Article

Mineralization of High-Concentration Aqueous Aniline by Hybrid Process

Haibing Zhang *, Yasong Zhou, Shaohui Guo, Zhipu Wang and Qing Wang

College of Chemical Engineering and Environment, China University of Petroleum–Beijing, Beijing 102249, China; zhys01@cup.edu.cn (Y.Z.); cupgsh@163.com (S.G.); 2019592037@cupk.edu.cn (Z.W.); wangqing961018@163.com (Q.W.)

* Correspondence: zhanghaibing@cupk.edu.cn; Tel.: +86-990-663-3303

Abstract: The efficient mineralization of high-concentration aqueous aniline (HCAA) is an issue needing to be resolved. In this study, a hybrid process of ozonation and electrochemical oxidation (ECO) was proposed for improving the mineralization of HCAA ($1000 \text{ mg} \cdot \text{L}^{-1}$). The results indicated that chemical oxygen demand (COD) removal by the hybrid process was far greater than that of a single ozonation or ECO process, revealing that the hybrid process might avoid low efficiency in late ozonation and initial ECO. Thus, a subsequent combination effect clearly existed. In this hybrid process, ozonation stage time was selected as 60 min for optimal COD removal. The main products of the ozonation stage were maleic and succinic acids, with declining pH which was beneficial to the following ECO stage. Nitrite and nitrate formed during ozonation, which acted as electrolytes for the ECO stage, in which maleic and succinic acids were fully degraded and pH thus increased. Moreover, the aniline degradation mechanism of the hybrid process was deduced, demonstrating the superiority of this hybrid process. Finally, more than 95% COD removal was achieved, which met the COD limit requirement and achieved pH control simultaneously, according to the discharge standards of water pollutants for dyeing and finishing of the textile industry in China (GB 4287–2012).

Keywords: aniline; hybrid process; mineralization; ozonation; ECO

Citation: Zhang, H.; Zhou, Y.; Guo, S.; Wang, Z.; Wang, Q. Mineralization of High-Concentration Aqueous Aniline by Hybrid Process. *Water* **2022**, *14*, 630. <https://doi.org/10.3390/w14040630>

Received: 11 January 2022

Accepted: 14 February 2022

Published: 18 February 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Aniline is commonly used by the chemical industry in several processes, such as for producing synthetic paints, antioxidants, herbicides, and varnishes [1–3]. Table 1 exhibits the main sources of aniline pollution in water. This chemical exhibits significant accumulation in nature due to its low degradability [4–6]. The carcinogenicity, teratogenicity, and mutagenicity of aniline have been widely reported due to its long-term persistence in the environment and potential for accumulating in organisms [7–9]. Strict standards have been set for the discharge of aniline wastewater (AW) in many countries and it is necessary for AW to be thoroughly treated before release to nature.

The treatment methods for AW mainly include adsorption, biodegradation, membrane separation, and photocatalytic oxidation [10–14]. Adsorption technology is suitable for low-concentration AW due to its limited adsorbing capacity [15], such that its adsorbing material requires frequent regeneration for treating high-concentration AW. Biodegradation needs a long culture cycle to achieve suitable results with existing biological strains and high-concentration AW and, thus, the degradation rate is slow [16]. Membrane separation can enrich low-concentration AW and act as a pretreatment process [17], but it rarely used for high-concentration AW. Photocatalytic oxidation requires additional artificial UV light to increase aniline mineralization, leading to high treatment costs [18]. Advanced oxidation processes (AOPs) have attracted increasing interest in recent years, owing to their high-degradation efficiency and short treatment period for organic wastewater treatment [19–21]. Among AOPs, ozonation and electrochemical oxidation (ECO) processes are widely used in wastewater treatment. In general, ozonation efficiency is high in its initial

period. However, ozone oxidizes high-concentration aniline incompletely, even though a catalyst is present [22–24], and efficiency clearly declines over time. ECO exhibits excellent degradation of refractory compounds in aqueous solution [25–28], but in the initial ECO stage, high-concentration aniline polymerization frequently occurs [29–31], which lowers anode oxidation ability. Thus, it is necessary to improve AOPs efficiency for thoroughly mineralizing HCAA.

Table 1. Main sources of aniline pollution in water.

Industries	Role of Aniline	Wastewater Kinds
synthetic paints	raw material	paint
dyestuffs	raw material of dyes and auxiliaries	dye
rubbers	vulcafor, ingredients raw material	rubber
pesticides	raw material	pesticide
plastics	intermediate	plastic
pharmaceuticals	raw material and intermediate	pharmaceutical

Based on the characteristics of ozonation and ECO for treating HCAA, a hybrid process of ozonation and ECO was examined here for possible improvement of the oxidation efficiency for HCAA. To the best of our knowledge, a hybrid process of ozonation and ECO has been little reported regarding the oxidation of such solutions and thus first proposed here. Additionally, the intermediate products and basic mechanism of this hybrid process needed to be revealed.

