Solar Boosting Pollutant Removal plus Hydrogen Production by Lifting-Heat and Lowering-Potential Chemical Synergy

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ABSTRACT: Solar-boosted oxidation plus hydrogen production for pollutant removal in wastewater, driven by a high thermal and low-potential electrochemical combination, is facilitated and demonstrated from theory to experiments. One sun fully offers both thermal and electrical energy powered thermo- and electrochemistry for pollutant oxidation. Solar thermal action provides high temperatures for the activation of the pollutant molecules to gear up for solar-driven electrochemical oxidation. Taking wastewater containing phenol as an example, the cyclic voltammetry (CV) curves display two redox processes at less than 100 °C, while only one redox process of single oxidation of phenol appears at more than 100 °C. The oxidation of phenol is accompanied by an efficient evolution of hydrogen, in which the yield of 0.627 mL at 30 °C is increased to 2.294 mL at 210 °C. The phenol removal is enhanced to 80.50% at 210 °C. Tracking the reaction progress shows that small molecular organic acids are detected as the only intermediate at the high temperatures, which suggests the easy realization of full mineralization. The kinetic reaction of the phenol oxidation is fitted to the first order with an increase of the rate constant of 10 times compared with that at low temperatures. Solar engineering of oxidation of organic pollutants not only solves the issue of energy demand for the tough wastewater treatment but also realizes fast and efficient oxidation of organic pollutants. This study opens up new avenues to achieve solar wastewater treatment and simultaneous hydrogen production.

1. INTRODUCTION

The interdependence of water and energy is a growing concern, as water resources become scarcer worldwide. Water resources have been in a state of mild water shortage for a long time, while water pollution has accelerated the process of water scarcity. Wastewater is a critical component of the water cycle; however, the types of contaminants discharged in wastewater and sewage are becoming diverse. Of particular concern are “organic contaminants”, newly developed compounds with novel negative effects on the environment and human health. Aromatic organic contaminants, containing one or more unsaturated cyclic carbon chains in the whole molecule, pose a great threat to aquatic life due to biomagnifications and bioaccumulation. Their negative biological impact has motivated governments to introduce legislation that prescribes and limits the emission of pollutants.

Many technologies have been developed for the treatment of organic wastewater. The pollutants can be removed using physical technologies such as natural forces, physical barriers, etc. Among physical technologies, membrane separation is considered to be the most efficient methods for oil and water separation because of its simple operation process. Biological technologies reproduce the natural degradation process, enhancing the removal of contaminants and the stability of sludge. Chemical technologies have been successfully applied for disinfecting and removing heavy metals. In terms of the removal of organic pollutants, advanced oxidation processes (AOPs) have been proved to be highly efficient for removing compounds. Numerous AOPs, including electrochemical oxidation, have been applied for generating hydroxyl radicals (•OH) to transform the organic matter into various inorganic minerals, water, and carbon dioxide. However, all these technologies demand a huge energy supply, which greatly constrained their industrial applications. Therefore, co-optimizing interdependent systems is necessary to understand the impact of energy on wastewater treatment.

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The goal of co-optimizing energy and wastewater treatment is to exploit potential investment and operational cost savings arising from high utilization of solar energy sources in wastewater treatment.10−12 In this paper, based on AOP theory and experiments, we propose a framework to identify the optimal investment mix for a co-optimized solar power system and apply it in AOP wastewater treatment. In terms of the solar power system, solar heat was used to lower the electropotential. As far as the solar spectrum distribution and the existing technologies for solar conversion to the other energy flux are concerned, the application of a substantial amount of solar heat is favorable for the enhancement of solar utilization. As stated in chemical thermodynamics, the electricity consumption in endothermic electrolysis can be decreased through increasing the solar thermal power. Coupling of the solar thermal and electric effects induces thermochemistry and electrochemistry for promoting the chemical rate and selectivity. The process has brought new hopes in the development of AOPs due to its considerably clean, renewable, and low-price method.13,14 One improvement toward AOPs is adjusting the energy matching of solar energy and organic compounds and also improve thermal efficiency, achieving full-scale cascade utilization of solar energy.15,16 Another improvement is utilizing infrared and visible spectra of solar radiation to improve the thermal effect on electrochemical processes. The single thermal oxidation of organic pollutants requires high temperatures, while single electro-oxidation of organic pollutants is accompanied by a high potential demand and inevitable water splitting. Therefore, coupling of thermo- and electrochemistry will greatly improve the efficiency of organic wastewater treatment. The conversion of solar energy to hydrogen energy has also attracted much attention in recent years.17−20 In our research, the oxidation of organic pollutants, driven by solar energy, can produce hydrogen products, which enable the conversion between renewable energy sources.
Phenol is highly poisonous and carcinogenic in all ecosystems, which has been considered models in many studies of AOP degradation.\textsuperscript{21−23} Generally speaking, purification of wastewater containing phenol is not easy, due to the high stability of small aromatic hydrocarbons. In this paper, we studied the oxidation of organic wastewater using solar energy driven by a high-heat and low-potential electrochemical combination. As shown in Figure 1, the solar thermal effect, energy matching principle, cascade control of coupling, and hydrogen production mechanism were studied. The notable benefits of the solar-boosted process are the ability to efficiently convert phenol to harmless products and the fact that it involves solar energy demand and hydrogen energy production that are environmentally friendly and safe to handle.

