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METHOD OF CORRELATION COEFFICIENT OPTIMIZATION USED IN UV-VIS SPECTROPHOTOMETRIC ANALYSIS FOR EFFLUENT IN CATALYTIC OZONATION**

Jing Feng [1,2], Honglin Chen [2*], Xiaoming Zhang [2]

[1] *Xihua University, Chengdu, 610039, Sichuan Province, China*
[2] *Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences,*
Chengdu, 610041, Sichuan Province, China; e-mail: hlchensubmission@yahoo.com

A wavelength selection method for spectrophotometric analysis, named correlation coefficient optimization (CCO), was employed for reagent-free analysis of organics (humic acid) in real sewage. The modeling set of CCO uses the effluent in the ozonation process of humic acid (HA) solution. In order to verify the relationship between HA concentration and absorbance at the selected wavelength, HA solutions with different mass concentrations were prepared as a validation set. The study showed that the absorbance at 300 nm could be a good quantitative indication of HA concentration. In addition, the absorbance at 300 nm was applied to analyze the HA concentration in the ozonation process. The decomposition of HA fits the pseudo-first-order kinetic model and has a linear relationship with pH and $(T - 20)^2$ (T is reaction temperature).

Keywords: *humic acid, UV-vis spectrophotometry, correlation coefficient optimization, regression analysis.*

МЕТОД ОПТИМИЗАЦИИ КОЭФФИЦИЕНТА КОРРЕЛЯЦИИ ДЛЯ СПЕКТРОФОТОМЕТРИЧЕСКОГО АНАЛИЗА СТОЧНЫХ ВОД ПРИ КАТАЛИТИЧЕСКОМ ОЗОНИРОВАНИИ

J. Feng [1,2], H. Chen [2*], X. Zhang [2]

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[1] *Университет Сихуа, Чэнду, провинция Сычуань, Китай*
[2] *Институт органической химии Чэнду Китайской АН,*
Чэнду, 610041, провинция Сычуань, Китай; e-mail: hlchensubmission@yahoo.com

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Для безреагентного спектрофотометрического анализа органических веществ (гуминовой кислоты) в сточных водах рабочая длина волны выбирается так называемым методом оптимизации коэффициента корреляции. Модельный набор оптимизированных коэффициентов корреляции охватывает все возможные состояния сточных вод в процессе озонирования раствора гуминовой кислоты. Для установления связи между концентрацией гуминовой кислоты и поглощением на выбранной длине волны использованы растворы гуминовой кислоты с различной концентрацией. Показано, что лучшим количественным показателем концентрации гуминовой кислоты является поглощение на 300 нм. Поэтому для анализа концентрации гуминовой кислоты в процессе озонирования использовалась оптическая плотность на длине волны 300 нм. Распад гуминовой кислоты соответствует кинетической модели псевдопервого порядка. Скорость распада линейно связана с pH и $(T - 20)^2$ (T – температура реакции).

Ключевые слова: *гуминовая кислота, спектрофотометрия в УФ и видимой областях, оптимизация коэффициента корреляции, регрессионный анализ.*

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Introduction. Ultraviolet-visible (UV-vis) spectrophotometer has been used for decades to monitor water quality in various locations, such as rivers, sewers, tap water in networks, effluents of factories, etc. [1, 2]. It has also been used for the measurement of chemical oxygen demand (COD) in aquatic solution [3]. Based on partial least squares regression (PLSR), calibration methods with spectra data could be used to estimate the concentration of organic compound [4]. The parameter used in these studies often is the absorbance at 254 nm (UV_{254}), which is related to properties of humic substances such as aromaticity [5], molecular weight [6], and formation potential for trihalomethane [7, 8]. In the ozonation reaction, the oxidizing species would attack aromatic structures and rapidly oxidize them. In the initial stage of reaction, these easily oxidized bonds would be destroyed while aquatic UV_{254} decline rapidly. UV_{254} would remain stable roughly after a few minutes.

Landfill leachate is a kind of wastewater containing many organics, which not only inflict serious harm to human health but also causes pollution of groundwater. The catalytic ozonation process is one of the most effective methods to deal with this wastewater, which has difficultly degradative organics. Humus (HS) in landfill leachate is composed of a great range of organic compounds, ranging from hydrophilic acids with low molecular weight to amphiphilic humic- and fulvic-like acid with higher molecular weight. Removing humus (HS) has long been a concern due to their high molecular weights and nonbiodegradability [9]. UV-vis absorbance has been widely used for the characterization of humus, with many practical advantages. It needs a short period of testing time and a small volume of sample. Besides, it does not require many analytical equipments and sophisticated sample pretreatment. Until now, few works have studied the selection of wavelength in UV-vis spectrophotometric analysis for the aqueous phase in the ozonation process. This is one of the main objectives of this work.

