

Analysis of the Effect of Erythromycin Wastewater Degradation by Fenton Method

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Erythromycin wastewater is a high chroma and concentration organic wastewater containing difficult biodegradable and more biologically toxic materials. In this paper, using Fenton method to pretreat erythromycin wastewater, analyzed the chemical compositions changes of wastewater before and after degradation. The experimental results showed that after treatment by Fenton method, removal rate of COD of wastewater was 40.88 %, sixteen-membered ring of erythromycin A was interrupted, macromolecules were degraded into eight kinds of smaller molecules, these substances caused high COD value and poor biodegradability of the effluent. This study aimed at providing certain theoretical basis for searching efficient treatment methods of erythromycin wastewater.

Key Words: Fenton method, Erythromycin wastewater, Degradation.

INTRODUCTION

Erythromycin is a kind of sixteen-membered ring macrolide antibiotics generated by *Streptomyces erythreus*, with broad spectrum antimicrobial effect, clinical application is very wide¹. The main component of erythromycin is erythromycin A (EA)². Molecular formula of erythromycin A is C₃₇H₆₇NO₁₃, molecular weight is 733.93, its molecular structure as shown in Fig. 1³.

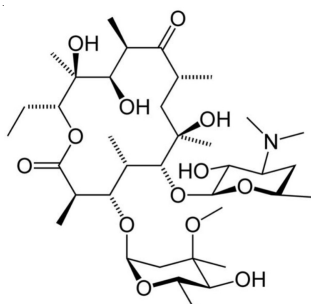


Fig. 1. Structure of erythromycin A

Wastewater produced in the production of erythromycin is of great quantity, high content of organic pollutants and

suspended solids, high pH changes, alkalinity, colour and water quality variation, *etc.*⁴. Because of bad biodegradability, the wastewater is difficult to drainage standard directly after treating by biochemical method⁵. So finding of erythromycin wastewater pretreatment method is needed based on the biochemical method. In this paper, Fenton method is adopted to erythromycin wastewater pretreatment, analysis of the changes of chemical composition before and after erythromycin wastewater degradation, providing certain theoretical basis for erythromycin wastewater treatment.

EXPERIMENTAL

Wastewater sources: Production workshop of erythromycin from Anyang Jiuzhou pharmaceutical factory in China.

Chemicals: Green copperas, hydrogen peroxide, sulfuric acid, sodium hydroxide, polyacrylamide (PAM), potassium dichromate, ferrous ammonium sulphate, sulphate mercury, silver sulphate and *o*-phenanthroline, all are analytical pure; deionized water.

Fenton method: 1000 mL wastewater was diluted to 2500 mL for Fenton experiments, COD_{Cr} 521 mg/L, experimental method and results were shown in Table-1.

TABLE-1
EXPERIMENTAL CONDITIONS AND RESULTS OF FENTON METHOD

Project	H ₂ O ₂ (mL/L)	10 % FeSO ₄ (mL/L)	pH value after dosing	Reaction time (h)	Adding liquid alkali (mL/L)	Aeration time (min)	1 % PAM (mL/L)	Effluent COD _{Cr}
Parameter	1.0	2.0	2.66	1	3	20	2	308

COD detection of water samples: On the basis of "Water quality-Determination of the chemical oxygen demand-potassium dichromate method" (GB11914 - 89).

Ultraviolet visible spectroscopy: The diluted raw wastewater and Fenton effluent were scanning in the range of 190-410 nm wavelength with Agilent 8453 UV spectrophotometer (Agilent Technologies Inc.), respectively.

Mass spectrometry⁶: The diluted raw water and Fenton effluent were analyzed by Agilent 1100 series LC/MSD Trap, Nebulizer: 6.0 psi, dry gas: 6.0 psi, temp.: 300 °C.

High performance liquid chromatography (HPLC)⁷: The diluted raw wastewater and Fenton effluent were analyzed by Waters 2487 high performance liquid chromatography. Stationary phase: RPC₁₈ column (5 μm, 250 mm × 4.6 mm), column temperature: 25 °C; mobile phase: methanol-acetonitrile = 1:1 (v/v); flow rate: 1.0 mL/min; injection volume: 40 μL; evaporative light scattering detector (ELSD).