2. EXPERIMENTAL SECTIONS

2.1. Chemicals and Materials. Phenol was received from KERMEL Chemical Co. of Tianjin. The dimensionally stable anode (DSA) Ti/SnO\textsubscript{2}−Sb\textsubscript{2}O\textsubscript{5} was purchased from Shanghai Precision Instrument Co., Ltd. Maleic acid, benzenediol, hydroquinone, and formic acid were used as received from Damao chemical of Tianjin. All chemicals were used as received without further purification. The aqueous solution is prepared with distilled water.

2.2. Solar-Boosted Pollutant Removal. 2.2.1. Experimental Setup. As shown in Figure 2, the electrical energy acquired is provided by silicon-based solar panels, and a DC transformer is used to adjust the voltage of the solar panel. The heat is provided by a point-focusing solar concentrator, and the reaction temperature is kept constant by adjusting the position of the spotting point and the flow rate of the oil bath. A thermocouple is inserted in the control cabinet to monitor the temperature in the reactor, and a pressure gauge is used to monitor the reaction pressure. The experiments of phenol oxidation were carried out in a cylindrical single-compartment cell, and the effective volume for the reactor is 100 mL, as shown in Figure 2. A poly(tetrafluoroethylene) (PTFE) O-ring is used to seal the connection between the cap and body of the reactor. The Ti/SnO\textsubscript{2}−Sb\textsubscript{2}O\textsubscript{5} anode had a surface of 2 cm × 2 cm, the nickel foil cathode had the same area, and the gap between the electrodes was 2 cm. For a test, the sample (phenol, 500 mg L\textsuperscript{−1}) was heated to 90 °C and was oxidized by a constant current intensity of 50 mA for 60 min. Sodium sulfate at 0.05 mol L\textsuperscript{−1} was selected as the electrolyte.

2.2.2. Analysis. The concentration of phenol was determined using an UV spectroscopic instrument (UV-1700, SHIMADZU). The detection wavelength was 270 nm. The COD\textsubscript{Cr} of organic compounds was determined by the potassium dichromate method (GB11914-1989). The reactant, intermediate, and products were monitored using high-performance liquid chromatography (LC-2010A HT) with a C18 reverse separation column (150 mm × 4.60 mm). The flow rate is 0.8 mL min\textsuperscript{−1}, the column temperature is 25 °C,
and the column pressure is 5.1 MPa. A sample of 10 μL was injected into the HPLC with methanol/water (v/v = 3:7) as the mobile phase. The wavelength of the UV detector was set at 254 nm. The compositions were identified by comparison with the retention time of pure samples. Cyclic voltammetry is used to determine the redox process of organic compounds, using the 1000B/W electrochemical workstation.

The gas products of phenol oxidation were analyzed by gas chromatography with separation on a 12-X gas chromatographic packed column with an inner diameter of 0.53 mm, a column length of 12 m, a column temperature of 50 °C, and a detector temperature of 170 °C.

According to the quantitative analysis of CO$_2$, the current efficiency can be calculated by the following formula.

$$\eta = \frac{m'}{m} \times 100\% = \frac{m'}{K \cdot I \cdot t} \times 100\%$$  \hspace{1cm} (1)

where $n$ is the number of electrons transferred; $\eta$ is the current efficiency, %; $m'$ is the actual quality of carbon dioxide, g; $m$ is the theoretical quality of carbon dioxide, g; $I$ is the current intensity, A; $t$ is the oxidation time, s; and $K$ is the electrochemical equivalent, g/C.

