Ce³⁺ triggers fenton-like processes in neutral solutions for effective catechol degradation

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ABSTRACT

Classical Fenton and Fenton-like processes destruct organic pollutants in water non-selectively to complete mineralization. However, the usage of classical Fenton or Fenton-like processes is often limited due to the narrow operational pH window, sludge accumulation, inefficient H₂O₂ and efficiency decline. To overcome these constraints, in this study, we used a homogeneous Fe³⁺-Ce³⁺-H₂O₂ Fenton-like process to degrade catechol at different experimental conditions. At pH 7, almost 97% of 10 mM catechol can be destructed within 60 min while the degradation by Classical Fenton or Fe³⁺-H₂O₂ Fenton-like process only 36.2% and 23.7%. The resultant solution after the degradation contains only traces of cerium ions. The sludge created by the process was extensively characterized by FTIR and XPS spectroscopy to elucidate the fate of cerium ions. Electron spin resonance (ESR) data confirmed •OH as the major free radical in Fe³⁺-Ce³⁺-H₂O₂ process. Our Fenton-like process widens the optimal pH values to neutral condition.

Keywords: Catechol, Cerium ion, Degradation, Fenton-like process, Precipitation

1. Introduction

Catechol released from chemical, petrochemical, and pharmaceutical industrial wastes is ubiquitous in the environment [1, 2]. It is listed as class B carcinogen by global health conventions, and therefore, its mitigation from the environment is a priority. Conventional wastewater treatment plants were never designed or did not completely remove non-biodegradable organic pollutants because of their persistence and resistance to biological attack and stability [3]. Treatment methods based on adsorption or membrane technology are inefficient to remediate organic pollutants because they merely concentrate them without destruction.

Advanced oxidation processes (AOP) based on •OH radicals offer an attractive alternative for the complete mineralization of recalcitrant organic pollutants [4-7]. Classical Fenton and Fenton-like processes have been used over three decades [8], which operate

in a narrow pH window with an inefficient use of H₂O₂. Irrespective of the presence of •OH radicals, the oxidation of Fe²⁺ → Fe³⁺ + e⁻ is rapid, which often results in sludge formation. However, the reduction process of Fe³⁺ is comparably slow, and therefore, it determines the overall efficiency of the Fenton Process [9]. Also, high ferrous iron consumption and large sludge production in the conventional Fenton reaction [10]. Many variants to classical Fenton processes such as photo-, electrochemical- or sono- assisted Fenton-like processes have been proposed to overcome the limitations mentioned above with limited success [3, 11-15]. Some researchers attempted to convert H₂O₂ → •OH directly for degradation of pollutants [16-18]. However, all of the above methods require additional energy or organic agents while the utilization rate of iron ions and the oxidation of the complexing agent are not satisfied. In view of this, it is of great significance to find a new method of Fenton to improve the utilization efficiency of H₂O₂, accelerate

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Received September 18, 2020 Accepted December 22, 2020

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the reduction rate of trivalent iron ions, and increase the concentration of ferrous ions in the oxidation system.

Herein, we propose a novel homogeneous system based on the classical Fenton process to overcome most of the limitations above. Compared with the classical Fenton process, the proposed system can operate in a wider pH window with high efficiency meanwhile minimizing contaminants in solution. The catechol was used as the model compound to assess the reaction efficiency. Cerium ($4f^6s^2$) is selected as the electron shuttling due to its well-known redox cycling properties between Ce^{3+} and Ce^{4+} state. Ce^{3+} is a strong reductant at alkaline conditions, and Ce^{4+} is a strong oxidant under acidic environments [19-22]. The Ce^{3+}/Ce^{4+} redox cycling was used for the in situ production of Fe^{2+} to facilitate the Fenton process. Further, we characterized the resultant solution and the sludge using ICP-MS and XPS/ FTIR, respectively.

2. Material and Methods

2.1. Materials

All chemicals used in this study were of analytical grade and used without further purification. Catechol ($C_6H_6O_2$), ferrous sulfate ($FeSO_4 \cdot 7H_2O$), iron(III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$), cerium(III) chloride heptahydrate ($CeCl_3 \cdot 7H_2O$), hydrogen peroxide (H_2O_2 , 30%), tert-butanol ($C_4H_{10}O$), sulfuric acid (H_2SO_4), and sodium hydroxide (NaOH) were purchased from Shanghai Chemical Reagent Co. Ltd, P. R. China. All sample pH adjustments were made either with 0.1M NaOH or 0.1M H_2SO_4 . Ultrapure deionized water (conductivity $\sim 18.25 \text{ M}\Omega \cdot \text{cm}$) was used for all sample preparations.

