Performance investigation of electrochemical assisted HClO/Fe²⁺ process for the treatment of landfill leachate

Zhihong Ye¹,² · Fei Miao¹ · Hui Zhang¹

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Abstract
The feasibility of removal of chemical oxygen demand (COD) and ammonia nitrogen \( (\text{NH}_4^+–\text{N}) \) from landfill leachate by an electrochemical assisted HClO/Fe²⁺ process is demonstrated for the first time. The performance of active chlorine generation at the anode was evaluated in \( \text{Na}_2\text{SO}_4/\text{NaCl} \) media, and a higher amount of active chlorine was produced at greater chloride concentration and higher current density. The probe experiments confirmed the coexistence of hydroxyl radical \( (\cdot\text{OH}) \) and \( \text{Fe(IV)}\text{-oxo complex} (\text{FeIVO}_2^+) \) in the HClO/Fe²⁺ system. The influence of initial pH, \( \text{Fe}^2+ \) concentration, and applied current density on COD and \( \text{NH}_4^+–\text{N} \) abatement was elaborately investigated. The optimum pH was found to be 3.0, and the proper increase in \( \text{Fe}^2+ \) dosage and current density resulted in higher COD removal due to the accelerated accumulation of \( \cdot\text{OH} \) and \( \text{FeIVO}_2^+ \) in the bulk liquid phase, whereas, the \( \text{NH}_4^+–\text{N} \) oxidation was significantly affected by the applied current density because of the effective active chlorine generation at higher current but was nearly independent of \( \text{Fe}^2+ \) concentration. The reaction mechanism of electrochemical assisted HClO/Fe²⁺ treatment of landfill leachate was finally proposed. The powerful \( \cdot\text{OH} \) and \( \text{FeIVO}_2^+ \), in concomitance with active chlorine and \( \text{M}(\cdot\text{OH}) \), were responsible for COD abatement, and active chlorine played a key role in \( \text{NH}_4^+–\text{N} \) oxidation. The proposed electrochemical assisted HClO/Fe²⁺ process is a promising alternative for the treatment of refractory landfill leachate.

Keywords Advanced oxidation process · Active chlorine · Electrochemical Fenton-type process · Landfill leachate · COD; \( \text{NH}_4^+–\text{N} \)

Introduction
Sanitary landfill disposal is the most widely used method for municipal solid waste treatment in the world due to its economic advantages (Wu et al. 2018). However, this disposal method leads to the production of complex liquids, namely landfill leachate, containing large amounts of organic pollutants, \( \text{NH}_4^+–\text{N} \), inorganic salts, and heavy metals (Fu et al. 2021). The generation of landfill leachate is expected to approach 330 million tonnes by 2025, posing great challenges to water environment and ecosystem worldwide (Abunama et al. 2018; Costa et al. 2019). The characteristics of leachate are affected by various factors including waste origin, seasonal precipitation, and, particularly, the age of landfill (Panizza et al. 2010). The old landfill leachate (more than 10 years) usually has stable water quality indexes, such as high fraction of recalcitrant organics, high \( \text{NH}_4^+–\text{N} \) concentration \( (2000–5000 \text{ mg L}^{-1}) \), and low biochemical oxygen demand \( (\text{BOD}) \) to chemical oxygen demand \( (\text{COD}) \) ratio \( (<0.1) \), making it difficult to be treated using traditional biological technology (Deng et al. 2021; Ghahrchi and Rezaee 2021). Many alternative physical and chemical methods have been applied for the treatment of landfill leachate, such as flocculation and sedimentation (Silva et al. 2004), adsorption (Reshadi et al. 2020), ozonation (Yang et al. 2021), advanced oxidation processes (Kwarcia-Kozłowska and Fijałkowski 2021),

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membrane technologies (Keyikoglu et al. 2021), and electrochemical technologies (Deng et al. 2020).