In this study, HCAA was degraded by a hybrid process, with the purposes of: (1) comparing the effects of the single processes and hybrid process; (2) investigate and optimize the key factors of the hybrid process; and (3) explore the decomposition mechanism of HCAA by the hybrid process.

2. Materials and Methods

2.1. Materials

Aniline (C_6H_7N , M_{av} 93.13 g/mol) sodium hydroxide (NaOH, M_{av} 40.01 g/mol) and activated carbon (AC; particle size $200 \pm 50 \mu m$) were obtained from Aladdin Industrial Corp., City Industry, CA, USA. All other chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. All chemicals were analytical grade and used as received without further purification. All solutions were prepared using ultrapure water.

2.2. Ozonation Device

The removal of aniline from aqueous solution by ozonation was carried out in a cylindrical laboratory-scale reactor (800 mL). In each experiment, the reactor was filled with 500 mL of $1000 \text{ mg} \cdot \text{L}^{-1}$ aqueous aniline (AA), with ozone produced from pure oxygen via an ozone generator (BMT 802X, BMT Messtechnik GmbH, Stahnsdorf, Germany). Experiments were performed at constant gas flow (measured at 25°C and 1 atm) and constant inlet ozone concentration ($50 \text{ g} \cdot \text{m}^{-3}$). Ozone entered the reactor through a gas distributor in the reactor bottom and was agitated in the solution. AA was prepared in purified water (Milli-Q Advantage A10, Millipore Corp., Billerica, MA, USA) and input to the reactor by a peristaltic pump. The ozone concentration was measured by an ozone analyzer (BMT 964, BMT Messtechnik GmbH, Stahnsdorf, Germany). In an experiment, 350 mg of modified AC (described below) were introduced in the reactor for promotion of ozonation reactions [32]. Ozone gas leaving the reactor was removed before venting in gas-washing bottles filled with 10% potassium iodide solution.

2.3. Electrochemical Oxidation Device

A 500 mL electrochemical reactor was assembled with a plate-shaped anode (Ti/SnO₂–Sb₂O₃, $10 \times 10 \text{ cm}$, Xinhengtai New Material Technology Co., Ltd., Xi'an, China) and cathode (SS316 plate, $10 \times 10 \text{ cm}$, Xinhengtai New Material Technology Co., Ltd., Xi'an, China),

which was vertically positioned in the electrochemical reactor, spaced 3 cm apart. One end of each electrode was connected to a direct current (DC) power supply, which supplied voltage and current density at 0–30 V and $25 \text{ mA} \cdot \text{cm}^{-2}$. Compressed air was introduced at the reactor bottom as the oxygen supply through a gas distributor and solution stirred at room temperature (25°C). For the hybrid process, the entering solution was from the ozonation device. For the single ECO process, the aniline concentration was the same as that in the ozonation experiment.

2.4. The Hybrid Process

The hybrid process was assembled by connecting the ozonation and ECO processes (Figure 1, dotted line). Initially, AA is treated by ozonation and then the resulting solution mineralized by ECO.

Figure 1. Schematic view of the ozonation process, ECO process, and hybrid process.

2.5. Modification of Activated Carbon (AC)

AC was modified using the following steps:

1. The material was washed with deionized water until the washing effluent was nearly colorless and then dried in a hot air oven at 105°C for 2 h;
2. A 40 mL volume of 30% (wt%) NaOH aqueous was added to 20 g of dried AC, oscillated for 2 h at 30°C , allowed to sediment for 24 h, and then filtered to remove retrieve the solid;
3. The modified AC was dried in an oven at 100°C for 2 h, rinsed with ionized water to neutrality, dried for 24 h at 105°C , and then dried.

The modified AC was labeled ACm. Before an ozonation experiment, ACm was soaked in the aqueous aniline ($1000 \text{ mg} \cdot \text{L}^{-1}$) for 24 h to eliminate adsorption effects.

2.6. Analytical Methods and Procedures

Conductivity was measured using a conductivity meter (Multi 3630, WTW, Xylem, Inc., Rye Brook, NY, USA). Aniline, COD, ammonia nitrogen ($\text{NH}_4^+\text{-N}$), nitrate-nitrogen ($\text{NO}_3^-\text{-N}$), and nitrous nitrogen ($\text{NO}_2^-\text{-N}$) were measured according to the standard protocol of the State Environmental Protection Administration of China [33].

Aniline oxidation products were detected using a liquid chromatograph with a mass spectrometer (LC-MS; LC-Orbitrap MS, Thermo Fisher Scientific Inc., Pittsburgh, PA, USA). Mobile phase A was ultrapure water containing 0.1-vol% formic acid and mobile phase B analytically pure grade methanol (distillation purified) with 0.1-vol% formic acid. The LC column was a UPLC C_{18} column (Hypersil Gold Vanquish, $1.9\ \mu\text{m}$, $100 \times 2.1\ \text{mm}$, Thermo Fisher Scientific, Inc., Waltham, MA, USA).