The catalytic ozonation process on active carbon (AC) was discovered by Kaptijn in 1997 [10]. Combied ozonation and AC offer a strong synergetic effect on the removal of many contaminants such as in leachate [11]. Jans presented different results obtained from the experiments with aquatic solutions at pH > 5 [12]. AC is an initiator of the radical-type chain reaction that transforms O_3 into HO• in the aqueous phase. The basal plane electrons and oxygenated surface groups in AC are mostly responsible for ozone decomposition into O-radicals [13, 14]. Ceria is a kind of storage material for oxygen and is widely used in catalytic oxidation [15]. Its surface has a certain amount of oxygen vacancies that are easy to transfer [16]. Studies show that a catalyst with ceria doped on AC has high activity in catalytic ozonation for fulvic acid in water [17].

A proper analysis method has always been a difficulty in the ozonation treatment of landfill leachate. In addition, different environment and seasons as well as different ages of landfills would cause the difference in the composition of organics. This problem seriously hinders the application of catalytic ozonation in the treatment of landfill leachate. Accordingly, we present a reliable CCO method to find out wavelength that can be used in quantitative analysis by a spectrophotometric method. Moreover, the application of its result in factor analysis and kinetic analysis proved its feasibility and prediction accuracy.

Experimental. *HA solution.* In order to control the repeatability of this study, HA was extracted from landfill leachate using the method proposed by Thurman [18]. The landfill leachate was collected from a landfill in Sichuan Province, China. The specific extraction process is shown in a supplementary publication.

The results of elemental analysis indicate that this HA has a high degree of unsaturation. This may be because it has a large number of benzene rings. The higher the atomic ratio of C/N, the higher its degree of humification [19]. The atomic ratio of C/N is 9.47 for this sample, indicating that it has a high degree of humification. The atomic ratio of O/C is considered as an indication of the content of oxygen functional groups, such as carboxylic acids [20]. The infrared spectrum of extracted HA, together with the results of elemental analysis, is also shown in the supplementary publication.

Catalytic ozonation reaction. Before the experiment, a certain weight of HA powder was dissolved in deionized water under mechanical agitation in order to provide homogeneous dissolution. The pH was adjusted to 7 by 0.5 mol/L NaOH solution. In catalytic ozonation, the virgin HA solution was 0.5 g HA in one volume of aqueous solution. The catalyst is the same as in our previous study [21]. The preparation process is shown in the supplementary publication. For statistical analysis, suitable time intervals of sampling were set, which requires wavelength selection and catalytic ozonation experiments. This work studies the reaction conditions, including pH, reaction time, and temperature.

The ozonation reaction was carried out in a 1.5-L quartz reactor equipped with a stirrer and a circulating heat-transfer medium in the interlayer. During the reaction, 1 L HA solution was added in it. When the temperature was stable, the reactor was bubbling with the mixture gas of ozone and oxygen from the bottom. Ozone dispersed rapidly and uniformly with a mechanical agitation of 150 r/min. Ozone was produced from pure O_2 by an ozone generator (Model CFG-1P, Jinan Sankang Co., Ltd., China). The experiments were performed at constant gas flow rate (0.2 L/min, measured at room *T* and *P*) and constant ozone concentration (8 g/L). At the same time of ozone admission, 0.5 g Ce/AC catalyst was added into the reactor. The COD and UV-vis spectra of aqueous solution were analyzed at suitable time intervals (COD measuring instrument: Model DB200 and D1010, Hach Co., Ltd., USA). Details of the procedure are shown in supplementary publication.

UV-vis spectrophotometry. Seventy-two aquatic samples were collected from the ozonation process at the same reaction temperature (T = 20°C) and the same pH (pH 7). The distribution of sample number for different COD values (ranging from 15 to 272 mg/L) was generally normal one. These samples were set as the modeling set. Figure 1 showed the UV-vis spectra and their COD distribution. UV-vis spectra were determined in 1-cm path length quartz cells by a spectrophotometer (Model 2600A, Unico Co., Ltd., USA). This study selected the wavelength range of ~190–800 nm and an interval of 1 nm.

It used deionized water as a blank because the HA was dissolved in deionized water. Using the extracted HA, thirty-six aqueous solutions with different mass concentrations were prepared precisely by an analytical balance (Connecticut HZ Co., Ltd., USA). They had mass concentrations in ~25–500 mg/L and COD in ~20–270 mg/L. These solutions had known mass concentrations and were tested for COD. They were set as a validation set to test the accuracy of the CCO method. The UV-vis spectra and COD distribution of validation set are shown in the supplementary publication.

