surface area of the electrode. The formed BDD electrode has a clear grain boundary, well crystal shape, less secondary nucleation and favorable diamond quality (Wei *et al.* 2011). According to the Raman spectra of the BDD electrode, characteristic peaks related to boron doping appeared nearly 467 and 1,195 cm^{-1} , indicating well boron doping (Li *et al.* 2010). As shown in the Raman spectra, there is a diamond first-order characteristic peak

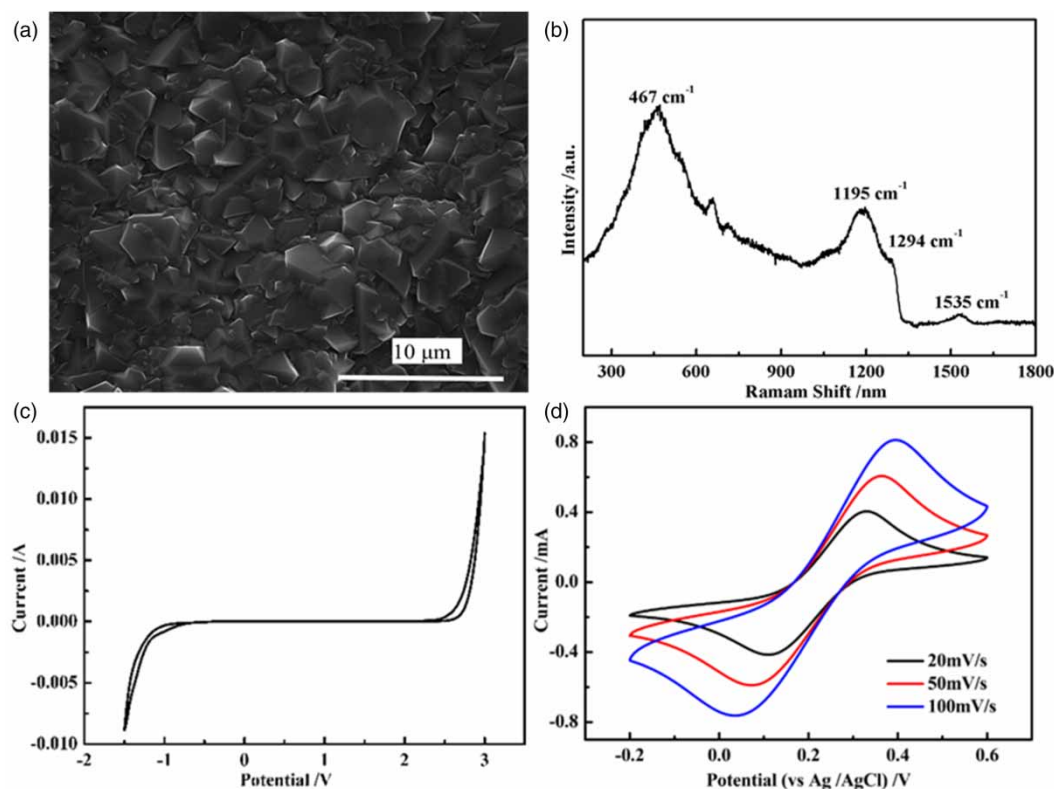


Figure 1 | Characterization of BDD electrodes. SEM images of BDD electrodes (a) and Raman spectra (b); (c) CV curves of BDD electrodes in 1 M H_2SO_4 ; (d) CV patterns of BDD electrodes in 1 mM $\text{K}_3\text{Fe}(\text{CN})_6 + 0.1 \text{ M KCl}$ solution at scan rates of 20, 50, and 100 mV s^{-1} .

at $1,294\text{ cm}^{-1}$ and a peak at $1,535\text{ cm}^{-1}$, caused by sp^2 phase (graphite structure) carbon. It can be seen that the sp^2 phase carbon peak of the electrode is very weak and almost negligible, indicating that the content of nondiamond phase of the BDD electrode is small. The reason is that the etching effect on the graphite phase is vital when the concentration of CH_4 is low, and the concentration of the H atom is relatively high. In this article, polysilicon is used as the substrate. Compared with monocrystalline silicon substrates, polysilicon is cheaper, easier to manufacture in large areas, and more suitable for the industrialization of BDD electrodes.

Figure 1(c) shows the CV curve of the BDD electrode in $1\text{ M H}_2\text{SO}_4$. As can be seen from the figure, the oxygen evolution potential of the BDD electrode is about 2.71 V , the potential window is about 3.38 V and the background current is about $3.99\text{ }\mu\text{A cm}^{-2}$. They prove that the BDD electrode prepared in this work has an excellent electrochemical performance. In the electrolysis process, the oxidation

potential of most pollutants is between 1.0 and 2.0 V . The oxygen evolution potential of the BDD electrode in this paper is higher than this range, which can effectively limit the oxygen evolution and other side reactions (Comninellis 1994; Comninellis *et al.* 2008). Figure 1(d) shows the CV diagram obtained from the BDD electrode in the solution containing $1\text{ mM K}_3\text{Fe(CN)}_6 + 0.1\text{ M KCl}$ at the scanning rates of $20, 50$ and 100 mV s^{-1} . The peak shape of the REDOX peak of the BDD electrode was symmetrical at different scanning rates. The ratio of the anode peak current to the cathode peak current was also close to 1, indicating its good reversibility.