Polymeric products formed in the initial ECO process were detected by gas chromatography with MS (GC-MS; Agilent 7890a, Agilent Technologies, Inc., Santa Clara, CA, USA and Waters GCT Premier, Waters Corp., Milford, MA, USA, respectively). Carrier gas was 99.999% nitrogen at $1\ \text{mL}/\text{min}$. Sample quantity was $0.2\ \mu\text{L}$ and inlet temperature $280\ ^\circ\text{C}$. The chromatographic column was a fused quartz capillary column (HP-5MS, $30\ \text{m} \times 0.25\ \text{mm} \times 0.25\ \mu\text{m}$, Agilent Technologies, Inc., Santa Clara, CA, USA). The column's initial temperature was $40\ ^\circ\text{C}$ for 5 min, programmed heating at $8\ ^\circ\text{C}/\text{min}$ to $240\ ^\circ\text{C}$, and then retained for 20 min.

The treatment effect of AA was assessed using the discharge standards of water pollutants for dyeing and finishing of textile industry in China (GB 4287-2012). The main indices are listed in Table 2.

Table 2. Main index limited in discharge standard (GB 4287-2012).

Index	Indirect Discharge Limited Value
pH	6–9
COD ($\text{mg}\cdot\text{L}^{-1}$)	200
BOD ₅ ($\text{mg}\cdot\text{L}^{-1}$)	50
Chroma	80
Ammonia-nitrogen ($\text{mg}\cdot\text{L}^{-1}$)	30
Total nitrogen ($\text{mg}\cdot\text{L}^{-1}$)	50
Total phosphorus ($\text{mg}\cdot\text{L}^{-1}$)	1.5
Aniline ($\text{mg}\cdot\text{L}^{-1}$)	1.0

It should be noted that indirect discharge means the act of enterprises discharging pollutants into a public sewage treatment system. In most cases, enterprises are inclined to indirect discharge and, therefore, meeting the indirect discharge standard is the treatment goal for AA in this study. In the discharge standard, COD is the important index and COD removal thus used here to evaluate oxidation effects.

3. Results and Discussion

3.1. Comparison of Three Oxidation Process

3.1.1. Aniline Concentration and COD Removal

In previous studies, phosphate buffer has been frequently added to AA to control ozonation pH [32,34,35]. However, added phosphate buffer increases the treatment cost and leads to the subsequent difficulties of biological dephosphorization. Therefore, in this study, all experiments were conducted without an aqueous buffer. Sodium chloride (NaCl , $0.5\ \text{g}/\text{L}$) was added as the electrolyte for ECO. In the hybrid process, the initial ozonation stage lasted 40 min and the following 120 min was the ECO stage. The evolution of the dimensionless aniline concentration and COD removal with time are shown in Figure 2.

Figure 2. Index changes during the three processes. Removal performance of aniline (a) and COD (b).

In all cases, a fast decay of aniline concentration was observed and complete removal achieved after ~60 min (Figure 2a). Considering only aniline removal, there was no great advantage in the hybrid process. However, when observing COD removal, the advantage of the hybrid process became clear (Figure 2b). When the effect of COD removal by the single ozonation process was compared with the single ECO process, it was observed that COD removal by the single ozonation process was higher than that of the single ECO in the first 75 min, while the opposite trend occurred after this period. According to previous reports, aniline is catalytically decomposed by $\cdot OH$ radicals in the initial single ozonation period. The oxidant species is highly reactive and degrades aniline in a short time, which shows that the indirect ozonation reaction has a dominant role. However, here, the direct ozonation reaction gradually took the leading role as intermediates formed which lowered the pH over time. As is well known, the reaction rate of direct ozonation is much less than that of indirect ozonation. Thus, in the single ozonation process of HCAA, COD removal was higher in the initial period than in later stages. In the single ECO process, COD removal was very low (<15%) in 40 min. It was found that polymeric products formed in the initial ECO stage might result in electrode fouling as a consequence of the adsorption of polymeric oxidation products on their surfaces, which can lead to low COD removal in initial times of single ECO (Figure 3) [36]. COD removal increased significantly once polymeric products were oxidized on the electrode surface from a constant electrode current supply over time.

Figure 3. GC-MS analysis of products formed in single ECO process in 10 min.

COD removal of $1000 \text{ mg}\cdot\text{L}^{-1}$ AA by the single ozonation, single ECO, and hybrid processes in 160 min was 62, 73, and 81%, respectively. This indicated that a subsequent combined process effect clearly existed. In the hybrid process, COD removal was higher than that of single ozonation and ECO processes after 40 min. The hybrid process was observed to combine the merits of the two processes and promote COD removal.