Among them, electrochemical methods are considered to be the most promising technologies that can effectively destroy refractory organics and increase the biodegradability of the leachate for the subsequent biological treatment (El Kateb et al. 2019). Electro-oxidation (EO), one of the electrochemical advanced oxidation processes (EAOPs), shows great priority for industrialization because of its stability, easy operation, and amenability to automation (Fernandes et al. 2015). During EO, the powerful physisorbed hydroxyl radical (M(•OH)) is generated via water oxidation on the surface of anode M (reaction 1), and it can be transformed into the chemisorbed active oxygen or superoxide MO from reaction (2), especially for active anodes like IrO$_2$ and RuO$_2$ (Moreira et al. 2017).

\[
M + H_2O \rightarrow M(\cdot OH) + H^+ + e^- \quad (1)
\]

\[
M(\cdot OH) \rightarrow MO + H^+ + e^- \quad (2)
\]

The presence of these active species allows efficient removal of refractory organics (R) in landfill leachate via the approaches of (i) electrochemical conversion, which arises from MO/M pair mediator via reaction (3) and (ii) electrochemical combustion, which is caused by the weakly interacted M(•OH) via reaction (4) (Sirés and Brillas 2012; Sirés et al. 2014).

\[
R + MO \rightarrow M + RO \quad (3)
\]

\[
R + M(\cdot OH) \rightarrow M + CO_2 + H_2O \quad (4)
\]

Unfortunately, the above active species play negligible roles in NH$_4^+$–N oxidation during the treatment of landfill leachate (Bunce and Bejan 2011). The high concentration of Cl$^-$ in the leachate can compete with water to be oxidized to dissolved chlorine via reaction (5), which is further converted into hypochlorous acid (HClO, $E^0 = 1.49$ V/SHE) at pH 3.0–8.0 through reaction (6). This gives rise to the so-called EO-HClO process (Murrieta et al. 2020; Sirés et al. 2014). The electro-generated active chlorine thus becomes HClO would consume H$_2$O$_2$ via the adverse reaction (10), resulting in a huge waste of oxidants (Aguilar et al. 2017; Murrieta et al. 2020; Shah et al. 2015). This can be overcome in the electro-Fenton-like process in which HClO is electro-generated and H$_2$O$_2$ could not be produced. Moreover, a recent work suggested that the high valent iron complex, Fe$^{IV}$O$_2^+$ ([Fe$^{IV}$] = 2.0 V/SHE), should be an important reactive species produced from the reaction between HClO and Fe$^{IV}$ (reaction 11), which was neglected by the previous studies (Liang et al. 2020).

\[
\text{HClO} + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{•OH} + \text{Cl}^- \quad (8)
\]

\[
\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+} \quad (9)
\]

\[
\text{HClO} + \text{H}_2\text{O}_2 \rightarrow \text{Cl}^- + \text{O}_2(g) + \text{H}_2\text{O} + \text{H}^+ \quad (10)
\]

\[
\text{HClO} + \text{Fe}^{2+} \rightarrow \text{Fe}^{IV}\text{O}^{2+} + \text{HCl} \quad (11)
\]

Recently, Kishimoto et al. (2015) proposed a new electrochemical assisted Fenton-like process to form *OH using Fe$^{3+}$ and HClO via reaction (8) for the decontamination of wastewater containing Cl$^-$, while Fe$^{2+}$ can be regenerated upon cathodic reduction of Fe$^{3+}$ through reaction (9). This electro-Fenton-like process shows numerous advantages over the conventional electro-Fenton. Firstly, HClO is generated by the chlorine-based reaction (5) and (6) at the anode, avoiding the competing cathodic reduction of O$_2$ to H$_2$O$_2$ and Fe$^{3+}$ to Fe$^{2+}$ occurred in the electro-Fenton system. Secondly, 2 mol of electrons can be used to generate 1 mol of *OH stoichiometrically, whereas the conventional electro-Fenton requires 3 mol for 1 mol of *OH. Finally, during the electro-Fenton treatment of wastewater with high Cl$^-$ content, the electro-generated HClO would consume H$_2$O$_2$ via the adverse reaction (10), resulting in a huge waste of oxidants (Aguilar et al. 2017; Murrieta et al. 2020; Shah et al. 2015). This can be overcome in the electro-Fenton-like process in which HClO is electro-generated and H$_2$O$_2$ could not be produced. Moreover, a recent work suggested that the high valent iron complex, Fe$^{IV}$O$_2^+$ ([Fe$^{IV}$] = 2.0 V/SHE), should be an important reactive species produced from the reaction between HClO and Fe$^{IV}$ (reaction 11), which was neglected by the previous studies (Liang et al. 2020).