2.2. Experiment Methods

Typically, Fenton or Fenton-like reactions were conducted in a batch reactor using a 100 mL glass flask. Catechol was used as a model compound to evaluate the degradation efficiency of various reactors presently tested. For all degradation experiments, kept the volume of solution at 100 mL and the concentration of catechol at 10mM. The pH was adjusted using 0.1 M H_2SO_4 or 0.1 M NaOH. The batch solution was stirred throughout an experimental cycle at 200 rpm in the dark at 25°C. The degradation of catechol by classical Fenton and Fenton-like processes were compared. Effect of pH (3, 5, 7), Fe^{2+} concentration (0, 4 mM), Fe^{3+} concentration (0, 1, 2, 3, 4 mM), Ce^{3+} concentration (0, 1, 2, 3, 4 mM), H_2O_2 dosage (5, 8, 10, 20, 30 mM), reaction time (0, 2, 5, 8, 10, 20, 30, 60 min) were investigated. After each reaction time, 5 mL sample aliquots were syringe-filtered (0.22 μm membrane pore) into sampling tubes containing tert-butanol as $\bullet\text{OH}$ scavenger and reserved them for chemical analysis. Each batch sequence experiment was repeated five times, and the average value was taken as the final value. UV and mass spectrometric methods analyzed the chemical composition of the treated water. Characterization of free radical products generated by our $Fe^{3+}\text{-}Ce^{3+}\text{-}H_2O_2$ and classical Fenton-like processes were characterized by ESR spectroscopy using DMPO as a spin trap. The sludge generated from the process was separated by filtration and centrifugation. The resultant solid substrate was oven-dried at 110°C, and processed for surface characterization

by FTIR and XPS.

2.3. Analytical Methods

The solution pH was monitored by pH meter calibrated with pH 4.00, 6.86, and 9.00 buffer solutions (PHS-3C, REX, Shanghai). UV-vis Spectrophotometric procedures were used to determine catechol and H_2O_2 concentration by direct ($\lambda = 275.3 \text{ nm}$) and titanium oxalate ($\lambda = 400 \text{ nm}$) methods (UV 2600 Shimadzu, Japan). The total carbon content was measured by TOC/TN analyzer (Multi N/C 3100, Germany). IR spectral analysis was carried out in transmission mode by Fourier Transform Infrared Spectrometer (Nicolet 67, Thermo Nicolet, USA) in the range of 4000-500 cm^{-1} at the scan speed of 20 scan/min with 4 cm^{-1} resolution, using 1:10 sample: KBr pellets. The near-surface elemental composition and oxidation states of the sludge were determined by X-ray Photoelectron Spectrometer (XPS, ESCALAB250 Xi, Thermo, USA). Electron spin spectral analysis was carried out by electron paramagnetic resonance spectrometer (EPR/ESR Spectrometer, JEOL, JES-FA 200).

3. Results and Discussion

3.1. Influences of Experimental Conditions on the Degradation of Catechol

3.1.1. Effect of initial pH and different process

The effect of initial pH on the degradation of catechol by five different Fenton or Fenton-like processes was investigated with a different ratio of Fe^{2+} , Fe^{3+} and Ce^{3+} . Keeping the H_2O_2 concentration constant (20 mM), five different processes were selected including the $Ce^{3+}\text{-}H_2O_2$ Fenton-like process, the classical Fenton process, the $Fe^{3+}\text{-}H_2O_2$ Fenton-like process, the $Fe^{2+}\text{-}Ce^{3+}\text{-}H_2O_2$ Fenton-like process and the $Fe^{3+}\text{-}Ce^{3+}\text{-}H_2O_2$ Fenton-like process. The catechol degradation was monitored for each process at different pH = 3, 5, 7 respectively (Fig. 1). For the $Ce^{3+}\text{-}H_2O_2$ Fenton-like process, the efficiency of catechol degradation increases with the pH and the highest degradation of catechol is observed around

Fig. 1. Effect of pH on the catechol degradation by five different Fenton or Fenton like processes (Conc. $H_2O_2 = 20 \text{ mM}$).