3.1.2. Variation of pH

Examination of pH evolution over time during ozonation, ECO, and hybrid processes showed that, due to aniline oxidation products, including carboxylic acid, organic aldehyde,

or alcohol, pH significantly decreased with ozonation reactions carried out without buffer conditions, which coincided with preliminary results (Figure 4) [37]. In the ECO reaction, H^+ was reduced to hydrogen gas on the cathode over time and OH^- accumulation raised alkalinity. In the hybrid process, pH was lowered in the ozonation stage and then gradually increased in the ECO stage, as H^+ was reduced to a gas. In ECO under low pH, the oxygen evolution reaction might be inhibited, as the oxidation potential of $\cdot OH$ was higher under acidic conditions (+2.85 V) than under alkaline conditions (+2.02 V). Under acid conditions, $\cdot OH$ has a stronger oxidation ability, which was beneficial for the following ECO stage and thus improved degradation efficiency [38].

Figure 4. Evolution of pH of HCAA by ozonation, ECO, and hybrid processes.

3.1.3. Variation of Nitrogen and Conductivity

The concentration variations of NH_4^+-N , NO_2^--N , and NO_3^--N were detected in the oxidation process (Figure 5). In all cases, NH_4^+-N concentrations were low, which indicated that only a little ammonia was converted to NH_4^+ and that most oxidized to NO_2^- or NO_3^- . The NO_2^--N concentration first increased and then declined over time, as in the initial stage, the formation amount of NO_2^--N was higher than the conversion to NO_3^--N , which led to NO_2^--N accumulation. After 80 min, most NO_2^--N was converted to NO_3^--N , with the concentration of NO_3^--N finally rose to $\sim 140 \text{ mg}\cdot\text{L}^{-1}$ (Figure 6). At the same time, most OH^- formed in ECO stage was neutralized by H^+ dissociated from carboxylic acid, which has little help to conductivity improvement.

Figure 5. Evolution of concentrations of NH_4^+-N , NO_2^--N , and NO_3^--N in single ozonation, single ECO, and hybrid processes.

Figure 6. Deduced evolution of NH_4^+ , NO_2^- , and NO_3^- in oxidation process.

Simultaneously, the conductivity of the solution was measured (Figure 7). In the single ozonation process, conductivity increased with increased NO_2^- -N and NO_3^- -N concentrations. In the single ECO process, the initial conductivity was high, which decreased in the first 40 min, and then increased over time. NaCl addition provided the high initial conductivity and the formation of chlorine or hypochlorous acid (Cl_2 or HClO , respectively; Equations (1)–(3) caused decreased conductivity in the first 40 min, but the subsequent generation of NO_2^- and NO_3^- finally improved conductivity. These results showed that the conductivity difference between single ozonation and ECO was $200\text{--}300\ \mu\text{S}\cdot\text{cm}^{-1}$ after 40 min. Thus, the formation of NO_2^- -N and NO_3^- -N played an important role in the late period of the single ozonation process and was beneficial for enhancing conductivity for ECO.

Figure 7. Evolution of conductivity of aniline oxidation by single ozonation, single ECO, and hybrid processes.

In the hybrid process, during the ozonation stage, conductivity gradually increased for the formation of NO_2^- and NO_3^- . During the hybrid ECO stage, conductivity increased

greatly from added NaCl and the following variation trend the same as for the single ECO process:

3.2. Optimized Influencing Factors of the Hybrid Process

3.2.1. Ozonation Time

In the hybrid process, ozonation time was crucial for aniline conversion and also impacted the ECO stage efficiency. The influence of different ozonation times on COD removal was examined and maximal COD removal in the hybrid process found to be with 60 min of ozonation (Figure 8), with COD removal at 95% of $1000 \text{ mg}\cdot\text{L}^{-1}$ AA and at 81 and 91% with 40 and 80 min, respectively. It may be seen from Figure 2b, when ozonation time was 40 min, 60 min, and 80 min in the single ozonation process, the COD removal was 37%, 47%, and 50% respectively. The COD removal improvement was 10% when ozonation time from 40 min prolonged to 60 min, but it was only 3% when ozonation time prolonged from 60 min to 80 min. It revealed that these ozonation products formed at 40 min ozonation may be degraded further by ozonation, while those products formed at 60 min ozonation were difficult to be degraded further by ozonation. On the other hand, Figure 8 indicated that these products formed in 40 min ozonation were more difficult to be degraded further in the next ECO stage than those products formed in 60 min or 80 min ozonation, which led to a stronger decrease of COD for 60 min and 80 min than that of 40 min. Therefore, the products formed with 60 min ozonation were ideal intermediates for the hybrid process. It was more efficient to select 60 min as the ozonation time for the whole COD removal in the same reaction time. At the same time, Figure 5 showed most of amino were converted to NH_4^+ , NO_2^- , or NO_3^- in 60 min ozonation stage which was close to these formed in 80 min ozonation, while these ions formed in 40 min ozonation were only half of those formed in 60 min ozonation, which would decrease the conductivity obviously. Thus, the 60 min was selected as the best ozonation time in the hybrid process.

Figure 8. Evolution of COD removal by hybrid process with different ozonation times.