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\]

The objective of this study was to investigate, for the first time, the performance of the electrochemical assisted HClO/Fe$^{2+}$ process regarding the treatment of old landfill leachate. The ability to generate HClO of the anode was firstly evaluated by conducting the electrolysis in NaCl or mixed Na$_2$SO$_4$+NaCl media at pH 3.0 with different chloride concentrations and current densities in the absence of Fe$^{3+}$. The formation of *OH and Fe$^{IV}$O$_2^+$ in the HClO/Fe$^{2+}$ system was further confirmed by using dimethyl sulfoxide (DMSO) and methyl phenyl sulfoxide (PMSO) as the radical probes, respectively (Shao et al. 2018). Then, the effect of initial pH, Fe$^{2+}$ concentration and current density on COD and NH$_4^+$–N decay was examined during the electrochemical assisted HClO/Fe$^{2+}$ treatment of landfill leachate. At last, a specific reaction mechanism for COD and NH$_4^+$–N removal was proposed.
Experimental

Landfill leachate characteristics

The old landfill leachate was collected from a municipal sanitary landfill located in Wuhan, China. The samples were stored in a refrigerator at 4 °C to maintain the characteristics unaltered, and they were directly used in electrochemical systems without any pre-treatment (Ye et al. 2016). The main characteristics of the leachate were summarized in Table 1.

Identification of •OH and FeIVO2+

DMSO was selected as a molecular probe for the detection of •OH in the HClO/Fe2+ system. It can react rapidly with •OH leading to the formation of methanesulfonic acid and methyl radicals, followed by several reactions to generate the final product formaldehyde (HCHO) (Tai et al. 2004; Zhang et al. 2020). Thus, the quantitative analysis of •OH in this study was conducted through the determination of the concentration of HCHO in the solution. In addition, it is generally believed that FeIVO2+ can oxidize PMSO through oxygen transfer to generate methyl phenyl sulfone (PMSO2), which is different from the •OH induced hydroxylated products (Fang et al. 2022). To figure out whether FeIVO2+ was generated in the HClO/Fe2+ system, PMSO was selected as the chemical probe to distinguish FeIVO2+ from •OH. The detailed procedures for the identification of •OH and FeIVO2+ in the HClO/Fe2+ system were described in Supplementary Material (Text S1). Further determination of •OH, FeIVO2+, and HClO in the electrochemical assisted HClO/Fe3+ process was conducted in NaCl solution or urban wastewater (COD 35 mg L−1, collected from municipal wastewater treatment works) matrices.

Electrochemical systems

A single-cell rectangular electrolytic reactor was used in the experiments, and the size of which was 12 cm × 10 cm × 20 cm. The anodic material was titanium coated by iridium dioxide, ruthenium dioxide, and titanium dioxide (Ti/IrO2–RuO2–TiO2, 75 cm2), and the cathodic material was titanium. The gap between the anode and the cathode was adjusted parallel at a distance of 2 cm. All trials were conducted under constant current conditions provided by a direct current (DC) power supply (LW-3030KD) under room temperature at 20 ± 3 °C, and the solution was vigorously stirred with a magnetic bar at 700 rpm. The assessment of the ability to generate HClO at the anode was firstly carried out with 400 mL NaCl or mixed Na2SO4+NaCl solutions at pH 3.0 in the absence or presence of Fe2+ under the conditions of different chloride concentration and current density. The trials for the treatment of landfill leachate were performed under galvanostatic conditions with the volume of 1000 mL and the electrodes working area of 75 cm2. Samples were collected to analyze the COD and NH4+-N concentrations at pre-selected time intervals.