RESULTS AND DISCUSSION

UV-visible spectral analysis of erythromycin A wastewater: COD_{Cr} of raw wastewater was 521 mg/L, COD_{Cr} of Fenton effluent was 308 mg/L (COD removal efficiency of 40.88 %). In Fig. 2, the raw wastewater had a strong absorption peak at 190-240 nm, this was because the erythromycin A molecule contained ring lactone (-COO-) and carbonyl group (-CO-), meanwhile existed the auxochrome of -OH and -O-. After Fenton treatment refractory materials of high content had strong absorption peak only at 190-220 nm, which explained it still contained ester or carboxyl group in molecules formed by degradation and no absorption at 220-240 nm, which explained sixteen-membered ring of erythromycin A was interrupted, causing auxochrome -OH and -O- out of action.

Mass spectral analysis of erythromycin A wastewater: From Figs. 3 and 4, it clearly showed that the high-intensity peak of m/z 743.7 was [M + 1]⁺ molecular ion peak of erythromycin A, this peak disappeared after Fenton treatment, indicating that erythromycin A molecules had been completely degraded. In mass spectra of effluent through Fenton treatment there were still two intensity peaks of m/z 579.2 and 301.0, indicating that after degradation it still had refractory macromolecular substances, which explained high COD value of erythromycin wastewater after Fenton oxidation.

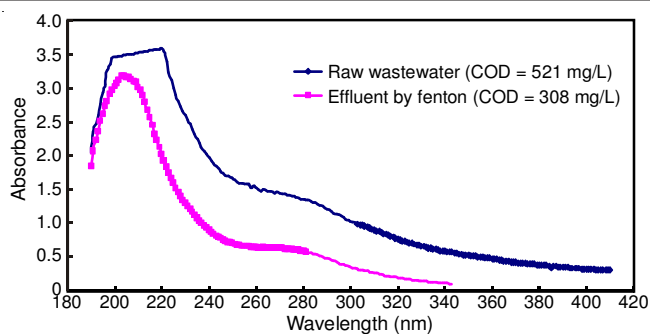


Fig. 2. UV-visible spectra changes of wastewater

HPLC spectral analysis of erythromycin A wastewater:

From Figs. 5 and 6, it showed that in HPLC spectrum of erythromycin raw wastewater it occurred a peak at 0.315 min which was the absorption peak of erythromycin A molecule, after Fenton treatment it appeared eight peaks in the spectrum, meanwhile the peak at 0.315 min had disappeared, illustrating after Fenton treatment erythromycin A molecules were degraded to eight smaller molecular substances, not fully degradation of water and carbon dioxide, it also explained after Fenton oxidation the COD value of erythromycin wastewater was still high. In next study we will separate and purify eight substances by preparative liquid chromatography for nuclear magnetic resonance experiment, determining the detailed chemical structure of each degradation products.