3.2.2. Nitrite and Nitrate as Electrolyte

In the ozonation stage, most of the amino groups were oxidized to nitrite and nitrate, with total concentrations of nitrite and nitrate increased to $\sim 600 \text{ mg}\cdot\text{L}^{-1}$ in the ECO stage, which also evidently enhanced conductivity. Thus, it was feasible that nitrite and nitrate replaced NaCl as the electrolyte at the ECO stage of the hybrid process. Comparison experiments with no electrolyte addition and different NaCl additions indicated that COD removal with $1 \text{ g}\cdot\text{L}^{-1}$ NaCl was superior to that added of $0.5 \text{ g}\cdot\text{L}^{-1}$ or no addition, particularly at 80 to 100 min, from promotion effects by HOCl (Equations (1)–(3); Figure 9). However, this superiority gradually shrank over time and, finally, COD removal differences between $1 \text{ g}\cdot\text{L}^{-1}$ and no addition were $\sim 2\%$ by 160 min. In consideration of corrosion resulting from chloride and desalination cost in the next treatment, the hybrid process with no electrolyte was concluded to be the best.

Figure 9. Evolution of COD removal by hybrid process with different NaCl concentrations.

3.2.3. Assessment on the Hybrid Process

The performance of the hybrid process on $1000 \text{ mg}\cdot\text{L}^{-1}$ AA was assessed by operating the hybrid process without electrolyte. The ozonation stage was 60 min and ECO for 100 min. Except for total nitrogen, the main indices of AA treated by the hybrid process were in the indirect discharge-limited range (Table 3). Notably, for COD removal and pH, it was difficult to achieve high COD removal and maintain pH at 6–9 simultaneously for the single processes (Figure 3). In the single ozonation process, pH decreased over time as COD removal increased. In contrast, in the single ECO process, pH increased to >9 when COD removal reached the discharge standard. However, the hybrid process appeared to improve COD removal and held the pH in the desired range simultaneously. This fortuitously settled the conundrum regarding high COD removal and pH controlled in a limited range.

Table 3. Effects of the hybrid process on $1000 \text{ mg}\cdot\text{L}^{-1}$ AA solution.

Item	Hybrid Process
pH	7.5
COD ($\text{mg}\cdot\text{L}^{-1}$)	189
BOD ₅ ($\text{mg}\cdot\text{L}^{-1}$)	46
Chroma	23
Ammonia–nitrogen ($\text{mg}\cdot\text{L}^{-1}$)	3.3
Total nitrogen ($\text{mg}\cdot\text{L}^{-1}$)	115.8
Anilines ($\text{mg}\cdot\text{L}^{-1}$)	0.8

3.3. The Merits and Mechanism of Hybrid Process

During the single ozonation process, the intermediate product variation was observed to include maleic and succinic (butanedioic) acids as the main products after 60 or 120 min ozonation (Figure 10, Table 4). At low pH, the formation of secondary oxidants, such as $\cdot\text{OH}$, were inhibited and direct oxidation acts as the main reaction for aniline degradation allowed [39]. However, the reaction rate of direct oxidation was much lower than that of $\cdot\text{OH}$ in indirect oxidation. At the same time, aniline was present in its molecular form in neutral or basic conditions. When the solution was acidic, protonated aniline predominated in solution, as the cation anilinium, which was less adsorbed by AC_m than the corresponding molecular form. Thus, aniline degradation efficiency in ozonation declined significantly when maleic and succinic acids accumulated in late ozonation.

Figure 10. LC–MS analysis of aniline oxidation products in ozonation process at 40 min. (a) maleic acid (a) and succinic acid (b).

Table 4. Peak chart area comparison of intermediates of aniline ozonation.

Intermediate Products	Ozonation Time, min				
	10	20	40	60	120
maleic acid	9,191,232	10,263,980	6,847,330	2,749,407	793,610
p-aminophenol	1,306,363				
succinic acid		585,062		3,029,264	361,816
p-nitrophenol		14,714,904	314,472		
benzoquinone			4,896,324		

In the initial times of single ECO, AA ($1000 \text{ mg}\cdot\text{L}^{-1}$) reactions were apt to form polymeric products (Table 5). The polymerization reactions were hardly conducive to COD removal, which resulted in electrode fouling and led to increased electrical potential of ECO (from 12.2 to 15.6 V). These polymeric products might have been decomposed to CO_2 and H_2O with a constant current supply. However, the potential of ECO was still high (from 14.7 to 15.5 V) due to fouled electrodes, which meant that increased energy consumption

was needed. Thus, the formation of polymeric products in the initial period of the single ECO process was a critical issue for HCAA treatment.

Table 5. Peak chart area comparison of intermediate products in single ECO process.