Analytical procedures

The solution pH was measured with a Metter-Toledo FE20 pH meter. Active chlorine was determined by the N, N-diethyl-p-phenylenediamine (DPD) colorimetric method using a UV/vis spectrophotometer (UV-5000, METASH) set at λ = 515 nm (Murrieta et al. 2020). The concentration of Fe2+ was analyzed by measuring the absorption of the reddish solutions resulting upon its complexation with 1,10-phenanthroline, whose maximum absorbance was at λ = 510 nm (Ye et al. 2020). COD was determined by a fast digestion-spectrophotometric method based on the Standard of the People’s Republic of China for Environmental Protection (Ye et al. 2016). NH4+-N concentration was measured using Nessler’s reagent colorimetric method. The concentration of HCHO was analyzed using acetylacetone method with a UV/vis spectrophotometer set at λ = 412 nm (Zhang et al. 2020). PMSO and PMSO2 were analyzed using a high-performance liquid chromatograph (HPLC, Shimadzu Co.) with a LC-20AB pump and a SPD-20A chromatograph equipped with a C-18 column (250 × 4.6 mm, 5 μm) and an SPD-10A UV–visible detector. The elution was achieved upon recirculation of an 80:20 (v:v) water (0.1% acetic acid)/acetonitrile mixture at 1.0 mL min−1. The detection wavelengths for PMSO and PMSO2 were set at 230 and 215 nm, respectively (Lai et al. 2020). The concentration of ClO3− and ClO4− was obtained by ion chromatography using a Dionex ICS-600 fitted with an IonPac AS16 anion column, coupled to a D5 conductivity detector.

Results and discussion

Active chlorine production on Ti/IrO2–RuO2–TiO2 anode

To clarify the ability for Ti/IrO2–RuO2–TiO2 anode to produce active chlorine, the variation of active chlorine content as a function of electrolysis time in the EO-HClO process
was monitored at various levels of chloride ion concentration (1.0 to 4.0 g L⁻¹) and different current densities (7.5 to 30 mA cm⁻²). The highest Cl⁻ concentration used in the simulated matrix was similar to that in the landfill leachate (3.8 g L⁻¹), in order to achieve valuable results to guide the subsequent practical treatment of landfill leachate. As depicted in Fig. 1a, the accumulated active chlorine content rapidly increased with the increase of Cl⁻ concentration from 1.0 to 3.0 g L⁻¹, and further increase of the Cl⁻ concentration to 4.0 g L⁻¹ led to the maximal active chlorine production (13.6 mmol L⁻¹), despite the enhancement was insignificant. The surface catalytic properties of anodes toward chloride ion oxidation have substantial relevance to the generation of active chlorine. The low adsorption properties of the active IrO₂–RuO₂–TiO₂ anode benefit the active chlorine production since a large number of empty active sites are available for Cl⁻ oxidation (Garcia-Espinoza et al. 2018). Thus, the increase in Cl⁻ concentration can accelerate the accessibility between Cl⁻ and active sites on the anode surface and promote active chlorine production.

The effect of current density on active chlorine generation was further investigated at 4.0 g L⁻¹ of Cl⁻ ion. As shown in Fig. 1b, a larger accumulation of active chlorine was achieved as the current density became higher. Only 7.8 mmol L⁻¹ active chlorine was yielded at the lowest current density 7.5 mA cm⁻², which was dramatically enhanced up to 13.6 and 19.7 mmol L⁻¹ at 15 and 20 mA cm⁻², respectively. The active chlorine concentration reached a maximum of 23.5 mmol L⁻¹ after 180-min electrolysis at 30 mA cm⁻². Obviously, the increase in current density could enhance charge transfer in the electrochemical process, thus, facilitating the Cl⁻ oxidation on the anode. However, the applied current was partly invested in the parallel parasitic reactions such as water oxidation at higher current density, resulting in the decreased current efficiency of active chlorine generation (Cornejo et al. 2020; Murrieta et al. 2020).

In order to better understand the electrochemical assisted HCIO/Fe²⁺ process, the evolution of active chlorine and Fe⁴⁺ concentrations was investigated in the presence of 4.0 g L⁻¹ of Cl⁻ ion and 5.6 mmol L⁻¹ of Fe²⁺ ion at current density of 15 mA cm⁻². Note that the molar mass of Fe³⁺ was much lower than that of electro-generated HCIO due to the continuous regeneration of Fe²⁺ at the cathode via reaction (9) and possible iron precipitation occurred at excessive iron dosage. Figure 2a highlights the much slower accumulation of active chlorine in the electrochemical assisted HCIO/Fe²⁺ system, which confirmed the continuous consumption of active chlorine by the Fenton-like reaction (8) and nonradical reaction (11). Worth noting, the accumulated active chlorine was lower than 0.6 mmol L⁻¹ during the initial 30-min reaction, whereas its counterpart reached up to 6.1 mmol L⁻¹ in the EO–HCIO system without Fe²⁺; the rapid consumption of active chlorine at the initial stage was due to the efficient reactions (8) and (11) occurred in the presence of abundant Fe²⁺. This is consistent with the result achieved on Fe²⁺ evolution in Fig. 2b, in which Fe⁴⁺ concentration underwent a very swift decay once the reaction was initiated and reached 96% disappearance at 30 min. Afterwards, Fe³⁺ species barely existed despite the continuous regeneration at the cathode due to the large accumulation of HCIO in the bulk. Therefore, it is believed that the ability of the cathode to reduce Fe³⁺ by reaction (9) became the rate-limiting factor after 30 min of the electrochemical assisted HCIO/Fe²⁺ process, rather than active chlorine concentration.