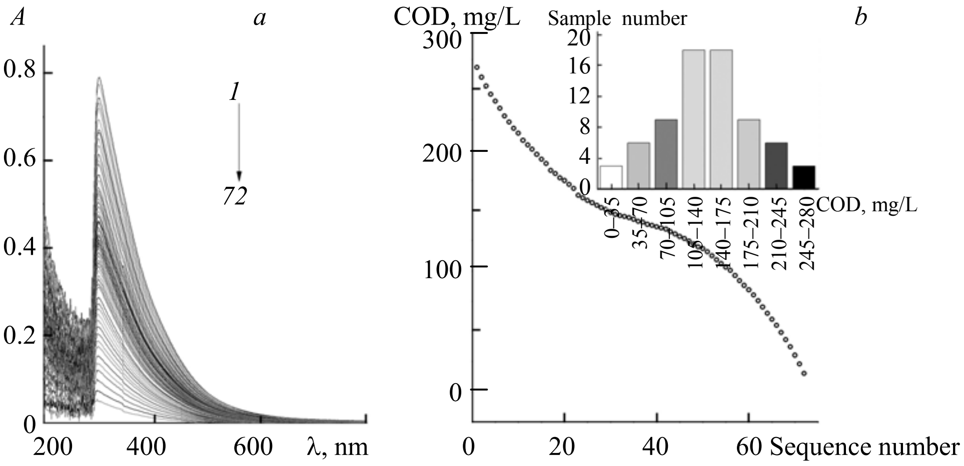

Fig. 1. The UV-vis spectra of the modeling set (a); the corresponding COD and distribution (b).

Wavelength selection by the CCO method. The correlation coefficient (R) between the organics concentration and the absorbance at each wavelength (λ) is defined by the following equation [22]:

$$R(\lambda) = \frac{\sum_{i=1}^{n}((A_i(\lambda) - A_{\text{ave}}(\lambda))(C_i - C_{\text{ave}})}{\sqrt{\sum_{i=1}^{n}((A_i(\lambda) - A_{\text{ave}}(\lambda))^2 \sum_{i=1}^{n}(C_i - C_{\text{ave}})^2}}, \quad (1)$$

where n is the number of samples; $A_i(\lambda)$ is the absorbance of the ith sample at wavelength of λ; C_i is the concentration of the ith sample; $A_{\text{ave}}(\lambda)$ and C_{ave} are the mean absorbance and mean concentration of all samples. The computer algorithms discussed below are designed using MATLAB 7.6 version software.

The statistical results of aquatic COD and mass concentration are given in the supplementary publication. COD and mass concentration are commonly used as quantitative characteristics of organics in water; they are taken as the basis for correlation coefficient analysis. In this calculation, the COD are taken as the concentration parameter of organics. According to the Lambert–Beer law, the absorbance of solution is proportional to the HA concentration in aqueous solution. The method of quantitative analysis for organics will be built up by finding the quantitative wavelength in the whole UV region. The linear relationship between absorbance and COD, which determine the accuracy of CCO method, can be established by regression analysis using the selected wavelength.

Kinetics of HA degradation. The HA degradation in water in the ozonation process undergoes two parallel reactions: 1) it directly reacts with dissolved ozone; 2) it reacts with hydroxyl radicals that are formed from ozone and promoted by catalyst. The concentrations of ozone and hydroxyl radical will be constant when the ozone inlet flow is continuous. The degradation of HA is a pseudo-first-order kinetic progress [21]

$$-dC_{\mathrm{HA}}/dt = k_{\mathrm{O_3}}^{\mathrm{HA}} C_{\mathrm{O_3}} C_{\mathrm{HA}} + k_{\mathrm{OH}}^{\mathrm{HA}} C_{\mathrm{OH}} C_{\mathrm{HA}} = (k_{\mathrm{O_3}}^{\mathrm{HA}} + k_{\mathrm{OH}}^{\mathrm{HA}} R_{\mathrm{ct}}) C_{\mathrm{O_3}} C_{\mathrm{HA}}, \qquad (2)$$

where $C_{\mathrm{O_3}}$ and C_{OH} represent the concentrations of dissolved ozone and hydroxyl radical in the solution; C_{HA} represents the residual concentration of HA. The ratio of the concentration of hydroxyl radical and dissolved ozone is a constant [23], named R_{ct} here.

The degradation efficiency of HA in catalytic ozonation reaction is calculated using the following equation:

$$C_{\mathrm{HA}}/C_{\mathrm{HA0}} = A_i/A_{i0}, \qquad (3)$$

where C_{HA0} and C_{HA} are the initial and residual concentration of HA; A_{i0} and A_i are absorbance at the wavelength of i nm at the initial time and after the reaction.