3. RESULTS AND DISCUSSIONS

3.1. Theoretical Study of Phenol Oxidation in the Solar Boosting System. The oxidation of phenol is completed by two half-cell reactions. As shown in eq 2, anodic oxidation was proved to produce intermediates and carbon dioxide. With the transfer of electrons, cathodic reduction (eq 3) undergoes a hydrogen evolution. The full-cell reaction of phenol oxidation is shown in eq 4.

The oxidation of phenol is as follows:

**Anodic reaction:** $\text{C}_6\text{H}_5\text{OH}(1) + 11\text{H}_2\text{O}(1)$

$\rightarrow 6\text{CO}_2(g) + 28\text{H}^+(1) + 28\text{e}^-$  \hspace{1cm} (2)

**Cathodic reaction:** $28\text{H}^+(1) + 28\text{e}^- \rightarrow 14\text{H}_2(g)$  \hspace{1cm} (3)

**Cell reaction:** $\text{C}_6\text{H}_5\text{OH}(1) + 11\text{H}_2\text{O}(1)$

$\rightarrow 6\text{CO}_2(g) + 14\text{H}_2(g)$  \hspace{1cm} (4)
The oxidation of phenol is common endothermic electrolysis, for example, \( \Delta r H_m^\Theta (298 \text{ K}) = 947.9 \text{ kJ mol}^{-1} \). By Kirchhoff’s rule, an increase in temperature can reduce the heat of the reaction, which in turn reduces the electrical energy driving the reaction. Such processes can be described by \( \Delta C_p \) (heat capacity at constant pressure), \( \Delta r S_m^\Theta \) (entropy), \( \Delta r H_m^\Theta \) (enthalpy), and \( \Delta r G_m^\Theta \) (Gibbs free energy). The thermodynamic data for phenol(l), H\(_2\)O(l), CO\(_2\) (g), and H\(_2\) (g) can be calculated from thermodynamic data sets, such as the NIST condensed phase and fluid property data. The results of thermodynamic calculation are shown in Table 1.

As shown in Table 1, the enthalpy (\( \Delta r H_m^\Theta \)) and the Gibbs free energy of phenol oxidation decrease with the increase of temperature from 25 to 210 °C. According to chemical thermodynamics, the theoretical potential of phenol electrolysis decreases from 0.109 to −0.035 V. The cyclic voltammetry data of phenol oxidation were measured with a scanning rate of 10 mV\( \text{s}^{-1} \) at different temperatures. The scanning potential ranged from −0.5 to 1.5 V, and the concentration of phenol was 500 mg L\(^{-1}\). Distilled water was used as a solvent with a supporting electrolyte of 0.25 mol L\(^{-1}\) Na\(_2\)SO\(_4\). The DSA electrodes (Ti/(SnO\(_2\) and Sb\(_2\)O\(_5\))) with an area of 2 cm \( \times \) 2 cm served as electrodes, and quasi-Ag was used as the reference electrode.

![Figure 3](https://via.placeholder.com/150)

**Figure 3.** Cyclic voltammogram of phenol oxidation at 90 °C. The results indicate that an oxidation peak is detectable at 0.7 V, which is attributed to the direct electrochemical oxidation of phenol to intermediates. The oxidation peak of 1.5 V was attributed to the oxidation of H\(_2\)O to O\(_2\). A reduction peak around −0.3 V is attributed to the reduction of intermediates to phenol. The reduction peak of −0.5 V is attributed to the reduction of H\(_2\)O to H\(_2\). The asymmetric redox current shows that the electrochemical oxidation of phenol is an irreversible redox process.

As seen from the cyclic voltammetry data at different temperatures in Figure 4, it is significant to note that the peak potential of phenol oxidation is 0.96 V at 30 °C, 0.84 V at 90 °C, 0.79 V at 150 °C, and 0.43 V at 210 °C. The potential of phenol oxidation decreased significantly from 0.96 to 0.43V with increasing temperature, and there was almost no reduction peak when the temperature was more than 100 °C, which is attributed to the decrease in activation energy and increase in reversibility.

**3.2.2. Heat-Dependent Removal Rate of Organic Contaminants.** Figure 5 shows that the removal rates of phenol can reach 12.3, 37.8, 69.8, and 80.5% at 30, 90, 150, and 210 °C, respectively, which reveal that the removal of phenol is much more easily realized by a high thermal and low-potential electrochemical combination.

As shown in Figure 6, the current efficiencies were 5.43, 21.18, 29.37, and 44.16% at 30, 90, 150, and 210 °C, respectively. It is proved that the thermal effect can not only...
improve the oxidation rate but also improve electrochemical efficiency.