Influence of current density (J)

The increase of current density leads to increasing mineralization efficiency of pollutants on or near the electrode surface, but it will also increase energy consumption. Figure 2 shows the degradation effect of the BDD electrode

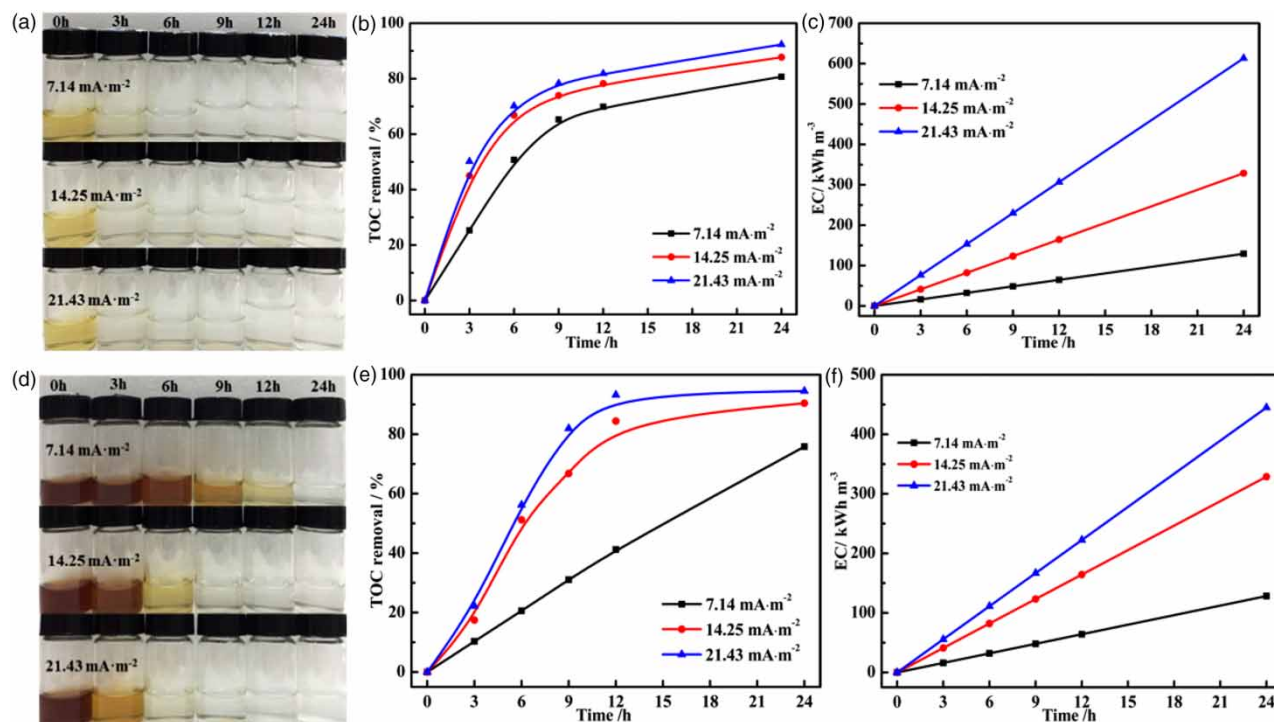


Figure 2 | The effect of different current densities ($J = 7.14, 14.25$ and 21.43 mA cm^{-2}) on the efficiency of BDD electrode degradation of high salt industrial wastewater. Color (a), TOC removal rate (b) and energy consumption (c) of NaCl industrial wastewater during BDD electrode degradation; Color (d), TOC removal rate (e) and energy consumption (f) of Na_2SO_4 industrial wastewater during BDD electrode degradation. Other degradation conditions: the initial pH of NaCl and Na_2SO_4 wastewater is 7, $T = 25^\circ\text{C}$. Please refer to the online version of this paper to see this figure in color: <http://dx.doi.org/10.2166/wqrj.2021.035>.

on NaCl and Na₂SO₄ industrial wastewater at the current density of 7.14, 14.25 and 21.43 mA cm⁻². The generation rate of ·OH and other strongly oxidizing substances (ROs) increases with the increase of current density, showing higher degradation efficiency. As shown in Figure 2(a) and 2(d), the color removal gradually gets better with the increase of current density. For NaCl industrial wastewater, the degradation time required to reach transparency under the current densities of 7.14, 14.25 and 21.43 mA cm⁻² was 6, 3 and 3 h, respectively. For Na₂SO₄ industrial wastewater, the degradation time required to reach transparency at the current densities of 7.14, 14.25 and 21.43 mA cm⁻² was 24, 9 and 6 h. As can be seen from Figure 2(b), 2(c), 2(e) and 2(f), with the increase of current density, the chroma removal rate and the TOC removal of NaCl and Na₂SO₄ industrial wastewater were gradually improved. Under the condition that the current density was increased from 7.14 to 21.43 mA cm⁻², the mineralization efficiency of NaCl and Na₂SO₄ industrial wastewater after the degradation of 24 h was increased from 80.70 to 92.32% and from 75.80 to 94.52%, respectively. However, the corresponding energy consumption also increased from 129.12 to 613.44 kWh m⁻³ and 128.4 to 444.96 kWh m⁻³. When the current density was increased from 7.14 to 14.25 mA cm⁻², the degradation effect was increased significantly. When the current density was 14.25 and 21.43 mA cm⁻², the degradation effect was similar. The yield of hydroxyl radicals on the surface of the electrode increased and the degradation improved with the increase of current density (Panizza & Cerisola 2006; Brito *et al.* 2016; Zambrano & Min 2020). Due to the limited electrochemical activity area, the generation of ·OH quickly reaches its maximum value with the increase of current density. The reaction process is controlled by diffusion, and the excess ·OH on the electrode surface reacts with itself to produce O₂ or H₂O₂ (El-Ghenymy *et al.* 2014). The degradation efficiency of the BDD electrode cannot be further improved (Mei *et al.* 2018).