At the same reaction temperature, the same amount of catalyst, the same pH, and the same stirring speed, the parameter R_{ct} would be the same and be a constant during the ozonation process. It is assumed that the concentration of dissolved ozone also remains constant due to the continuous bubble, which was verified by measuring the dissolved ozone concentration during the experiments. Accordingly, Eq. (3) and

$$\ln(C_{\mathrm{HA0}}/C_{\mathrm{HA}}) = k_{\mathrm{app}}t. \qquad (4)$$

could be used to calculate the k_{app} (the apparent pseudo-first-order rate constant).

Regression analysis. Regression analyses are carried out to assess the effects of reaction conditions. Because the reaction conditions can affect the reaction result, they have certain quantitative relationships with the residual HA, both in the average sense and statistical significance. Seeking expressions of these relationships is the main task of regression analyses. Confirming the primary and secondary relationship of influence factors is another task of this study. The design of the catalytic ozonation reaction could be optimized both in the optimization of catalyst and in the choice of reaction conditions. Here, the absorbance at selected wavelength is taken as the characterization of the organics concentration in water.

The estimated value of the dependent variable y is denoted by $\hat{y}$, and independent variables are denoted by x_i. The equation of linear multiple regression is as follows:

$$\hat{y} = b_0 + b_1x_1 + b_2x_2 + \ldots + b_kx_k. \qquad (5)$$

Standardized equations:

$$\begin{cases} a_1 + a_2\overset{*}{r}_{x_1x_2} + a_3\overset{*}{r}_{x_1x_3} + \ldots + a_k\overset{*}{r}_{x_1x_k} = \overset{*}{r}_{yx_1} \\ a_1\overset{*}{r}_{x_2x_1} + a_2 + a_3\overset{*}{r}_{x_2x_3} + \ldots + a_k\overset{*}{r}_{x_2x_k} = \overset{*}{r}_{yx_2} \\ \qquad \ldots \\ a_1\overset{*}{r}_{x_kx_1} + a_2\overset{*}{r}_{x_kx_2} + a_k\overset{*}{r}_{x_kx_k} + \ldots + a_k = \overset{*}{r}_{yx_k} \end{cases} \qquad (6)$$

Algorithms using SPSS statistical software are employed to calculate the above standardized equations. After calculating these expressions, the optimal variables of a_1, a_2, …, a_k are determined. The square of the regressed multiple variable is also determined:

$$R^2 = a_1\overset{*}{r}_{yx_1} + a_2\overset{*}{r}_{yx_2} + \ldots + a_k\overset{*}{r}_{yx_k}\ . \qquad (7)$$

Results and discussion. *Wavelength selection.* Figure 2 presents the correlation coefficients (R) between COD and absorbance from 190 to 700 nm of the modeling set. In the spectrum of correlation coefficients (CCS), there are some peaks at wavelengths of 251, 280, 300, and 342 nm. The maximum peak of CCS is at 300 nm. The ultraviolet absorption peak of the conjugated bond has a blue shift from 254 to 251 nm, which indicates that the conjugated bond may connect with electron withdrawing groups.

The interference from environment is smaller where the absorbance is stronger. This principle is also called "less absorbance and greater interference". For further consideration, the quantitative wavelength is chosen as 300 nm. Figure 3a shows the linear relationship between the absorbance and measured COD of the validation set. The linear relationship between the absorbance and mass concentration of validation set is shown in Fig. 3b. Their squared correlation coefficients (R^2) are 0.994 and 0.997. This is consistent with the correlation coefficient of the validation set shown in the supplementary publication. The validation set includes 36 solutions with different HA concentrations and without ozonation treatment; therefore, the absorbance and concentration characteristics also have a good linear correlation at 300 nm.

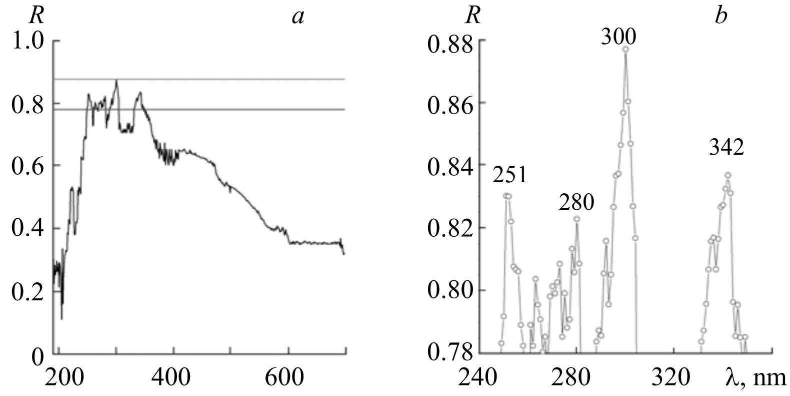

Fig. 2. The spectrum of correlation coefficient-CCS (a); the maximum peak of CCS (b).