4. MECHANISM OF SOLAR-BOOSTED REMOVAL OF POLLUTANTS

4.1. Kinetics of Organic Contaminant Oxidation. The concentrations of phenol in the solar thermo/electrochemical process are shown in Table 2.

Table 2. Concentrations of Aqueous Phenol

| T (°C) | C_{0\text{max}} (mg·L^{-1}) | C_{2\text{min}} (mg·L^{-1}) | C_{4\text{min}} (mg·L^{-1}) | C_{6\text{min}} (mg·L^{-1}) | C_{10\text{min}} (mg·L^{-1}) |
|-------|------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| 30    | 500                          | 476                          | 452                          | 436                          | 415                          | 394                          |
| 90    | 500                          | 435                          | 390                          | 338                          | 300                          | 261                          |
| 150   | 500                          | 376                          | 274                          | 185                          | 131                          | 102                          |
| 210   | 500                          | 331                          | 223                          | 147                          | 97                           | 74                           |

According to the rate equation of the overall reaction, the oxidation of phenol can be expressed as eq 5.

\[
r = k[C_6H_5OH][H_2O]^p
\]  

\[r = k[C_6H_5OH]^q\]  

As the concentration of water in the reaction system was changed slightly, \([H_2O]^p\) can be regarded as a constant. The rate equation of phenol oxidation is only related to the concentration of the reactant phenol. The equation can be simplified to eq 6.

\[
r = k[C_6H_5OH]^q
\]  

The trial method can be used to obtain the coefficients \(k'\) and \(\alpha\), the sum of the residuals squared, and the standard errors of the kinetic constants.

Table 3. Kinetic Equation of the First-Order Reaction of Phenol Oxidation

| T (°C) | kinetic equation | \(R^2\) | k/min^{-1} |
|--------|-----------------|---------|------------|
| 30     | \(\ln(C_0/C_t) = 0.00143t + 0.00234\) | 0.997   | 0.00143    |
| 90     | \(\ln(C_0/C_t) = 0.00644t + 0.00171\) | 0.998   | 0.00644    |
| 150    | \(\ln(C_0/C_t) = 0.01643t - 0.02024\) | 0.996   | 0.01643    |
| 210    | \(\ln(C_0/C_t) = 0.01941t + 0.02578\) | 0.995   | 0.01941    |

Figure 7. Plot of \(t\) and \(\ln(C_0/C_t)\) at 30 °C (a), 90 °C (b), 150 °C (c), and 210 °C (d).
The values of $C_t$ and $t$ at different temperatures were substituted into the rate equations of different order reactions. The results show that the oxidation process is in accordance with the rate equation of the first-order reaction. The first-order kinetic curves at different temperatures were obtained by plotting $t$ with $\ln \left( \frac{C_0}{C_t} \right)$, as shown in Figure 7a−d.

Figure 7 shows the linear relationship between $\ln \left( \frac{C_0}{C_t} \right)$ and reaction time $t$. The first-order kinetic equation of phenol oxidation is obtained as shown in Table 3.

The kinetic constant $k$ increases with increasing temperature. The results in Table 3 show that the kinetic constant at 210 °C is 13.5 times that at 30 °C. The relationship of $\ln k$ and $1/T$ is shown in Figure 8.

According to the Arrhenius equation

$$\ln k = -\frac{E_a}{RT} + \ln A$$

where $k$ is the rate constant, $E_a$ is the activation energy, $T$ is the temperature, and $A$ is the prefactor, $R = 8.314$ J mol$^{-1}$K$^{-1}$. Equation 8 can be obtained from Figure 8.

$$k = 9.2534e^{-23.56x10^3/(RT)}$$

4.2. Intermediates and Proposed Reaction Pathway. Figure 9a shows a UV spectrogram of phenol oxidation at 30 °C. As the characteristic peaks of phenol ($\lambda_{max}$ 220, 270 nm) decrease, two new absorptions appear in the two wavelength bands of 273−289 and 290−310 nm. Compared with the absorptions of phenol, the two new absorptions move in the long-wave direction, which indicates the growth of the $\pi \rightarrow \pi^*$ conjugate system. Benzenediol, benzoquinone, maleic acid, formic acid, and oxalic acid were detected by high-performance liquid chromatography (HPLC). Even after electrolysis for 240 min, organic molecules have not been completely oxidized at 30 °C. Figure 9b shows a UV spectrogram of phenol oxidation at 210 °C. New absorption peaks appear in the wavelength band of 230−265 nm and then disappear, which indicate the shortening of the $\pi \rightarrow \pi^*$ conjugate system. The results of HPLC showed that only one peak was detected in the process of phenol oxidation, corresponding to maleic acid. Gas products of phenol oxidation were analyzed by gas chromatography, as shown in Table 4.