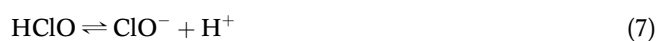
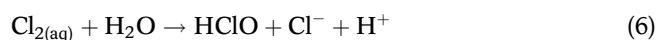
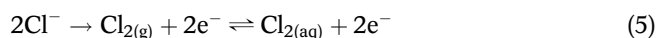
Influence of pH

The hydroxyl radicals (·OH) tend to be extremely sensitive to pH value (Enache *et al.* 2009). The pH of the solution has a significant effect on the electrochemical degradation of industrial wastewater. For example, Zhu *et al.* (2018)

studied the degradation of alizarin red dye by the BDD electrode in the solution of acidic, neutral and alkaline. The result shows that with the pH value between 4.97 and 7.86, the degradation effect of alizarin red is best and the condition of acid or alkali is against degradation.

Use HCl and NaOH to adjust the initial pH value of NaCl industrial wastewater, and use H₂SO₄ and NaOH to adjust the initial pH value of Na₂SO₄ industrial wastewater. Figure 3 shows the effect of different initial pH values on the degradation effect of industrial wastewater. As shown in Figure 3(a) and 3(e), with the increase of pH value, the degradation effect of industrial wastewater was improved. When the pH value of NaCl industrial wastewater was 2, 7 and 10, the required degradation time to reach transparency was 3, 6 and 6 h, respectively. When the pH value of Na₂SO₄ industrial wastewater was 2, 7 and 10, the required degradation time to reach transparency was 12, 24 and 24 h, respectively. It can be seen from Figure 3(b) and 3(f) that the TOC removal rate of industrial wastewater is the best under acidic conditions. After the degradation of 24 h, the mineralization efficiency of NaCl and Na₂SO₄ reached 83.21 and 85.72%, respectively. The corresponding energy consumption is 115.2 and 118.32 kWh m⁻³. The degradation effect is higher and the energy consumption is lower under acidic conditions, showing great advantages in the degradation of wastewater. Considering comprehensiveness and reducing efficiency, the better pH value in this paper is 2. pH values can change the charge and adsorption abilities on the electrode surface, which changes the reaction activity of the electrode (Enache *et al.* 2009). Therefore, the degradation efficiency of the medium acidic solution is the highest under the same condition.

During the degradation process, there are some special reactions in NaCl industrial wastewater. The oxidation reaction of Cl⁻ occurs at the anode shown in formulas (5)–(7) (Szpyrkowicz *et al.* 2000; Rajkumar & Kim 2006; Rajkumar *et al.* 2007):