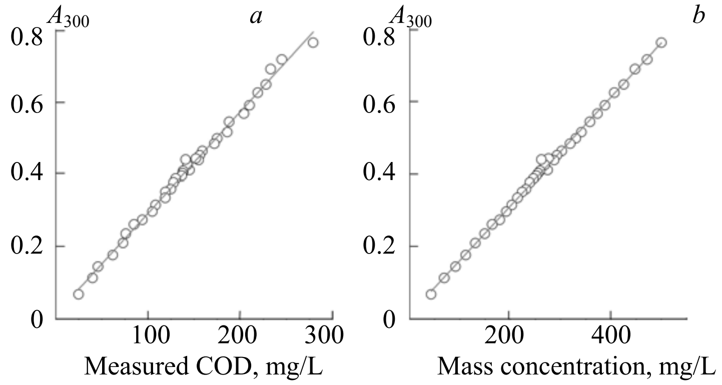

Fig. 3. The linear relationship between the absorbance at 300 nm and the measured COD (a) and the mass concentration of solution (b).

HA degradation by catalytic ozonation. The HA concentration in aqueous solution decreased drastically at the first 30 min of ozonation reaction. The catalyst accelerated the HA decomposition; accordingly, the decline was quicker in catalytic ozonation than that in single ozonation: 91 and 86% of HA were removed in the early 30 min, respectively. Two hours later, the removal rates were 96 and 93% in catalytic ozonation and single ozonation, respectively.

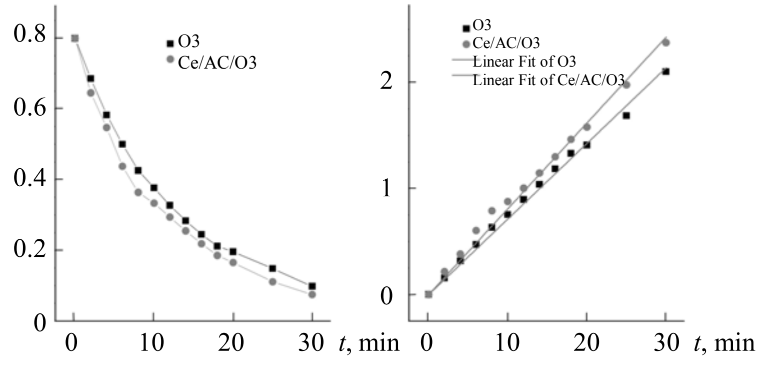

Fig. 4. Evolution of the absorbance of HA solution with reaction time (a) and the pseudo-first-order decay of HA in water (b)

As shown in Fig. 4, the HA decomposition by ozone fits the pseudo-first-order kinetic model both with catalyst and without catalyst. The square of the correlation coefficient (R^2) is above 0.98. The results of linear fitting are as follows:

$$\ln(C_{\mathrm{HA0}}/C_{\mathrm{HA}}) = k_{\mathrm{app}}t = \begin{cases} 0.08088t \ (\mathrm{O_3}) \\ 0.07124t \ (\mathrm{Ce/Ac/O_3}) \end{cases} \qquad (8)$$

Due to the fact that the time unit in the above equation is minutes, the rate constants for the single ozonation and catalytic ozonation are 1.30×10^{-3} and 1.19×10^{-3} s^{-1}, respectively. These results are consistent with the rate constants in the single ozonation for commercial HA, which ranged from 7.42×10^{-4} to 3.22×10^{-3} s^{-1} at different initial HA concentrations [24].

Regression analyses for reaction conditions. The reaction conditions that are analyzed by linear multiple regression are pH, temperature (T), and reaction time (t). The three input parameters are $X_1 = \mathrm{pH}$, $X_2 = (T - 20)^2$, and $X_3 = e^{-0.07118t}$.

Because of Eq. (3) and the results of the COO method, the absorbance at 300 nm is taken as an indication of the HA concentration. Accordingly, the output parameter is the absorbance at 300 nm (denoted y). The results of catalytic ozonation for HA are presented in the supplementary publication. The results of multiple linear regression analysis are as follows:

$$Y = -0.011X_1 + 0.001X_2 + 0.662X_3 + 0.080. \qquad (9)$$

The R^2 of this model is 0.963. According to the above equation, the pH shows a linear relationship with the HA concentration in catalytic ozonation. Besides, a relationship also exists between the HA concentration and the quadratic of reaction temperature. At the same pH and temperature, the HA concentration shows an exponential relationship with reaction time. This model also validates the law of HA decomposition with time in catalytic ozonation.