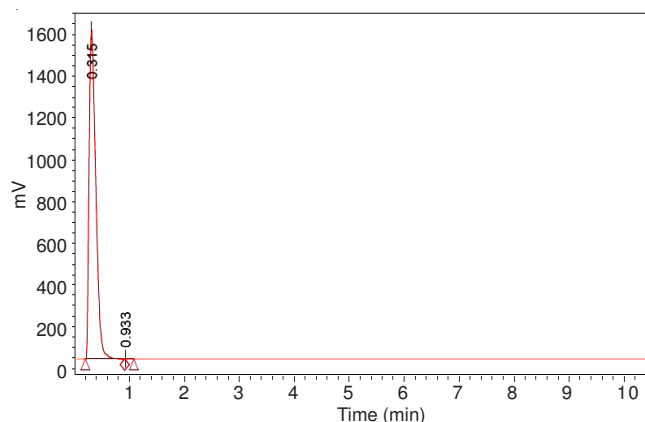


Fig. 5. HPLC spectrum of erythromycin A raw wastewater

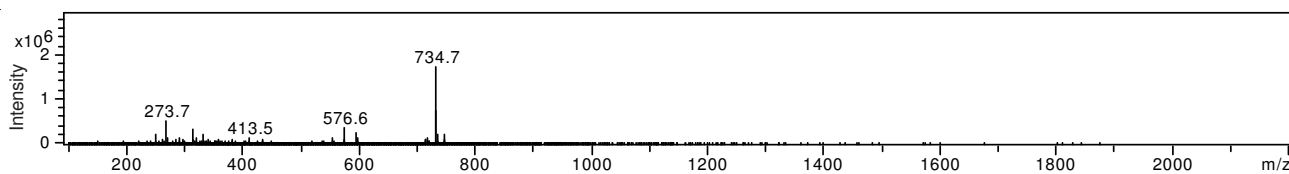


Fig. 3. Mass spectrum of erythromycin A raw wastewater

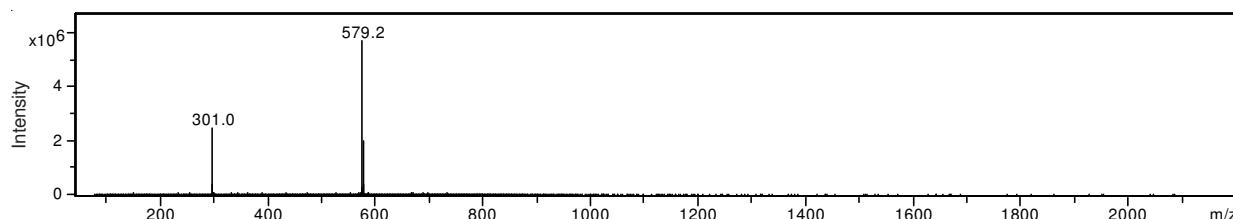


Fig. 4. Mass spectrum of Fenton effluent

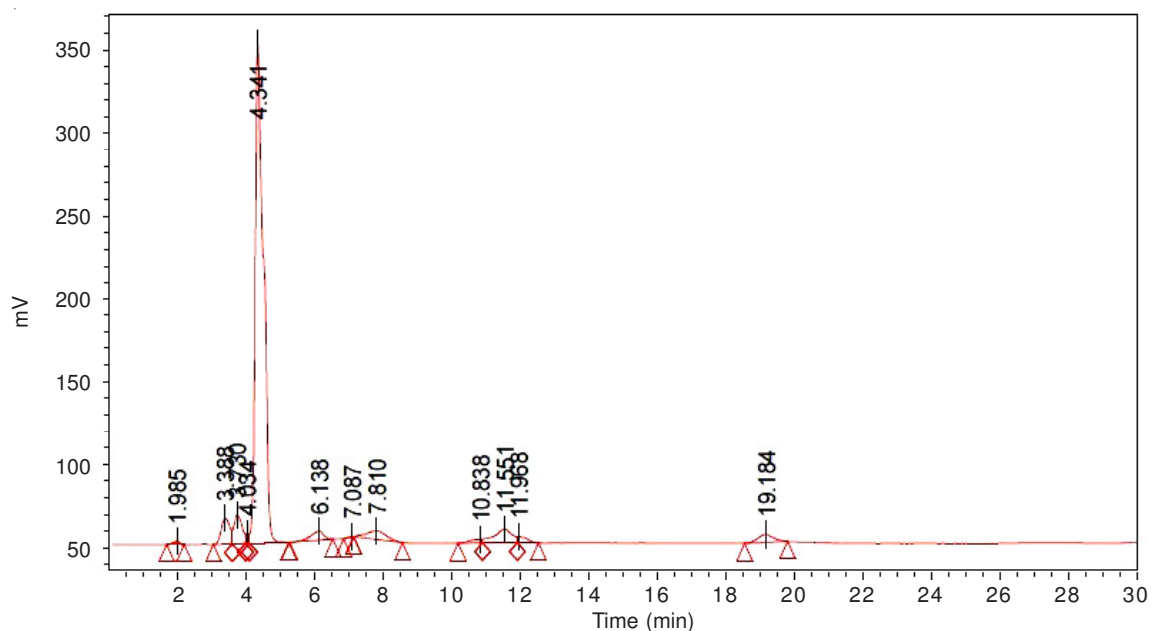


Fig. 6. HPLC spectrum of Fenton effluent

Conclusion

After Fenton treatment of erythromycin wastewater, sixteen-membered ring of erythromycin A molecule is interrupted, macromolecules are degraded into eight kinds of smaller molecules, these substances cause COD value of effluent still on the high side, biodegradability still poor. In next study we will use preparative liquid chromatography to collect each peak ingredients for nuclear magnetic resonance experiment, determining the detailed chemical structure of degradation products, in order to providing certain theoretical basis for finding efficient methods of erythromycin wastewater treatment.

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