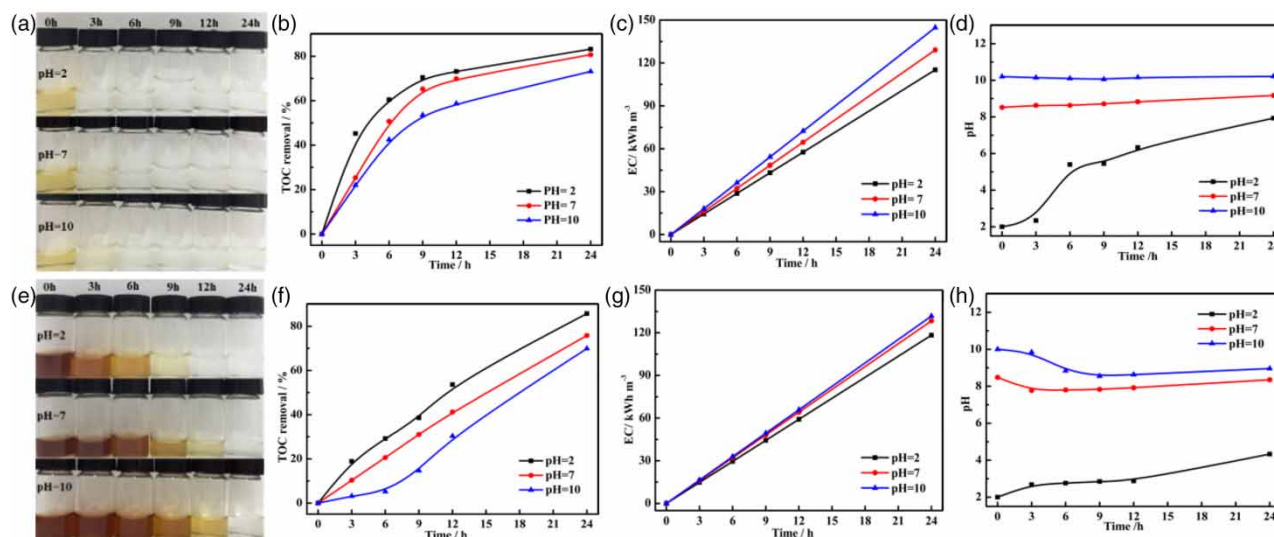


Figure 3 | Effect of different pHs on the efficiency of BDD electrode degradation of high salt industrial wastewater. Color (a), TOC removal rate (b), energy consumption (c) and pH (d) of NaCl industrial wastewater during BDD electrode degradation; Color (e), TOC removal rate (f) energy consumption (g) and pH (h) of Na₂SO₄ industrial wastewater during BDD electrode degradation. Other degradation conditions: $J = 7.14 \text{ mA cm}^{-2}$, $T = 25^\circ\text{C}$. Please refer to the online version of this paper to see this figure in color: <http://dx.doi.org/10.2166/wqrj.2021.035>.

In the acid solution, the main substances generated are Cl_2 and HClO . ClO^- mainly exists in alkaline conditions. The standard potential of $\text{Cl}_{2(\text{aq})}$ ($E^0 = 1.36 \text{ V vs. SHE}$) and HClO ($E^0 = 1.49 \text{ V vs. SHE}$) is higher than that of ClO^- ($E^0 = 0.89 \text{ V vs. SHE}$). Therefore, these substances oxidize organic matter indirectly faster in acidic media than in alkaline media (Boxall & Kelsall 1992). In addition, a small amount of toxic by-products such as chlorite, chlorate and perchlorate may be produced during the degradation process.

During the degradation process, some special reactions will also occur in the Na_2SO_4 industrial wastewater. The oxidation reaction of SO_4^{2-} occurs at the anode, as shown in formula (8) (Zambrano & Min 2019). In the solution, H^+ gradually decreases, and it generally approaches weakly alkaline conditions.

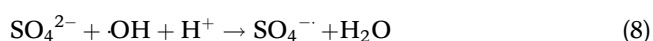


Figure 3(d) and 3(h) show the change of pH value of solution during the electrolysis process. The pH value of NaCl and Na_2SO_4 industrial wastewater was approaching weak alkaline during the degradation process. The formation of OH^- and H^+ is generated by the hydrogen evolution reaction of the cathode and oxygen evolution

reaction of the anode, respectively (Calzares et al. 2009; Souza & Ruotolo 2013). The reaction mechanism is shown in Equations (9) and (10) (El-Ghenymy et al. 2014):



Influence of temperature (T)

Temperature influences the diffusion of microscopic particles and the reaction rate between oxidized groups and pollutants in wastewater, and influences the conductivity of the whole degradation system, thus affecting the energy consumption of the degradation process (Degaki et al. 2014).

Figure 4 shows the effects of temperatures (25, 40 and 60°C) on the degradation result of industrial wastewater. As shown in Figure 4(a) and 4(d), the required degradation time of NaCl industrial wastewater to reach transparency at temperatures of 25, 40 and 60°C is 6, 3 and 3 h, respectively. The required degradation time of Na_2SO_4 industrial wastewater to reach transparency at 25, 40 and 60°C is 24, 24 and 12 h, respectively. According to Figure 4(b), 4(c), 4(e) and 4(f), with the increase of temperature, the