16.7% in pH 7 reactor. Also, we observed higher catechol degradation rate in classical Fenton process when compared to the Ce^{3+} - H_2O_2 Fenton-like process. The addition of Ce^{3+} to classical Fenton or Fenton-like processes showed an increasing catalytic activity as pH grows from 3 to 7 where the efficiency of catechol degradation nearly doubled in the presence of Ce^{3+} at pH 7. Out of the reactors examined, the Fe^{3+} - Ce^{3+} - H_2O_2 process at pH 7 shows the highest catechol degradation ($\sim 97\%$). This process not only improves catechol degradation but also broadens the operational pH window to environmentally compatible values. We suggested when the solution pH increased from 3 to 7, the catalytic role played by Ce^{3+} becomes significant. In neutral solutions, both classical Fenton and Ce^{3+} - H_2O_2 Fenton-like processes produce $\bullet\text{OH}$ and $\text{OOH}\bullet/\text{O}_2\bullet$ radicals, which can degrade the catechol [23].

3.1.2. Effect of Fe^{3+} : Ce^{3+} ratio

The effect of Fe^{3+} : Ce^{3+} ratio on catechol degradation by Ce^{3+} - Fe^{3+} - H_2O_2 Fenton-like process was examined as a function of Fe^{3+} and Ce^{3+} concentration. As shown in Fig. 2(a), with the Ce^{3+} concentration increased from 0 to 2 mM, the catechol degradation has steadily increased, and reaching an optimal at 2 mM.

Fig. 2. The removal of catechol by $\text{Fe}^{3+}/\text{Ce}^{3+}$ Fenton-like process with different addition of Ce^{3+} or Fe^{3+} . (a) Ce^{3+} , (b) Fe^{3+} . (Conc. $\text{H}_2\text{O}_2 = 20$ mM).

After that, the degradation efficiency remains stable with a further increase of Ce^{3+} . Similarly, the catechol degradation by our Fenton-like process was also examined as a function of Fe^{3+} concentration, and the results are shown in Fig. 2b. With the increasing of Fe^{3+} , the removal of catechol increased reaching a maximal catechol degradation at 4 mM Fe^{3+} . Finally, we concluded $\text{Fe}^{3+}:\text{Ce}^{3+} = 2:1$ optimal ratio for maximum catechol degradation ($96.70\% \pm 0.12\%$). As can be seen, Ce^{3+} has a more significant effect than Fe^{3+} . The reason for this is likely to be the introduction of Ce^{3+} reinforces the $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox cycle, and the Fe^{2+} generated in situ can promote the Fenton process [24].

3.1.3. Effect of H_2O_2 concentration

Optimal H_2O_2 concentration required to maximize catechol degradation was also evaluated using Fe^{3+} - Ce^{3+} - H_2O_2 keeping $\text{Fe}^{3+}:\text{Ce}^{3+} = 2:1$ ratio. The results thus obtained within 60 min. are shown in Fig. 3. The degradation of catechol by our process is increased with the H_2O_2 concentration reaching an optimal value at 20 mM. When H_2O_2 concentration increases further, the degradation efficiency shows a mild decline due to the $\bullet\text{OH}$ quenching process. The H_2O_2 concentration reaches a steady state after within the first 20 min (Fig. S1). Therefore, we concluded that a typical reaction cycle is essentially completed within 20 min.

Fig. 3. The removal of catechol by Fe/Ce Fenton-like process with different addition of hydrogen peroxide. The H_2O_2 concentrations were 5, 8, 10, 20, and 30 mM, separately.

3.1.4. COD and TOC removal capacity by cerium-iron-based Fenton-like process

In the reaction condition, $\text{Fe}^{3+}:\text{Ce}^{3+}:\text{H}_2\text{O}_2 = 4:2:20$ and pH = 7, TOC and COD in the solution before after the reaction were determined. The reaction results are shown in Fig. 4. The removal performance of both TOC and COD in iron cerium-based Fenton for removal of catechol in solution is excellent. With the removal of TOC reaching 97.5% and COD reaching 94.2%.