Moreover, the formation of ClO₃⁻ and ClO₄⁻ during EO and electrochemical assisted HCIO/Fe²⁺ processes in Fig. 2a.
was investigated. The EO process gave rise to 12.83 mg L⁻¹ ClO₃⁻ after 120 min, while the concentration of ClO₃⁻ during the electrochemical assisted HClO/Fe²⁺ process was below the limit of quantification (<0.01 mg L⁻¹), which was due to the slow accumulation of HClO in the presence of Fe²⁺. No ClO₄⁻ was detected in both systems.

Identification of reactive species involved in the HClO/Fe²⁺ process

It has been reported that •OH is believed to be the predominant reactive species generated in the HClO/Fe²⁺ process via Fenton-like reaction (8) (Aguilar et al. 2017; Kishimoto et al. 2015). However, most recently, some researchers suggested that Fe⁴⁺O²⁺ could also make a significant contribution to wastewater decontamination (Liang et al. 2020). Therefore, to fully identify the potential reactive species involved in the HClO/Fe²⁺ process, DMSO was used as a capturing agent for •OH, and PMSO was selected to determine Fe⁴⁺O²⁺ by measuring the conversion rate of PMSO to PMSO₂ in this work.

DMSO has been widely employed in the detection of •OH in advanced oxidation processes due to its high reactivity with •OH (k = 4.5–7.1 × 10⁹ M⁻¹ s⁻¹) forming methanesulfinic acid and methyl radicals via reaction (12); the generated methyl radicals were further converted to HCHO thorough reactions (13) and (14) (Tai et al. 2004). Thus, the presence of HCHO could provide convictive evidence for the formation of •OH.

As shown in Fig. 3a, around 400 nmol •OH was finally detected in the HClO/Fe²⁺ system in the presence of excess DMSO after 30-min reaction at pH 3.0, indicating the formation of •OH via Fenton-like reaction (8).

Moreover, identification of Fe⁴⁺O²⁺ was performed using PMSO as the probe according to reaction (15), the formation of Fe⁴⁺O²⁺ species could be assessed on the basis of the yield of PMSO₂ (mole of PMSO₂ formed per mole of PMSO consumed, \( \eta \)PMSO₂ = \[PMSO₂ formed] /[PMSO] consumed×100%), and high production of Fe⁴⁺O²⁺ was suggested when \( \eta \)PMSO₂ approached 100% (Gao et al. 2020).

As depicted in Fig. 3a, the \( \eta \)PMSO₂ value was quantified to be as high as 100%, suggesting the significant role of high-valent iron species in the HClO/Fe²⁺ system. Note that, although Fe(IV) is less reactive than •OH, it is more inert to the interference of coexisting anions (Cl⁻, NO₃⁻, and CO₃²⁻) and can selectively oxidize target refractory organic contaminants in wastewater (Zong et al. 2021). This finding is consistent with the previous work documenting Fe⁴⁺O²⁺ as the main oxidant in the HClO/Fe²⁺ system (Liang et al. 2020). Summarily, the coexistence of HClO-simulated one-electron pathway to •OH and two-electron nonradical transformation of Fe²⁺ to Fe⁴⁺O²⁺ is identified, and these two reactive species may together contribute to the degradation of organic pollutants during wastewater treatment.