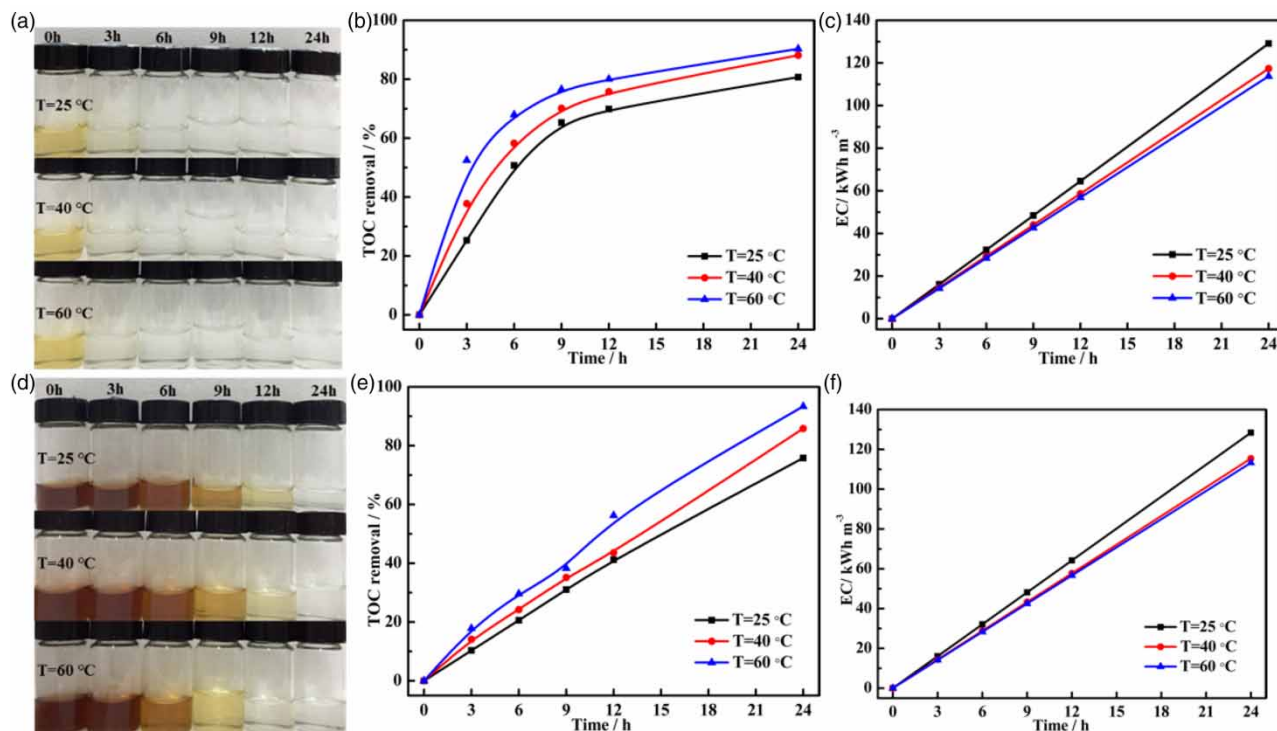


Figure 4 | Effects of different temperatures ($T = 25, 40$ and $60\text{ }^{\circ}\text{C}$) on the efficiency of BDD electrode degradation of high salt industrial wastewater. Color (a), TOC removal rate (b) and energy consumption (c) of NaCl industrial wastewater during BDD electrode degradation; Color (d), TOC removal rate (e) and energy consumption (f) of Na_2SO_4 industrial wastewater during BDD electrode degradation. Other degradation conditions: the initial pH of NaCl and Na_2SO_4 wastewater is 7, $J = 7.14\text{ mA cm}^{-2}$. Please refer to the online version of this paper to see this figure in color: <http://dx.doi.org/10.2166/wqrj.2021.035>.

TOC removal rate of the NaCl and Na_2SO_4 industrial wastewater was increased. The mineralization efficiency of the NaCl and Na_2SO_4 industrial wastewater was increased from 80.70 to 90.34% and 75.80 to 93.36% after degradation of 24 h. With the increase of temperature, the mineralization efficiency of NaCl and Na_2SO_4 industrial wastewater after degradation of 24 h was increased by 9.64 and 17.56%, respectively. The corresponding energy consumption was reduced from 129.12 to 113.76 kWh m^{-3} and 128.4 to 113.28 kWh m^{-3} . Considering comprehensiveness and reducing efficiency, the better temperature in this paper is $60\text{ }^{\circ}\text{C}$. As can be seen from Figure 4(d) and 4(e), when the temperature of Na_2SO_4 industrial wastewater was increased from 25 to $40\text{ }^{\circ}\text{C}$, the mineralization efficiency was increased from 75.80 to 85.85% after degradation of 24 h. However, its chroma removal rate changed less, indicating that temperature significantly impacts on the mineralization of organic pollutants and minor impact on the chroma removal. The

temperature has a greater influence on the mineralization of organic matter, making organic matter change from large molecules to small molecules, even inorganic salts, CO_2 and H_2O . However, it has little effect on the color-developing functional groups in organic matter, so the decolorization is not obvious (Petrucci & Montanaro 2011). Compared with the chroma removal rate, the TOC removal rate is more representative of the degradation efficiency of organic pollutants.

The higher the temperature is, the higher the diffusion rate and reaction rate of ions in the wastewater, which increases the rate of degradation of wastewater (Chen 2013; Korbahti & Demirbeken 2017). With the increase of temperature, the generation rate of hydroxyl radicals increases (Zhu et al. 2018). Wastewater contains high concentrations of sodium chloride or sodium sulfate. As the temperature increases, the electrical conductivity of NaCl and Na_2SO_4 solution will increase significantly, which reduces energy consumption for degradation.

Influence of persulfate additive

Persulfate (PS) itself has a certain oxidation property, which it reacts slowly with organic pollutants. Persulfate can be activated easily by the BDD electrode to produce highly active free radical, sulfate radical $\text{SO}_4^{\cdot-}$. Its oxidation approaches even beyond $\cdot\text{OH}$, the strong oxidizing group produced by the BDD electrode (Wang & Wang 2016).

Figure 5 shows the degradation effect of NaCl and Na_2SO_4 industrial wastewater in the process of single electrochemical advanced oxidation (BDD), external electric field-activated persulfate (BDD + PS) and nonactivated persulfate (PS). According to Figure 4(a), 4(b), 4(d) and 4(e), the comparative results about the removal effect of chroma and TOC is $\text{BDD} + \text{PS} > \text{BDD} > \text{PS}$. The mineralization efficiency of NaCl industrial wastewater degraded by BDD + PS and BDD were 90.09 and 80.7%, respectively. The mineralization efficiency of Na_2SO_4 industrial wastewater degraded by BDD + PS and BDD were 91.42 and 75.80%,

respectively. Compared with BDD technology, the mineralization efficiency of NaCl and Na_2SO_4 industrial wastewater under BDD + PS technology was increased by 9.39 and 15.62%, respectively. Single persulfate has the worst degradation effect due to the low production of activated sulfate radical and the degradation efficiency is weak at room temperature (Yousefi et al. 2019). An external electric field activates persulfate (its reaction mechanism is shown in Equations (11) and (12) (Chen et al. 2014)), and the degradation effect on organic compounds by coupling of $\text{SO}_4^{\cdot-}$ with $\cdot\text{OH}$ was higher than the single $\cdot\text{OH}$ (Li et al. 2018). It can be seen from Figure 4(c) and 4(f) that the energy consumption of degradation by BDD + PS is lower than that by BDD, showing great advantages in the process of wastewater degradation.