Fig. 4. COD and TOC before and after the reaction (10 mM catechol, $\text{Fe}^{3+}:\text{Ce}^{3+}:\text{H}_2\text{O}_2=4 \text{ mM} : 2 \text{ mM} : 20 \text{ mM}$)

3.2. Reaction Mechanism and Degradation Path Analysis

3.2.1. Sediment characterization

FTIR and XPS spectroscopy characterizes the sludge created by our Fenton-like process. Fig. S2(b) shows the XPS survey scan showing the presence of Ce3d, O1s, C1s, and Fe2p peaks in the sludge sample. As in Fig. S2(b), the C1s band resolved into three peaks correspond to C-C (284.74 eV), C-O (286.3 eV), and C=O (288.55 eV) indicate catechol in solution. In agreement with IR data, the O1s band resolves as C-O (532.6 eV) and O-H (531.5 eV), which confirms the presence of water. It has been destroyed by the oxidation of the Fenton reaction and forms a precipitate under the action of coagulation precipitation. The Ce 3d band resolves into seven peaks (Fig. S2(d)). The peaks correspond to spin-orbital states $3d_{5/2}$, and $3d_{3/2}$ are labeled as V and U, respectively. The mixed oxidation states of cerium, viz. +3 and +4 are also present (901.2 eV and 882.5 eV) [25]. The interactions between the Ce3d orbitals result in rapid transitions between Ce^{3+} and Ce^{4+} . Fig. S2(e) shows the XPS spectrum of Fe 2p. The binding energies of 711.3 eV and 714 eV belong to the Fe $2p_{3/2}$ orbitals, but the binding energy of 724.8 eV belongs to the Fe $2p_{1/2}$ orbital [26]. Our data confirm the presence of Fe^{2+} and Fe^{3+} in the sludge.

We pay particular attention to determine sorbed catechol or other degraded products in the sludge. The IR bands marked in Figure S3 results due to trace degraded organic moieties. The characteristic broad IR band around $3300 - 2,500 \text{ cm}^{-1}$ is due to bending and stretching modes of water. However, the bands specific to catechol, viz. $3,375 \text{ cm}^{-1}$ due to phenolic -OH stretching, or $1,466$ and $1,360 \text{ cm}^{-1}$ bands due to aromatic ring vibrations, are absence confirming its complete mineralization by our method.

3.2.2. Free radical generation mechanism

To identify possible free radical products of the $\text{Ce}^{3+}\text{-Fe}^{3+}\text{-H}_2\text{O}_2$ Fenton-like reaction, we used electron spin resonance (ESR) method with DMPO spin trap. ESR experiments were performed in optimized $\text{Ce}^{3+}\text{-Fe}^{3+}\text{-H}_2\text{O}_2$ and $\text{Fe}^{3+}\text{-H}_2\text{O}_2$ Fenton-like processes. After five minutes, DMPO was added to scavenge $\bullet\text{OH}$ radical [27]. As shown in Fig. 5, four adsorption peaks correspond to $\bullet\text{OH}$ with an intensity 1:2:2:1 are observed in $\text{Fe}^{3+}\text{-Ce}^{3+}\text{-H}_2\text{O}_2$ Fenton-like process, while no evidence is found for the formation of $\bullet\text{OH}$ in

Fig. 5. ESR spectra of the $\text{Fe}^{3+}\text{-Ce}^{3+}\text{-H}_2\text{O}_2$ Fenton-like process and $\text{Fe}^{3+}\text{-H}_2\text{O}_2$ Fenton-like process.

$\text{Fe}^{3+}\text{-H}_2\text{O}_2$ process. This result confirms that Ce^{3+} acts synergistically with Fe^{3+} for $\bullet\text{OH}$ production.

Based on the data so far presented, we devised a degradation mechanism of catechol by our $\text{Fe}^{3+}\text{-Ce}^{3+}\text{-H}_2\text{O}_2$ Fenton-like process, as illustrated in Fig. 6. The Fe^{3+} is transformed into Fe^{2+} through the $\text{Ce}^{3+}/\text{Ce}^{4+}$ redox cycle. Afterward, the classical Fenton process is operative with H_2O_2 for the degradation of catechol into CO_2 and H_2O at neutral pH. To determine the most efficient radical out of $\bullet\text{OH}$, and $\text{HO}_2\bullet/\text{O}_2^{\bullet-}$, TBA and IPA were used as $\bullet\text{OH}$ quenchers, and chloroform was used as the $\text{HO}_2\bullet/\text{O}_2^{\bullet-}$ quencher [28] (Fig. S4). Our data confirm the efficiency of the $\bullet\text{OH}$ radical when compared to $\text{HO}_2\bullet/\text{O}_2^{\bullet-}$, and the also take part in the $\text{Ce}^{3+}\text{-Fe}^{3+}\text{-H}_2\text{O}_2$ Fenton-like reaction.

Fig. 6. $\text{Ce}^{3+}\text{-Fe}^{3+}\text{-H}_2\text{O}_2$ homogeneous Fenton-like process schematic. (a) Generation of Activated radicals. (b) Degradation of organic compounds.