Conclusion. The method of correlation coefficient optimization is an accurate algorithm for finding the appropriate walvelength in the UV-vis spectrophotometric method, which is used to measure the concentration of organics in ozonation reaction. From the result of CCO calculation, the absorbance at 300 nm is a good quantitative indication for the HA concentration in landfill leachate. Accordingly, it was applied to analyze the HA concentration in the ozonation process. It was found that HA decomposition by ozone fits the pseudo-first-order kinetic model. The HA concentration shows a linear relationship with pH and $(T-20)^2$. It is easier to evaluate the reaction conditions with a simple and rapid spectrophotometric method. The CCO method provides a new approach for selecting the quantitative wavelength in the UV-vis spectrophotometric method, which is applied to the determination of organic compounds in water.

Supplementary

Extraction of HA

The landfill leachate was collected from a landfill in Sichuan province, China. It was filtrated with filter paper and 0.45μm microporous film. Subsequently, the pH of filtrate was adjusted to 1 by using 0.1 mol/L HCl. After precipitating for 24 h and centrifugation, the precipitate was dissolved in 0.1 mol/L KOH solution which volume was as little as possible, followed by adding solid KCl to make sure that the $\mathrm{K^+}$ concentration was 0.3 mol/L. Then, this solution was standing four hours and adjusted pH to 1~2 as well as stored at 70 °C for one hour. After that, it was centrifuged for 15 minutes. The obtained sediment was added into dialysis solution (0.1 mol/L HCl together with 0.3 mol/L HF) and placed in a dialysis bag until no $\mathrm{Cl^-}$ in it. At last, the purified HA was freeze-dried and grinded to powder. The obtained powder was HA. This is a mixture of humic substances and its molecular weight distribution is from tens to thousands.

The results of elemental analysis of the extracted HA were shown in the following table (the elemental analyser equipment: vario MICRO select, Elementar Co., Ltd., Germany). In this sample, the atomic ratio of H/C is 1.39. This indicated that it has a high degree of unsaturation. This may be because that it has a large number of benzene rings. A higher atomic ratio of C/N, a higher degree of humification it has. The atomic ratio of C/N is 9.47 for this sample, indicating that it has a high degree of humification. This is related to the age of landfill. The atomic ratio of O/C is considered as an indication of the content for oxygen functional groups, such as carboxylic acids. It is commonly used to compare the humus in different environments. The atomic ratio of (N+O)/C is considered as an indication of the polarity of HA. The smaller of the value, the less polar functional groups it has, such as: COOH, OH, $\mathrm{NHCO{-}CH_3}$, SH, CO- and COOR.

TABLE S1. Elemental Analysis of the Extracted HA

Element content/%							Atomic ratio			
C	H	O	N	S	P	ash	H/C	C/N	O/C	(N+O)/C
46.25	5.32	35.35	5.70	0.95	0.08	6.35	1.39	9.47	0.57	0.679

The infrared spectrum of extracted HA is shown in following (the FT-IR equipment: Model 6700, Nicolet Co., Ltd., USA). There are strong absorptions at 3399.7 and 1694.5 cm^{-1}, moderate absorption at 1320.2 cm^{-1}. They indicate the existence of carboxyl groups. The strong absorptions at 3399.7 and 1175.0 cm^{-1}, and the moderate absorption at 659.0 cm^{-1} indicate that there may be hydroxyl groups. There may be carbonyl groups because of the moderate absorption at 1694.5 and 826.3 cm^{-1}. Meanwhile, there may be the double bond because of the moderate adsorption at 3152.8 and 987.8 cm^{-1}.

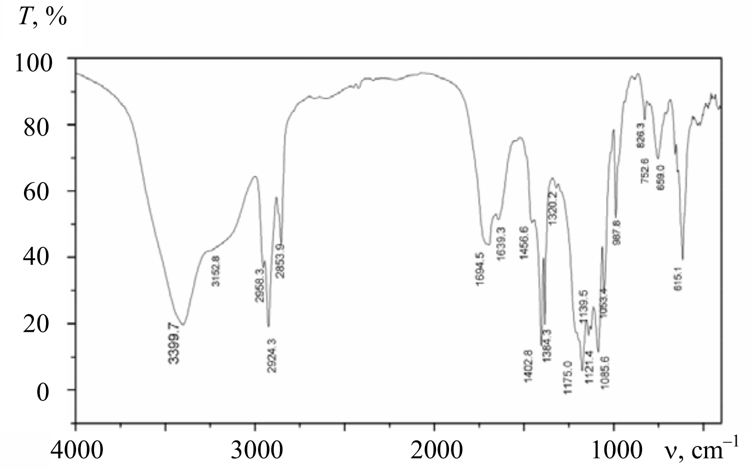

Fig. S1. The infrared spectrum of obtained HA.