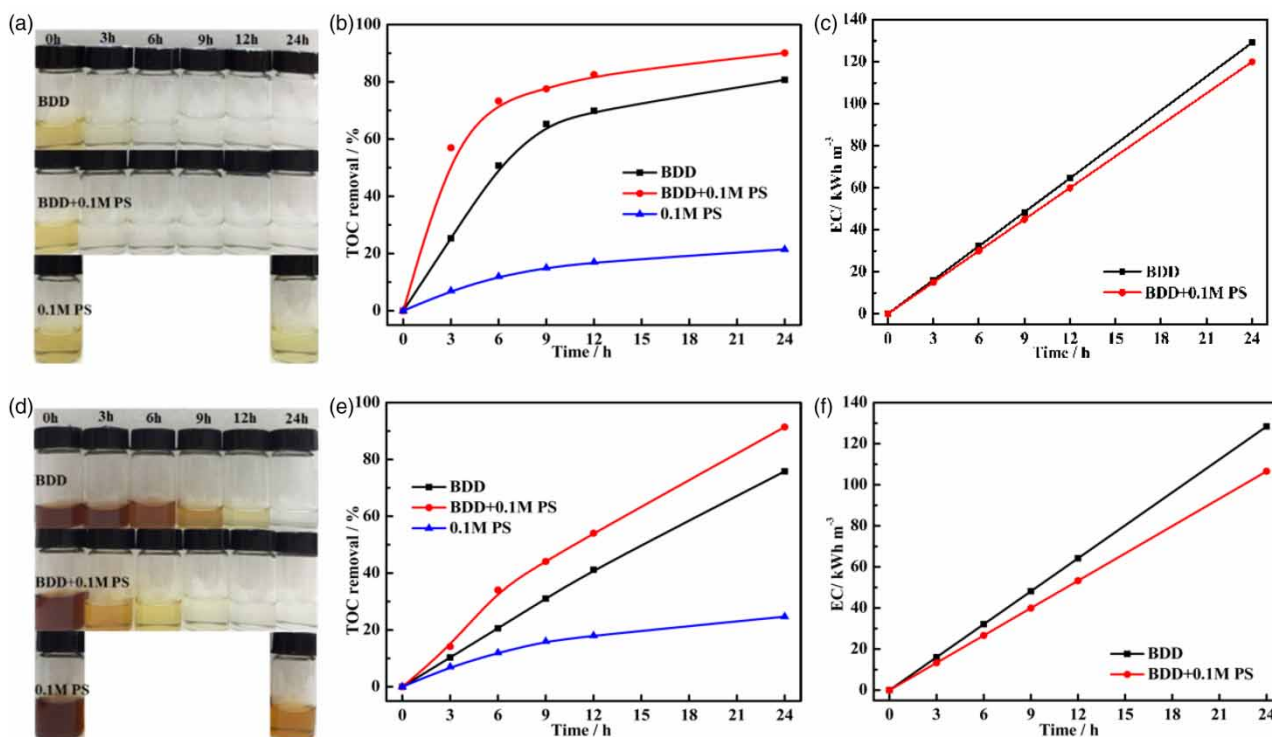
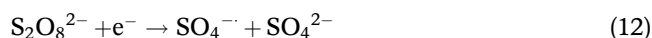


Figure 5 | Comparison of single electrochemical advanced oxidation (BDD), external electric field-activated persulfate (BDD + 0.1 M PS) and unactivated persulfate (0.1 M PS) degradation of high salt industrial wastewater. Color (a), TOC removal rate (b) and energy consumption (c) of NaCl industrial wastewater during degradation; Color (d), TOC removal rate (e), and energy consumption (f) of Na_2SO_4 industrial wastewater during degradation. Other degradation conditions: the initial pH of NaCl, Na_2SO_4 industrial wastewater is 7, $T = 25^\circ\text{C}$, $J = 7.14 \text{ mA cm}^{-2}$. Please refer to the online version of this paper to see this figure in color: <http://dx.doi.org/10.2166/wqrj.2021.035>.

Cost assessment

Degradation costs are critical for industrial applications. Figure 6 shows the energy consumption required for the BDD electrode to degrade 0.5 L high salt industrial wastewater to 80% mineralization under different conditions ($J = 21.43 \text{ mA cm}^{-2}$, $\text{pH} = 2$, $T = 60^\circ\text{C}$, BDD + 0.1 M PS). As can be seen from Figure 6, whether it is NaCl industrial wastewater or Na_2SO_4 industrial wastewater, the relationship of energy consumption in different conditions is $\text{EC}_{\text{BDD}+0.1\text{MPS}} \approx \text{EC}_{T=60^\circ\text{C}} < \text{EC}_{\text{pH}=2} < \text{EC}_{J=21.43 \text{ mA cm}^{-2}}$. The results showed that under laboratory conditions, raising the temperature and adding a certain amount of sodium persulfate could significantly improve the TOC removal rate of industrial wastewater and greatly reduce energy consumption, showing great energy conservation advantages.