3.2.3. Analysis of catechol degradation pathway

The composition of the catechol solution before and after treatment with our Fenton-like process was determined by GC-MS. Fig. 7(a) is the raw water sample of untreated catechol, and Fig. 7(b) is the water sample after the reaction. The catechol fragments into a large number of small molecules. The catechol degradation pathway is multi-facet [29]. A possible degradation pathway is postulated based on mass spectral data in Fig. 8.

On the basis of previous discussion, the process for the enhanced Fenton-like processes of cerium can be described as follows [23]:

As shown in reactions (1) to (5), the Ce^{3+} - H_2O_2 Fenton-like process triggers $\text{Ce}^{3+} \rightleftharpoons \text{Ce}^{4+}$ redox cycle, which also can quench $\bullet\text{OH}$ and $\text{OOH}\bullet$ radicals [30]. However, the complete elimination of $\bullet\text{OH}$ by this process is not possible due to the reversibility of the reactions [30, 31]. When compared to $\bullet\text{OH}$, $\text{OOH}\bullet$ radical is a weak oxidant, and the production of $\text{OOH}\bullet$ is larger than $\bullet\text{OH}$ by $\text{Ce}^{3+}/\text{H}_2\text{O}_2$ at neutral pH [32]. $\text{OOH}\bullet$ radical shows poor ability to degrade organic compounds [33]. Therefore, the standalone Ce^{3+} - H_2O_2 Fenton-like process results in inefficient degradation of catechol, particularly at acidic conditions.

Further, as shown in reaction (6), the Ce^{4+} to Ce^{3+} conversion is also thermodynamically feasible ($\text{Fe}^{3+}/\text{Fe}^{2+}$ 0.77 V; $\text{Ce}^{4+}/\text{Ce}^{3+}$ 1.44V). Therefore, it appears that at acidic pH, the role of Ce^{3+} in Fenton or Fenton-like processes are not significant. As solution pH increases, the catalytic role played by Ce^{3+} becomes significant. In neutral solutions, dual-mode Fenton-like processes, namely classical Fenton and Ce^{3+} - H_2O_2 Fenton-like processes, seem active.

Fig. 7. Comparative GC-MS Diagram of Catechol solution (a) before and (b) after reaction.

Fig. 8. Schematic diagram of the reaction mechanism of the oxidation of catechol.

Herein, both processes produce $\bullet\text{OH}$ and $\text{OOH}\bullet/\text{O}_2\bullet$ radicals. The $\bullet\text{OH}$ radical is active for catechol degradation. Although $\text{OOH}\bullet/\text{O}_2\bullet$ is a weak radical for the degradation of catechol, it can readily convert $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ by Ce^{3+} generating in situ Fe^{2+} for the Fenton process.

4. Conclusions

We have developed a homogeneous Fenton-like process using Fe^{3+} - Ce^{3+} - H_2O_2 to destruct organic pollutants efficiently. Our process operates in a wide pH range (3 to 7) with the highest efficiency for catechol degradation at pH 7. The Fe^{2+} required for the Fenton process is generated in situ, which minimizes $\bullet\text{OH}$ and Fe^{2+} recombination. Under the optimal conditions: pH = 7, Fe^{3+} : Ce^{3+} : H_2O_2 = 4 mM: 2 mM: 20 mM, almost 97% of 10 mM catechol can be destructed. The wide operation pH window, minimal contaminants in solution, and high efficiency offer our Fenton-like process a promise in the advanced water treatment industry.

Acknowledgments

The authors acknowledge the financial support from National Basic Research Program of China (Grant No. 2019YFC0408500), National Natural Science Foundation of China (Grant No. 21777164), Fundamental Research Funds for the Central Universities (Grant No. PA2019GDQT0019), Changfeng County-Hefei University of Technology Industrial Innovation Guidance Fund Key Project, and Suzhou Science and Technology Plan Project (2019056).

Author Contributions

X.C. (Professor) contributed to the conception of the study and the data analyses, and revised the manuscript. X.L. (Ph.D. student) performed the experiment and wrote the manuscript. H.W. (M.S. student) performed the experiment and contributed significantly to manuscript preparation. K.C. (Professor) contributed to the data analyses with constructive discussions. R.W. (Professor) revised the manuscript. S.H. (Associate Professor) contributed to the data analyses with constructive discussions. G.L. (Engineer) contributed to the data analyses. J.P. (Engineer) contributed to the data analyses. K.Z. (Engineer) contributed to the data analyses.

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