The occurrence of reactions (8) and (11) during the electrochemical assisted HClO/Fe²⁺ process was further...
verified by determining *OH, FeIVO2+, and active chlorine in NaCl solution or urban wastewater matrices. As can be observed in Fig. 3b, high amounts of *OH and FeIVO2+ were detected after 20-min reaction during the electrochemical assisted HClO/Fe2+ process in NaCl solution, while only 0.3 mmol L⁻¹ active chlorine was accumulated, attesting the effectiveness of reactions (8) and (11). The concentrations of *OH and HClO were significantly decreased when urban wastewater was employed due to the presence of organics, such as humic and fulvic acids, which, however, scarcely affected the accumulation of FeIVO2+. This results from the low organic concentrations and, more importantly, the relatively weak and selective oxidation properties of Fe(IV) (Liang et al. 2021).

Summarily, the electrochemical assisted HClO/Fe2+ system is particularly applicable to treat the refractory wastewater with high Cl⁻ content, and the electrodes with satisfactory chlorine-evolution polarization characteristics, such as IrO₂-based dimensionally stable anodes, are preferred to produce a high amount of HClO and avoid its further oxidation to HClO₃ and HClO₄ as much as possible. In addition, the selection of cathodes that can efficiently regenerate Fe²⁺ is of great significance.

**Electrochemical assisted HClO/Fe²⁺ treatment of landfill leachate**

The old landfill leachate was firstly treated by EO-HClO in the absence of Fe²⁺ at different current densities (7 and 14 mA cm⁻², respectively). As shown in Fig. S1, only 8.1% COD abatement was obtained after 2-h treatment at low current density 7 mA cm⁻², and further increase in the current density to 14 mA cm⁻² led to slight enhancement on COD removal (13.7%). The old landfill leachate is usually characterized by complex refractory organic compounds, such as humic and fulvic acids, which are highly resistant to the oxidation. The active anode, Ti/IrO₂–RuO₂–TiO₂, used in this study presents low oxygen evolution potential and allows the generation of a small amount of unstable M(*OH), which is too weak to yield efficient oxidation of organic pollutants (Sirés et al. 2014). On the other hand, despite the excellent ability to form active chlorine from the oxidation of chloride at the anode, as displayed in Fig. 1, the oxidative power of HOCl (E° = 1.49 V vs. SHE) is barely satisfactory to acquire quick COD abatement due to the accumulation of persistent chloroderivatives (Panizza et al. 2010).

Similar results were achieved for NH₄⁺–N treatment in the EO–HClO system, i.e., 7.3% and 9.1% removal efficiency at current density of 7 and 14 mA cm⁻², respectively. As reported, the contribution of *OH on NH₄⁺–N oxidation is assumed as negligible; active chlorine thus became the dominant active species for the elimination of NH₄⁺–N, which was also competitively consumed by high amounts of organics in landfill leachate (Mandal et al. 2020). Summarily, the single EO-HClO process failed to achieve powerful performance on landfill leachate treatment. The feasibility of the electrochemical assisted HClO/Fe²⁺ system was therefore explored.

**Effect of initial pH**

To investigate the effect of initial pH on COD and NH₄⁺–N removal, experiments were carried out with a current density of 14 mA cm⁻² and Fe²⁺ dosage of 4.0 mmol L⁻¹ at different initial pH (2.0, 3.0, and 9.0). The decay of COD and NH₄⁺–N as a function of time is displayed in Fig. 4. Similar COD removal efficiencies, 55.2% and 55.8%, were achieved after 8-h treatment at initial pH 2.0 and 3.0, whereas the value was dropped to 28% when the pH increased to 9.0. Worth noting, the initial 30-min treatment already led to 45% COD abatement at pH 3.0, which was much higher than that obtained in the EO-HClO process (3%), and the following
that initial pH exerted little impact on COD removal at initial pH 9.0. However, several previous studies stated that initial pH exerted little impact on COD removal at initial pH 9.0 (Ye et al. 2016). The generation of FeIVO2+ that were generated Fe3+ at the cathode. Further increasing the pH to 9.0 resulted in massive precipitation of hypochlorite ion (ClO−, pKa for HClO/ClO− was 7.5); these clearly explained the poor performance on COD decay at initial pH 9.0. hampered due to the massive precipitation of ion species at alkaline pH. 7.5-h treatment only contributed 10.8% more COD removal. This highly agrees with the results achieved in Fig. 2, where it has been demonstrated that the production of •OH and FeIVO2+ from reactions (8) and (11) largely occurred during the initial stage due to the presence of high concentration of Fe2+, but these two reactions became inefficient afterwards because of the limited cathodic reduction of Fe3+. In consequence, the COD abatement in the electrochemical assisted HClO/Fe2+ process occurred in two consecutive stages: (i) the first one, where the •OH and FeIVO2+ had the leading role, followed by (ii) the second one, where COD was mainly destroyed by M(•OH) and HClO, coupled with poor contribution of ”OH and FeIVO2+ that were generated due to the gradual reduction of Fe3+ at the cathode. Further increasing the pH to 9.0 resulted in massive precipitation of iron species and transformation of HClO to weaker oxidant hypochlorite ion (ClO−, pKa for HClO/ClO− was 7.5); these clearly explained the poor performance on COD decay at initial pH 9.0 (Ye et al. 2016).