Can the parameters studied in this chapter be used in actual production? We conducted the following studies:

1. The current Chinese status of waste treatment: the treatment price of hazardous waste (refers to solid or liquid wastes that have one or more hazardous properties, such as corrosiveness, toxicity, inflammability, reactivity and infectivity, or may cause harmful effects on the environment or human health) is 1,237.6–1,547.0 USD per ton. The price of solid waste (refers to the solid and semi-solid waste materials produced by human beings in production, construction, daily life and other activities, which cannot be used at a certain time and place and are discarded to pollute the environment) is 309.4–618.9

USD per ton. Figure 7 shows the picture of industrial salt precipitated by evaporation, which is degraded for the different duration (0, 3 and 24 h) by the BDD electrode. After degradation, evaporation and crystallization, the purified salt can be used as industrial salt. Approximately 140 g of salt is produced after evaporation of a liter of industrial salt wastewater. The direct evaporation product of high salt industrial wastewater is usually miscellaneous salt containing a large amount of organic matter, which can only be treated as hazardous waste. After the high salt industrial wastewater treated by electrochemical oxidation with the BDD electrode, the direct evaporation product is common mixed salt, which can be treated as solid waste.

2. At present, according to different seasons and the time of peak and valley demand, Chinese power supply companies set the electricity prices of peak, flat and valley period. The electricity price of industrial power is 0.166–0.279 USD·(kWh)^{−1} during the peak period, 0.093–0.155 USD·(kWh)^{−1} during the flat period and 0.045–0.074 USD·(kWh)^{−1} during the valley period. Factories can choose to use electricity during the valley period. The price of sodium persulfate is 1,674 USD per ton, and 1.71 ton of $\text{Na}_2\text{S}_2\text{O}_8$ is added to deposit 1 ton of industrial salt, which cost 284.586 USD. In industrial production, industrial waste heat can be used to increase the reaction temperature to achieve the degradation effect, and the cost can be ignored. The price of H_2SO_4 is 139.5 USD per ton, and 3.57 kg of H_2SO_4 is added to deposit 1 ton of industrial salt, which cost 0.499 USD.

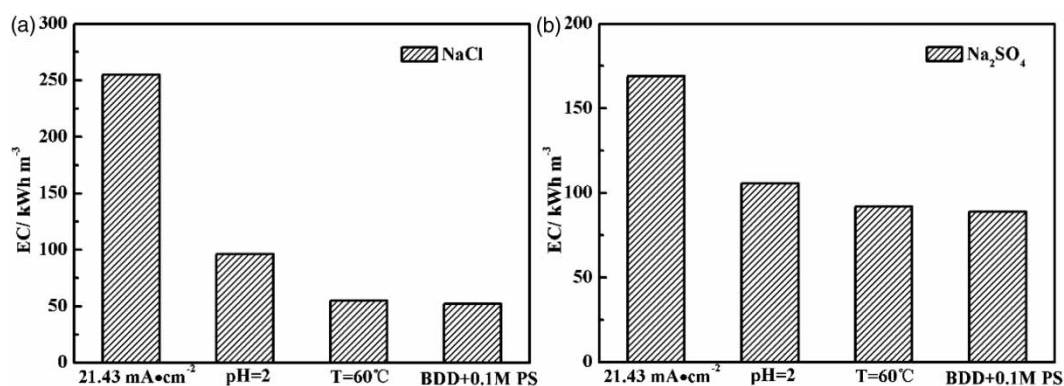


Figure 6 | Comparison of energy consumption required for the BDD electrode to degrade 0.5 L of high salt industrial wastewater to achieve a mineralization efficiency of 80% under different conditions ($J = 21.43 \text{ mA cm}^{-2}$, $\text{pH} = 2$, $T = 60^\circ\text{C}$, BDD + 0.1 M PS). (a) NaCl industrial wastewater and (b) Na_2SO_4 industrial wastewater.



Figure 7 | Comparison of industrial salts evaporated from high salt industrial wastewater after electrochemical degradation of BDD electrodes at different times (0, 9 and 24 h). (a) NaCl industrial wastewater and (b) Na₂SO₄ industrial wastewater. Degradation conditions: $J = 7.14 \text{ mA cm}^{-2}$, $T = 25^\circ\text{C}$, $\text{pH} = 7$.

It can be ignored. Similarly, the cost of the HCl is negligible. The equipment has a long service life, and the cost is negligible. There will be no gas emissions if it is hazardous waste treatment or solid waste treatment after electrochemical oxidation. No additional calculation is required for the treatment cost of exhaust gas.

The specific calculation results are shown in Table 1. It can be seen from the table that the total cost (F_2 in the table) required for the treatment of high salinity wastewater by electrochemical oxidation technology is significantly lower than the cost of hazardous waste treatment (2,200–3,000 USD per ton). So the content studied in this chapter is feasible in industrial production.