Intermediate Products	ECO Time, min				
	10	20	40	60	200
maleic acid	3,732,405	4,341,021	6,001,241	11,612,253	2,994,023
<i>p</i> -aminophenol	4,041,304				
quinoline	1,633,427				
dimethylbenzidine	1,134,261				
diphenylamine ethylene diketone		1,214,627			

In the hybrid process, the main products of the ozonation stage were maleic and succinic acids, which clearly decreased the pH and inhibited radical $\cdot\text{OH}$ formation from O_3 . Simultaneously, low pH might inhibit the oxygen evolution reaction and improve the oxidation potential of $\cdot\text{OH}$. Thus, the ozonation stage laid a perfect foundation for the ECO stage. In the ECO, in which maleic and succinic acids were completely mineralized to CO_2 and H_2O , providing excellent degradation of carboxylic acids [40–42], and avoiding the formation of polymeric products. The decomposition mechanism of the hybrid process is shown in Figure 11. In the ozonation stage, aniline first reacted with $\cdot\text{OH}$ to form *p*-aminophenol, which was then gradually oxidized to *p*-nitrophenol, hydroquinone, and benzoquinone, with maleic and succinic acids the main products by the end of the ozonation stage. In the ECO stage, maleic and succinic acids were decomposed thoroughly to CO_2 and H_2O . The hybrid process combined the merits of the ozonation and ECO processes and effectively avoided the low COD removal efficiency in late ozonation as well as in initial ECO.

Figure 11. Aniline decomposition mechanism in the hybrid process.

4. Conclusions

A hybrid process, including ozonation and ECO stages, was successfully used to mineralize HCAA and the overall process investigated. The subsequent combination effects on COD removal of the hybrid process were clearly observed. The ozonation stage time was selected to be 60 min for optimal COD removal. Nitrite and nitrate were considered to be excellent electrolytes for the hybrid process because of self-formation and no corrosion. The results showed that the hybrid process achieved 95% COD removal and settled the issue between COD removal and pH range (6–9) limits in the discharge standards. The aniline decomposition mechanism of the hybrid process indicated that maleic and succinic acids were the main products by the end of the ozonation stage, which were subsequently thoroughly decomposed to CO₂ and H₂O in the ECO stage. The hybrid process combined the merits of single ozonation and ECO processes and effectively avoided low efficiency in late ozonation and initial ECO.

Author Contributions: Y.Z. performed the conceptualization; S.G. carried out the design of methodology and analyses; H.Z. and Z.W. contributed process validation; H.Z. and Q.W. performed the investigation; H.Z. wrote the original draft, including preparation, review, and editing; and H.Z. acquired the funding. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by Science Foundation of China University of Petroleum-Beijing At Karamay (No. RCYJ2016B-02-005 and RCYJ2016B-02-005), the Natural Science Foundation (Tian Shan Qing Nian) of Xinjiang (No. 2020Q021).

Acknowledgments: The authors are thankful for the analysis support by The State Key Laboratory of Heavy Oil. All authors are grateful for the support of the Research Foundation of China University of Petroleum-Beijing at Karamay.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Khan, A.H.; Aziz, H.A.; Khan, N.A.; Dhingra, A.; Ahmed, S.; Naushad, M. Effect of seasonal variation on the occurrences of high-risk pharmaceutical in drain-laden surface water: A risk analysis of Yamuna River. *Sci. Total Environ.* **2021**, *794*, 148484. [\[CrossRef\]](#) [\[PubMed\]](#)
2. Khan, N.A.; Ahmed, S.; Farooqi, I.H.; Ali, I.; Vambol, V.; Changani, F.; Yousefi, M.; Vambol, S.; Khan, S.U.; Khan, A.H. Occurrence, sources and conventional treatment techniques for various antibiotics present in hospital wastewaters: A critical review. *Trends Anal. Chem.* **2020**, *129*, 115921. [\[CrossRef\]](#)
3. Dias, N.C.; Bassin, J.P.; Sant'Anna, G.L.; Dezotti, M. Ozonation of the dye reactive red 239 and biodegradation of ozonation products in moving-bed biofilm reactor: Revealing reaction products and degradation pathways. *Int. Biodeterior. Biodegrad.* **2019**, *144*, 104742. [\[CrossRef\]](#)
4. Cui, D.; Shen, D.; Wu, C. Biodegradation of aniline by a novel bacterial mixed culture AC. *Int. Biodeterior. Biodegrad.* **2017**, *125*, 86–96. [\[CrossRef\]](#)
5. Fana, Y.; Chen, X.; Yao, Z. A novel inhibition mechanism of aniline on nitrification: Aniline degradation competes dissolved oxygen with nitrification. *Sci. Total Environ.* **2021**, *770*, 145205. [\[CrossRef\]](#)
6. Chen, H.; Sun, C.; Liu, R. Enrichment and domestication of a microbial consortium for degrading aniline. *J. Water Process Eng.* **2021**, *42*, 102108. [\[CrossRef\]](#)
7. Ferreiro, C.; Villota, N.; Lombraña, J.I.; Rivero, M.J. An efficient catalytic process for the treatment of genotoxic aniline wastewater using a new granular activated carbon-supported titanium dioxide composite. *J. Clean. Prod.* **2019**, *228*, 1282–1295. [\[CrossRef\]](#)
8. Gan, Y.; Chen, G.; Sang, Y.; Zhou, F.; Man, R.; Huang, J. Oxygen-rich hyper-cross-linked polymers with hierarchical porosity for aniline adsorption. *Chem. Eng. J.* **2019**, *368*, 29–36. [\[CrossRef\]](#)
9. Xue, G.; Wang, Q.; Qian, Y. Simultaneous removal of aniline, antimony and chromium by ZVI coupled with H₂O₂: Implication for textile wastewater treatment. *J. Hazard. Mater.* **2019**, *368*, 840–848. [\[CrossRef\]](#)
10. Koyuncu, H.; Kul, A.R. Removal of aniline from aqueous solution by activated kaolinite: Kinetic, equilibrium and thermodynamic studies. *Colloids Surf. A* **2019**, *569*, 59–66. [\[CrossRef\]](#)
11. Zhang, W.; Zhang, Q.; Li, M. Microbial community and function evaluation in the start-up period of bioaugmented SBR fed with aniline wastewater. *Bioresour. Technol.* **2021**, *319*, 124148. [\[CrossRef\]](#) [\[PubMed\]](#)
12. Shao, M.; Li, Y.; Meng, L. Simultaneous removal of antimony, chromium and aniline by forward osmosis membrane: Preparation, performance and mechanism. *Desalination* **2021**, *520*, 115363. [\[CrossRef\]](#)
13. Jin, R.; Qiu, Z.; Cheng, W. Photocatalytic degradation of aniline by magnetic nanomaterials Fe₃O₄@SiO₂@BiO_{1.8}·0.04H₂O/Ag₃PO₄. *Chem. Phys. Lett.* **2020**, *755*, 137747. [\[CrossRef\]](#)