Table 4 shows the gas products of phenol oxidation. The presence of CO$_2$ indicates that portions of phenols were oxidized completely to carbon dioxide, and the volume of CO$_2$ increases with the increase of temperature. The volume of CO$_2$ is 0.081 mL at 30 °C, 0.31 mL at 90 °C, 0.48 mL at 150 °C, and 0.65 mL at 210 °C, which indicates that the production rate of carbon dioxide increases with increasing temperature. The precipitation of H$_2$ indicates the existence of hydrogen evolution on the cathode surface, which proved that hydrogen energy can be obtained while dealing with organic pollutants with a high thermal and low-potential electrochemical combination.
Considering the UV spectrum, HPLC, and gas chromatography, the phenol oxidation under different thermal effects was deduced as shown in Figure 10.

The oxidation of phenol to CO$_2$ undergoes either an indirect production of intermediates (B, C, or D) or direct mineralization. The oxidation of phenol is generally matched with an indirect conversion by the following coreaction at the low temperature: phenol $\rightarrow$ hydroquinone/hydroquinone $\rightarrow$ maleic acid $\rightarrow$ CO$_2$. The appearance of benzoquinone and catechol indicates that the benzene ring has undergone a hydroxylation reaction, and then, a series of organic substances, even CO$_2$ and water, are obtained. However, the oxidation of phenol to CO$_2$ undergoes direct conversion by the following coreaction at the high temperature: phenol $\rightarrow$ maleic acid $\rightarrow$ CO$_2$. The direct conversion of phenol to maleic acid indicated that the phenol molecules collide with the anode and lose electrons; the removal of an electron from a bonding orbital will weaken the C–C chemical bond. This can lead to the loss of a substituent or rearrangement of phenol molecules, followed by the generation of maleic acid or carbon dioxide. Compared with the low-temperature process, this process is fast and efficient, which opens up a wider application range of the solar thermo-electrochemical process. Corresponding to the oxidation of phenol, the reduction of water was induced on the surface of the cathode, which provides a new way for the production of hydrogen energy. The combination of solar energy and hydrogen energy will be a new way for future energy development.

5. CONCLUSIONS

Solar-boosted oxidations of pollutants plus hydrogen production were studied concerning theoretical and methodological problems, which utilized infrared and visible spectra of solar radiation energy to improve the thermal effect on electrochemical processes. The removal rate of phenol can reach 80.5% at 210 °C, which is improved significantly relative to

| Table 4. Gas Products of Phenol Oxidation ($I = 50$ mA) |
|-----------------------------------------------|
| temperature (°C) | total gas volume (mL) | volume percentage of gases (%) | volume of generated gas (mL) | the quality of CO$_2$ (g) |
|------------------|----------------------|--------------------------------|----------------------------|--------------------------|
|                  |                      | N$_2$ | O$_2$ | H$_2$ | CO$_2$ | H$_2$ | CO$_2$ |                        |
| 30               | 99.84                | 78.65 | 20.641 | 0.628 | 0.081 | 0.627 | 0.081 | 1.591 $\times 10^{-4}$ |
| 90               | 100.21               | 77.81 | 20.095 | 1.78  | 0.315 | 1.781 | 0.316 | 6.207 $\times 10^{-4}$ |
| 150              | 101.36               | 77.92 | 19.728 | 1.92  | 0.432 | 1.946 | 0.438 | 8.604 $\times 10^{-4}$ |
| 210              | 102.75               | 77.89 | 19.239 | 2.23  | 0.641 | 2.294 | 0.659 | 1.294 $\times 10^{-3}$ |

Figure 10. Oxidation routes of phenol under different thermal effects.
that of the low-temperature process, 12.3% at 30 °C. The high thermal and low-potential electrochemical combination makes the reaction rate increase dramatically from 0.00143 at 30 °C to 0.01941 at 210 °C, which is according to the Arrhenius equation. Solar-boostered oxidations of phenol realized connecting sustainable energy with wastewater treatment, which provides a new way for the development of the two fields.

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**Notes**

The authors declare no competing financial interest.

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