Persulfate has been regarded as a potential method because it can improve the degradation efficiency of wastewater. However, the actual cost assessment found that although the use of persulfate improves the degradation efficiency of high salt wastewater, the cost comparison actually does not have much advantage over other optimization methods.

The process parameters studied in this chapter are conducive to significantly reducing the treatment cost of high salt industrial wastewater by electrochemical degradation of the BDD electrode, laying a foundation for efficient industrial degradation of high salt industrial wastewater.

In Table 1, W_1 is the electricity consumed by 1 ton of wastewater reaching 80% mineralization efficiency and the unit is kWh; W_2 is the electrical energy consumed by

Table 1 | Comparison of the electricity consumption and various costs of the BDD electrode under different conditions ($J = 21.43 \text{ mA cm}^{-2}$, $\text{pH} = 2$, $T = 60^\circ\text{C}$, BDD + 0.1 M PS) after degrading high salt industrial wastewater to evaporate 1 ton of industrial salt

Types of wastewater Optimized process	NaCl industrial wastewater				Na ₂ SO ₄ industrial wastewater			
	$J = 21.43 \text{ mA cm}^{-2}$	$\text{pH} = 2$	$T = 60^\circ\text{C}$	BDD + 0.1 M PS	$J = 21.43 \text{ mA cm}^{-2}$	$\text{pH} = 2$	$T = 60^\circ\text{C}$	BDD + 0.1 M PS
W_1 (kWh)	269.12	95.35	56.13	53.82	171.93	108.37	93.45	91.83
W_2 (kWh)	1,921.52	680.80	400.77	384.27	1,227.58	773.76	667.23	655.67
F_0 (USD)	0	0	0	284.586	0	0	0	1,020.02
F_1 (USD)	155.47–257.33	55.08–91.17	32.43–53.67	31.09–50.63	99.32–164.40	62.61–103.62	53.99–89.36	53.05–87.81
F_2 (USD)	713.47–1,373.33	613.08–1,207.17	590.43–1,169.67	873.68–1,451.21	657.32–1,280.40	620.61–1,219.62	611.99–1,205.34	895.64–1,488.39

generating 1 ton of salt (about 140 g salt can be produced after evaporation of 1 L high salt industrial wastewater) and the unit is kWh; F_0 is the cost of PS consumed by 1 ton of salt and the unit is USD; F_1 is the electricity cost consumed by 1 ton of salt (calculated using electricity prices during valley period) and the unit is USD. Because the treatment prices of solid waste and hazardous waste are calculated in 1 ton, the electricity cost is calculated based on the cost of 1 ton of salt produced by the electrochemical degradation. F_2 is the sum of the solid waste treatment cost for 1 ton of salt, electricity cost and persulfate cost, and the unit is USD.

CONCLUSION

In this work, BDD electrodes were prepared using HFCVD technology. The effects of current density, temperature, pH, external electric field activation of persulfate technology and other environmental conditions on the degradation effect of NaCl and Na₂SO₄ industrial wastewater were studied. The specific conclusions are as follows:

1. As the current density increased, the degradation effect of BDD electrodes on NaCl and Na₂SO₄ industrial wastewater gradually increase. With the increase of current density from 7.14 to 21.43 mA cm⁻², the mineralization efficiency of NaCl and Na₂SO₄ industrial wastewater was increased by 14.40 and 24.70% after 24 h degradation, respectively.
2. The pH value affects the degradation of high salt industrial wastewater by the BDD electrode. Acidic conditions are favorable for degradation, followed by neutrality and alkaline conditions are the worst. Under the condition of pH = 2, the required degradation time for the NaCl and Na₂SO₄ industrial wastewater to reach transparency is 3 and 12 h, and the mineralization efficiency after degradation for 24 h is 83.21 and 85.72%, respectively.
3. As the temperature increased, the degradation effect of BDD electrodes on NaCl and Na₂SO₄ industrial wastewater gradually increased. With the increase of temperature from 25 to 60 °C, the mineralization efficiency of NaCl and Na₂SO₄ industrial wastewater after degradation for 24 h was increased by 9.64 and 17.56%, respectively.
4. Compared with single electrochemical oxidation (BDD), the external electric field-activated persulfate technology

(BDD + PS) is more dominant in terms of degradation of wastewater. Compared with BDD technology, the mineralization efficiency of NaCl and Na₂SO₄ industrial wastewater using BDD + PS technology was increased by 9.39 and 15.62%, respectively.

5. In actual production, the results of the comparison of the total cost to electrochemically degrade 1 ton of high salt industrial wastewater by the BDD electrode under better conditions are as follows: $F_{T=60^{\circ}\text{C}} < F_{\text{pH}=2} < F_{J=21.43\text{ mA cm}^{-2}} < F_{\text{BDD}+0.1\text{M PS}}$. After degradation, evaporation and crystallization, the purified salt can be used as industrial salt. The use of persulfate improves the degradation efficiency of high salt wastewater, but there is no advantage compared with other methods from the cost comparison. The total cost is significantly lower than the cost of hazardous waste treatment.

The process parameters studied in this work help significantly reduce the treatment cost of high salt industrial wastewater degraded by electrochemical oxidation of BDD electrodes and lay the foundation for the high-efficiency industrial degradation of high salt industrial wastewater.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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