14. Chena, J.; Shena, C.; Guoa, B. Photocatalytic oxidation of aniline over MO/TiO₂ (M = Mg, Ca, Sr, Ba) under visible light irradiation. *Catal. Today* **2019**, *335*, 312–318. [\[CrossRef\]](#)
15. Ghosh, S.; Malloum, A.; Bornman, C. Novel green adsorbents for removal of aniline from industrial effluents: A review. *J. Mol. Liq.* **2022**, *345*, 118167. [\[CrossRef\]](#)
16. Wang, H.; Li, C.; Xu, Q. Mass transport and pervaporation recovery of aniline with high-purity from dilute aqueous solution by PEBA/PVDF composite membranes. *Sep. Purif. Technol.* **2021**, *268*, 118708. [\[CrossRef\]](#)
17. Durán, A.; Monteagudo, J.M.; Martín, I.S. Solar photo-degradation of aniline with rGO/TiO₂ composites and persulfate. *Sci. Total Environ.* **2019**, *697*, 134086. [\[CrossRef\]](#)
18. Chhaya, V.; Rekhate, J.K. Srivastava. Recent advances in ozone-based advanced oxidation processes for treatment of wastewater—A review. *Chem. Eng. J. Adv.* **2020**, *3*, 100031.
19. Xie, H.; Li, J.; Wang, Y. Influencing factors for the Fenton-like of biological sponge iron system and its degradation mechanism of aniline. *Process Biochem.* **2021**, *101*, 230–236. [\[CrossRef\]](#)
20. Ou, B.; Wang, J.; Wu, Y. A highly efficient cathode based on modified graphite felt for aniline degradation by electro-Fenton. *Chemosphere* **2019**, *235*, 49–57. [\[CrossRef\]](#)
21. Ahmadi, M.F.; da Silva, Á.R.L.; Martínez-Huitle, C.A. Understanding the electro-catalytic effect of benzene ring substitution on the electrochemical oxidation of aniline and its derivatives using BDD anode: Cyclic voltammetry, bulk electrolysis and theoretical calculations. *Electrochim. Acta* **2021**, *369*, 137688. [\[CrossRef\]](#)
22. Qi, Y.; Guo, C.; Xu, X. Co/Fe and Co/Al layered double oxides ozone catalyst for the deep degradation of aniline: Preparation, characterization and kinetic model. *Sci. Total Environ.* **2020**, *715*, 136982. [\[CrossRef\]](#) [\[PubMed\]](#)
23. Li, Y.; Zhu, J.; Hu, J. Catalytic ozonation for effective degradation of aniline by sulfur-doped copper–nickel bimetallic oxide in aqueous solution. *J. Environ. Chem. Eng.* **2021**, *9*, 104953. [\[CrossRef\]](#)
24. Chen, C.; Jia, N.; Song, K. Sulfur-doped copper–yttrium bimetallic oxides: A novel and efficient ozonation catalyst for the degradation of aniline. *Sep. Purif. Technol.* **2020**, *236*, 116248. [\[CrossRef\]](#)
25. Zhang, Z.; Yi, G.; Li, P. Electrochemical oxidation of hydroquinone using Eu-doped PbO₂ electrodes: Electrode characterization, influencing factors and degradation pathways. *J. Electroanal. Chem.* **2021**, *895*, 115493. [\[CrossRef\]](#)
26. Sato, Y.; Zeng, Q.; Meng, L. Importance of Combined Electrochemical Process Sequence and Electrode Arrangements: A Lab-scale Trial of Real Reverse Osmosis Landfill Leachate Concentrate. *Water Res.* **2021**, *192*, 116849. [\[CrossRef\]](#) [\[PubMed\]](#)
27. Lee, J.; Cho, W.-C.; Poo, K.-M.; Choi, S.; Kim, T.-N.; Son, E.-B.; Choi, Y.-J.; Kim, Y.M.; Chae, K.-J. Refractory oil wastewater treatment by dissolved air flotation, electrochemical advanced oxidation process, and magnetic biochar integrated system. *J. Water Process Eng.* **2020**, *36*, 101358. [\[CrossRef\]](#)