The Preparation of Ce/AC Catalyst

Ce/AC catalysts were prepared by impregnation method. 50 ml deionized water was added in a flask and dispersed 5 g of AC by mechanical stirring. Subsequently, it was slowly dropped with 4 mL $Ce(NO_3)_3$ solutions with 3.187 mg/L Ce^{3+}. After stirring half an hour, the speed was slow down to 100 r/min for reducing the abrasion of AC. This stirring process continued 12 hours. After filtering and washing, the resultant samples were dried at 110 °C for 24 h and calcined in a tube furnace under a flow of N_2+H_2 (40 cm^3/min N_2 and 10 cm^3/min H_2) for 3 h at 450 °C. The obtained catalyst was named as Ce/AC, and used in the catalytic ozonation.

The Precise and Accurate measurement of COD

COD (chemical oxygen demand) is one indication for the total emission of organics in wastewater. It also reflects the pollution degree of water by reducing substances, including iron sulfide and organic nitrite. At the same time, COD is taken as one index of relative content for organics in water. Using "the fast digestion spectrophotometric method" to measure the COD, the national standard of China (HJ/T 399-2007) gives the details for measurement. And instruments used in this test are Model DB200 and D1010 of Hach from USA.

The colorimetric tube method and low measurement range (COD ~15–150 mg/L) were used to test COD. Each water sample was diluted to a certain multiple, to ensure the COD was in the range of ~15–150 mg/L. Before the determination, each photometric colorimetric tube was added 5ml deionized water and tested its absorbance at 440 nm. The absorbance difference of used tube should be in 0.005. The COD measurement needed the colorimetric tube to be almost conformance.

In COD measurement, each sample was measured for three times. And the measurement which standard deviation is less than Ex is the effective data. At this moment, its average value could be the measured COD. This was also referenced to the national standard to control the precision and the accuracy for the low range method.

TABLE S2. Standard Deviation of COD

COD, mg/L	~0–50	~25–75	~75–125	~125–175	~175–225	~225–275
Ex, %	3.525	2.900	2.275	1.650	1.000	0.375

The Validation Set

Using the extracted HA, 35 aqueous solutions with different mass concentrations were prepared by an analytical balance (Connecticut HZ Co., Ltd., USA). The concentration range was ~25–500 mg/L. The number in different COD rang obeyed the gaussian distribution (which is also called normal distribution). These solutions were set as a validation set to test the accuracy of CCO method. The absorbance at 300 nm (A_{300}) and the correspondent COD of validation set are as following.

TABLE S3. Analysis Data of Validation Set

No	Measured COD, mg/L	Mass concentration, mg/L	A_{300}	A_{342}
1	279.24	500.00000	0.76616	0.50512
2	245.32	472.01493	0.71938	0.49985
3	233.11	447.76119	0.69277	0.47619
4	228.08	425.37313	0.64993	0.42856
5	219.15	406.71642	0.62709	0.41236
6	210.04	388.0597	0.59194	0.39843
7	204.31	373.13433	0.56889	0.37607
8	188.17	358.20896	0.54609	0.35996
9	186.22	341.41791	0.51753	0.34350
10	175.14	330.22388	0.50010	0.33257
11	172.02	319.02985	0.48531	0.32061
12	159.09	302.23881	0.46533	0.31951
13	156.22	292.77612	0.45329	0.30371
14	155.05	287.31343	0.43979	0.28895
15	151.98	275.85075	0.44418	0.28084
16	145.12	274.38806	0.41205	0.27104
17	142.98	268.65672	0.42654	0.28229
18	140.86	261.92537	0.44113	0.29390
19	138.24	259.32836	0.40985	0.27283
20	137.55	255.59701	0.40319	0.26591
21	136.72	251.86567	0.39675	0.25811
22	130.12	246.26866	0.38871	0.25198
23	127.82	238.80597	0.37807	0.24465
24	124.92	231.34328	0.36037	0.23297
25	119.05	223.8806	0.35287	0.22536
26	118.86	214.55224	0.33644	0.21488
27	108.33	203.35821	0.31657	0.20188
28	104.89	192.16418	0.29822	0.19061
29	94.08	179.10448	0.27552	0.17061
30	85.00	164.1791	0.26265	0.15812
31	76.23	149.25373	0.23690	0.14114
32	73.08	130.59701	0.21068	0.11296
33	61.98	111.9403	0.17771	0.10183

Continue Table S3

No	Measured COD, mg/L	Mass concentration, mg/L	A_{300}	A_{342}
34	46.06	91.41791	0.14555	0.08030
35	40.05	69.02985	0.11384	0.06143
36	25.00	42.91045	0.06792	0.03044