Figure 4 also illustrates approximately 25% NH4+-N removal at initial pH 2.0 and 3.0, slightly higher than that achieved at pH 9.0. However, several previous studies stated that initial pH exerted little impact on NH4+-N degradation due to the fact that NH4+-N removal mainly takes place close to the anode surface where the local pH is minimally affected by initial pH (Vanlangendonck et al. 2005; Zhang et al. 2018). The different results obtained in this study could be attributed to the formation of complex between ammonia and FeIV species, as reported in the literature, which reduced the amount of detectable NH4+-N in the solution (Feng et al. 2017). The generation of FeIVO2+ was significantly hampered due to the massive precipitation of ion species at alkaline pH.

Effect of Fe2+ concentration

The influence of Fe2+ concentration, ranging from 2.0 to 8.0 mmol L−1, on the performance of electrochemical assisted HClO/Fe2+ treatment of landfill leachate was examined at initial pH 3.0 and current density 14 mA cm−2. As can be observed in Fig. 5, the COD removal efficiency increased from 48.5 to 55.8% when Fe2+ dosage increased from 2.0 to 4.0 mmol L−1, but further increase in Fe2+ concentration to 8.0 mmol L−1 led to negligible promotion in COD decay. The enhancement of HClO decomposition to active •OH and FeIVO2+ species can be achieved by appropriate increase in Fe2+ concentration, but excess Fe2+ also gave rise to the competitive consumption of •OH and FeIVO2+ via reactions (16) and (17), especially at the initial stage when HClO accumulation was insufficient, negatively affecting the COD destruction (Murrieta et al. 2020; Wang et al. 2018).

Fe2+ + •OH → Fe3+ + OH− (16)

FeIVO2+ + Fe2+ + 2H+ → 2Fe3+ + H2O (17)

In addition, the aforementioned rate-limiting factor after the disappearance of added Fe2+ is the Fe3+ reduction ability of the cathode, rather than the total concentration of iron species. The generated excess Fe3+ from reactions (8) and (11) tended to precipitate on the cathode surface due to the formation of OH− by water splitting reaction, which retarded the regeneration of Fe2+ via reaction (9).

The profiles of NH4+-N removal with different Fe2+ dosage possessed similar trends during 8-h treatment, as depicted in Fig. 5. This is because NH4+-N elimination is mainly attributed to the indirect oxidation by active chlorine
generated via chloride oxidation at the anode, rather than •OH and FeIVO2+ species, whose production highly relied on Fe2+ concentration.

**Effect of current density**

Figure 6 displayed the trends of the COD and NH4+–N with electrolysis time during the treatment of landfill leachate at different current densities (7.0, 14, and 28 mA cm−2) with 4.0 mmol L−1 Fe2+ at initial pH 3.0. The COD decay was accelerated at higher current density, achieving 43.7% and 51.8% removal efficiencies at 7.0 and 14 mA cm−2, respectively. This enhancement could be attributed to the increase in the rate of reactions (1), (5), and (9), leading to the formation of larger amounts of M(•OH), active chlorine, and faster regeneration of Fe2+, which consequently promoted the production of active •OH and FeIVO2+ via reactions (8) and (11). However, the COD abatement was barely upgraded when the current density further increased to 28 mA cm−2, attaining a final COD removal of 53.4%. Although the increase in current density gave rise to more efficient active chlorine accumulation, as depicted in Fig. 1, the destruction of refractory organics by active chlorine was fairly limited as mentioned previously, and excessive HClO can act as a scavenger of •OH via reaction (18) (Ye et al. 2016). Furthermore, higher current density also caused a greater extent of parasitic reactions (19) and (20), competing with the electrolysis of water to form M(•OH) at the anode and the reduction of Fe3+ to regenerate Fe2+ at the cathode, respectively (Cornejo et al. 2020; Sirés et al. 2014).