28. Deng, Y.; Chen, N.; Feng, C. Degradation of nitrogen-containing refractory organic wastewater using a novel alternating-anode electrochemical system. *Sci. Total Environ.* **2019**, *697*, 134161. [\[CrossRef\]](#)
29. Karthikeyan, S.; Viswanathan, K.; Boopathy, R. Three dimensional electro catalytic oxidation of aniline by boron doped mesoporous activated carbon. *J. Ind. Eng. Chem.* **2015**, *21*, 942–950. [\[CrossRef\]](#)
30. Nie, C.; Ao, Z.; Duan, X. Degradation of aniline by electrochemical activation of peroxydisulfate at MWCNT cathode: The proofed concept of nonradical oxidation process. *Chemosphere* **2019**, *206*, 4324–4338. [\[CrossRef\]](#)
31. Ferreira, M.; Pinto, M.F.; Neves, I.C. Electrochemical oxidation of aniline at mono and bimetallic electrocatalysts supported on carbon nanotubes. *Chem. Eng. J.* **2015**, *260*, 309–315. [\[CrossRef\]](#)
32. Faria, P.C.C.; Órfão, J.J.M.; Pereira, M.F.R. Ozonation of aniline promoted by activated carbon. *Chemosphere* **2002**, *67*, 809–815. [\[CrossRef\]](#) [\[PubMed\]](#)
33. Chinese, N. *Water and Wastewater Monitoring Methods*; Chinese Environmental Science Publishing House: Beijing, China, 2002.
34. Tekle-Rötter, A.; von Sonntag, C.; Reisz, E. Ozonation of anilines: Kinetics, stoichiometry, product identification and elucidation of pathways. *Water Res.* **2019**, *98*, 147–159. [\[CrossRef\]](#) [\[PubMed\]](#)
35. Oyama, S.T. Chemical and catalytic properties of ozone. *Catal. Rev.* **2000**, *42*, 279–322. [\[CrossRef\]](#)
36. Li, X.; Shao, D.; Xu, H. Fabrication of a stable Ti/TiO_xH_y/Sb-SnO₂ anode for aniline degradation in different electrolytes. *Chem. Eng. J.* **2016**, *285*, 1–10. [\[CrossRef\]](#)
37. Zhao, J.; Zhu, C.Z.; Lu, J. Electro-catalytic degradation of bisphenol A with modified Co₃O₄/β-PbO₂/Ti electrode. *Electrochim. Acta* **2014**, *118*, 169–175. [\[CrossRef\]](#)
38. Arts, A.; de Groot, M.T.; van der Schaaf, J. Current efficiency and mass transfer effects in electrochemical oxidation of C₁ and C₂ carboxylic acids on boron doped diamond electrodes. *Chem. Eng. J. Adv.* **2021**, *6*, 100093. [\[CrossRef\]](#)
39. Von Gunten, U. Ozonation of drinking water: Part I. Oxidation kinetics and product formation. *Water Res.* **2000**, *37*, 1443–1467. [\[CrossRef\]](#)
40. Kesavan, L.; Kalekar, A.M.; Damlin, P. Reduced graphene oxide supported palladium nano-shapes for electrooxidation of oxalic acid. *J. Electroanal. Chem.* **2019**, *847*, 113167. [\[CrossRef\]](#)
41. de Queiroz, J.L.A.; da Silva, A.R.L.; de Moura, D.C. Electrochemical study of carboxylic acids with Nb-supported boron doped diamond anode. Part 1: Potentiodynamic measurements and bulk oxidations. *J. Electroanal. Chem.* **2017**, *794*, 204–211. [\[CrossRef\]](#)
42. Shih, Y.J.; Huang, C.P.; Chan, Y.H. Electrochemical degradation of oxalic acid over highly reactive nanotextured γ- and α-MnO₂/carbon electrode fabricated by KMnO₄ reduction on loofah sponge-derived active carbon. *J. Hazard. Mater.* **2019**, *379*, 120759. [\[CrossRef\]](#) [\[PubMed\]](#)