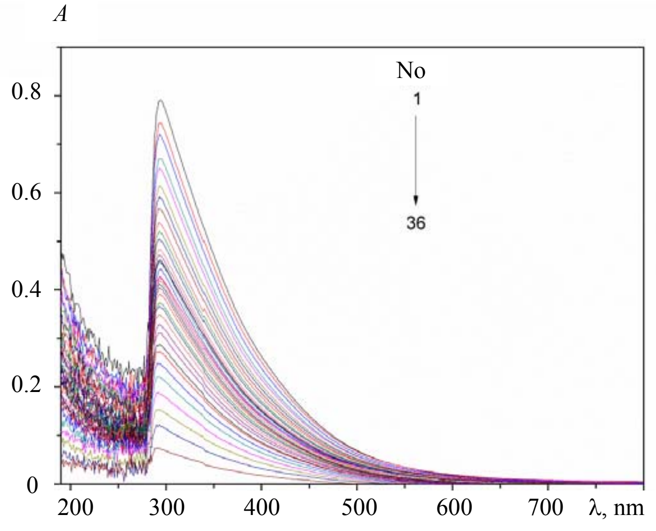

Fig. S2. The UV-vis spectra of validation set.

Regression analyses for reaction conditions

The reaction conditions which were analyzed by regression analyses included pH, temperature (*T*) and reaction time (*t*). The results of catalytic ozonation for HA were presented in following. These data were used for the regression analyses for reaction conditions.

TABLE S4. Results of Catalytic Ozonation

No	pH	T, °C	t, min	X_1	X_2	X_3	A_{300}
1	6	15	5	6	25	0.7005	0.5467
2	6	15	10	6	25	0.4908	0.3659
3	6	15	15	6	25	0.3438	0.2534
4	6	15	20	6	25	0.2408	0.1880
5	6	15	30	6	25	0.1182	0.0923
6	6	20	5	6	0	0.7005	0.5325
7	6	20	10	6	0	0.4908	0.3717
8	6	20	15	6	0	0.3438	0.2425
9	6	20	20	6	0	0.2408	0.1738
10	6	20	30	6	0	0.1182	0.0802
11	6	25	5	6	25	0.7005	0.5905
12	6	25	10	6	25	0.4908	0.3597
13	6	25	15	6	25	0.3438	0.2570
14	6	25	20	6	25	0.2408	0.1901
15	6	25	30	6	25	0.1182	0.0940
16	7	15	5	7	25	0.7005	0.4279
17	7	15	10	7	25	0.4908	0.3071
18	7	15	15	7	25	0.3438	0.2478
19	7	15	20	7	25	0.2408	0.1792

Continue Table S4

No	pH	T, °C	t, min	X_1	X_2	X_3	A_{300}
20	7	15	30	7	25	0.1182	0.0885
21	7	20	5	7	0	0.7005	0.4037
22	7	20	10	7	0	0.4908	0.2829
23	7	20	15	7	0	0.3438	0.2337
24	7	20	20	7	0	0.2408	0.1650
25	7	20	30	7	0	0.1182	0.0744
26	7	25	5	7	25	0.7005	0.5117
27	7	25	10	7	25	0.4908	0.3509
28	7	25	15	7	25	0.3438	0.2517
29	7	25	20	7	25	0.2408	0.1830
30	7	25	30	7	25	0.1182	0.0924
31	8	15	5	8	25	0.7005	0.4585
32	8	15	10	8	25	0.4908	0.3591
33	8	15	15	8	25	0.3438	0.2397
34	8	15	20	8	25	0.2408	0.1712
35	8	15	30	8	25	0.1182	0.0805
36	8	20	5	8	0	0.7005	0.3843
37	8	20	10	8	0	0.4908	0.2948
38	8	20	15	8	0	0.3438	0.2257
39	8	20	20	8	0	0.2408	0.1573
40	8	20	30	8	0	0.1182	0.0664
41	8	25	5	8	25	0.7005	0.4423
42	8	25	10	8	25	0.4908	0.3429
43	8	25	15	8	25	0.3438	0.2437
44	8	25	20	8	25	0.2408	0.1572
45	8	25	30	8	25	0.1182	0.0762
46	9	15	5	9	25	0.7005	0.4397
47	9	15	10	9	25	0.4908	0.3483
48	9	15	15	9	25	0.3438	0.2491
49	9	15	20	9	25	0.2408	0.1804
50	9	15	30	9	25	0.1182	0.0797
51	9	20	5	9	0	0.7005	0.4535
52	9	20	10	9	0	0.4908	0.3351
53	9	20	15	9	0	0.3438	0.2339
54	9	20	20	9	0	0.2408	0.1572
55	9	20	30	9	0	0.1182	0.0655
56	9	25	5	9	25	0.7005	0.4325
57	9	25	10	9	25	0.4908	0.3411
58	9	25	15	9	25	0.3438	0.2419
59	9	25	20	9	25	0.2408	0.1722
60	9	25	30	9	25	0.1182	0.0816

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