\[
\text{HClO} + \cdot \text{OH} \rightarrow \cdot \text{ClO} + \text{H}_2\text{O} \quad (18)
\]

\[
\text{2H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 + 4\text{e}^- \quad (19)
\]

\[
\text{2H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \quad (20)
\]

On the contrary, more rapid NH4+–N oxidation was observed at higher current density due to the enhanced generation of active chlorine, which proved again that NH4+–N elimination dominantly arose from the active chlorine oxidation, but was barely affected by M(•OH), •OH, and FeIVO2+ species.

**Proposed reaction mechanism**

Based on the results summarized in this work, the abatement mechanism of COD and NH4+–N during the electrochemical assisted HClO/Fe2+ treatment of old landfill leachate was proposed in Fig. 7. The active anode allowed effective electro-generation of active chlorine from the oxidation of chloride ions and the formation of a small amount of adsorbed M(•OH), while the cathode supported the continuous reduction of Fe3+ to Fe2+. The key reactions occurred between HClO and Fe2+ gave rise to highly active •OH and FeIVO2+ in the bulk solution, and the generated chloride ions can be circularly oxidized at the anode. Therefore, COD in the leachate was mainly destructed by •OH and FeIVO2+ in concomitance with partial oxidation by HClO and M(•OH). On the other hand, active chlorine should be responsible for the NH4+–N oxidation during the electrochemical treatment of landfill leachate.

![Diagram of proposed mechanism](image)

Fig. 7 Proposed mechanism for COD and NH4+–N removal during electrochemical assisted HClO/Fe2+ treatment of landfill leachate
Conclusion

The electrochemical assisted HClO/Fe²⁺ process has been demonstrated as an effective technology for the treatment of old landfill leachate. The active anode, Ti/IrO₂–RuO₂–TiO₂, showed superior ability to generate active chlorine, which was more rapid in the presence of a greater Cl⁻ concentration or at a higher current density. The production of both •OH and Fe⁴⁺O⁵⁺⁺ species was verified in the HClO/Fe²⁺ system by employing DMSO and PMSO as the probes, respectively; despite the lower oxidizing potential of Fe⁴⁺O⁵⁺⁺ compared with •OH, it is advantageous due to the high selectivity and activity for the oxidation of pollutants. The addition of Fe²⁺ to construct an electrochemical assisted HClO/Fe²⁺ system led to more rapid abatement of COD especially at the initial stage than that in the EO-HClO process. Acidic pH was found to favor better COD and NH₄⁺–N removal due to the fact that hypochlorous acid was the dominant active chlorine species at pH 3.0–8.0. The decay of COD was enhanced with the increase in Fe²⁺ dosage and current density to some extent; excessive high Fe²⁺ concentration and current density adversely caused the parasitic reactions, retarding either the accumulation of •OH and Fe⁴⁺O⁵⁺⁺ in bulk or the reduction of Fe⁴⁺ at the cathode. Meanwhile, Fe²⁺ dosage showed a negligible effect on NH₄⁺–N oxidation, which, nevertheless, could be largely promoted by increasing the applied current density. It is believed that various active species, including •OH, Fe⁴⁺O⁵⁺⁺, active chlorine, and M(•OH), could contribute to the COD abatement, and NH₄⁺–N removal highly relied on the oxidation by active chlorine during the electrochemical assisted HClO/Fe²⁺ treatment of landfill leachate. In conclusion, this new approach is environmentally friendly and vitally promising for the treatment of wastewater containing high chloride content.

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Data availability All data and materials used during this study are included in the submitted manuscript and the supplementary files.

Declarations

Ethics approval This study follows all ethical practices during writing.

Consent to participate Not applicable

Consent for publication Not applicable

Competing interests The authors declare no competing interests.

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