Study on UV–Visible Spectra Characteristic of Dissolved Organic Matter during Municipal Solid Waste Composting

Dan Li1,a, XiaoSong HE1,b, BeiDou XI1,c, ZiMin WEI2,d, HongWei PAN2,e and DongYu CUI1,f

1State Key Laboratory of Environmental Criteria and Risk Assessment, Chinese Research Academy of Environmental Science, Beijing 100012, China
2Northeast Agricultural University College of Life Science, Harbin 150030, China

a)lidangaga@126.com, b)hexs82@126.com(corresponding author),
c)xibeidou@263.net(corresponding author), d)weizimin691120@126.com, e)phw103@163.com,
f)222221cdy@163.com

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Abstract: This paper aims to characterize the evolution of organic matter during the composting of municipal solid waste (MSW). During the 46-day composting process, six samples with different composting time were collected from Songjiang Solid Waste Biological Treatment Plant in Shanghai, China. Dissolved organic matter (DOM) was extracted by ultra-pure water, and the UV-Visible (UV-Vis) spectra of DOM were scanned and investigated. The results showed that, during the composting process, non-humus substances in DOM were gradually transformed into humus substances, the aromatization, molecular weight and humification of humus substances increased. Correlation analysis showed that the absorbance value at 280 nm (SUVA280), and the area of 226~400 nm (A226~400) correlated positively with each other. The dissolved organic carbon (DOC) concentration exhibited a negative correlation with the parameters S275~295, SUVA280 and A200~226, and the correlation coefficients between the DOC content and the A220~226 value was the best (r=-0.976, P=0.001). The absorbance ratio between 465 and 665 nm (E465/E665) showed a significant correlation with SUVA280 (r=-0.892, P=0.017), A226~400 (r=-0.909, P=0.012) and DOC (r=0.840, P=0.036). The absorbance ratio of 250 to 365 nm (E250/E365) correlated significantly with DOC (r=-0.880, P=0.021), and showed no correlation with the other parameters. Absorption curve slope in the range of 275~295nm (S275~295) showed a significantly positive correlation with the DOC content (r=0.961, P=0.002). Among all parameters, the A200~226, A226~400 and S275~295 values reflected compost maturity best.

Introduction

Aerobic composting is one of the most important ways for reusing organic solid wastes such as municipal solid wastes (MSW), food wastes, municipal sludges, livestock and poultry manures. As an efficient treatment method for MSW, composting is widely used in China because of its waste
reduction, minimum pollution and maximum reuse [1]. Indigenous microorganisms and artificial inoculation are used for the degradation of organic matter in urban domestic refuse treatment sites, and biodegradable organic matter is transformed to humic substance. All of these processes occur in a thin layer of liquid membrane on the particle surface of the organic wastes, so only the dissolved organic matter (DOM) could be used. The evolution of DOM can reflect the transformation process of compost matter during the composting process. There is a close relation between the maturity of compost and the content of humic organic matter, which has been evidenced by many investigators [2, 3, 4].

Currently, spectroscopy methods have been widely used to study the material transformation during the composting process of livestock and poultry manure. However, this method is limited during the composting process of MSW. Among the different analytical techniques that could be used to characterize the humification degree of organic materials, UV-visible spectroscopy presents clear potentialities [5, 6, 7]. Although some authors consider DOM absorption spectra of little usefulness because of its apparent featureless character, a number of studies have shown that an adequate analysis of these spectra may provide highly important information on the chemical structure of DOM [8]. As far as UV-visible spectroscopy is concerned, classical indexes such as the ratios between the absorbance at 465 and 665 nm ($E_{465}/E_{665}$) or the absorbance at 254 nm or 280 nm per organic carbon (OC) unit (SUVA$_{254}$ and SUVA$_{280}$) have proven to be qualitatively related, to a certain extent, to certain structural features of different components [5, 6, 9, 10]. This fact has facilitated the development of several indexes that seem to provide a valuable means to quantify the humification degree of diverse organic materials [11].

In this paper, UV-Vis spectra were used to investigate the structural transformation characteristics of DOM extracted from different stages of MSW composting. The aims of the current work are (1) to find the most suitable characterization of indicators of maturity; and (2) to avoid the compound pollution and provide a theoretical basis for process control of a garbage treatment plant.

**Materials and Methods**

**Sampling and pretreatment.** The composting samples used in this experiment were obtained from Shanghai Songjiang Biological Treatment Plant, Shanghai, China. The composted materials were mainly comprised of MSW in the plant, and the fermentation process was conducted in storehouses. The entire composting process lasted approximately 46 days, during which time the composted materials were forked over several times to maintain aeration. We did not control the composting operation or attempt to influence the course of the composting process. During the composting process, samples of different composting stages were collected in duplicate on day 1, 4, 8, 16, 32, and 46.

**Extraction of DOM and analysis of dissolved organic carbon (DOC).** Compost samples were freeze-dried at -54 °C, ground and sieved. Particles that were smaller than 2 mm in diameter were chosen for analysis. Each sample (20 g) was extracted with 200 mL ultrapure water (solid to liquid ratio of 1:10, w/v), shaken at 200 rpm for 24 h, at room temperature. Extracts were centrifuged at 12,000 rpm for 20 min and then filtered through a 0.45 μm membrane filter, the organic matter in filtrate was DOM. The DOC concentration in the filtrates was measured with TOC analyzer (Analytik Jena Multi N/C 2100, Jena, Germany). A portion of the filtrates was freeze-dried at -54°C,
and the rest was stored in dark at 4°C in acid-washed oven-dried amber glass flasks for further analyses.

**UV-Vis spectra.** For UV-Vis spectroscopy, the DOC concentrations of all samples were adjusted to 7.0 mg L\(^{-1}\), in accordance with the result of the pre-experiment. UV–Vis absorption spectra were recorded with a UV-4802 spectrophotometer (Unico, Shanghai, China) at a wavelength range of 190–700 nm. The integral area was calculated from 200 to 226 and from 226 to 400 nm, designated as \(A_{200-226}\) and \(A_{226-400}\). Specific ultraviolet absorbance at 280 nm (SUVA\(_{280}\)) was calculated as the absorbance divided by the DOC concentration. The \(E_{250}/E_{365}\) ratio was calculated as the ratio of absorbance at 250 and 365 nm, the \(E_{465}/E_{665}\) ratio was calculated as the ratio of absorbance at 465 and 665 nm, and the \(E_{253}/E_{203}\) ratio was calculated as the ratio of absorbance at 253 and 203 nm. In addition, the slope of the 275–295 nm region (\(S_{275-295}\)) was obtained as described by Helms et al (2008). The correlation of each characteristic ultraviolet absorbance parameter was analyzed with the SPSS 17.0 statistical analysis system.

**Results and discussion**

**DOC change at different stages during composting.** The changes of DOM were more sensitive than the solid phase component to reflect the transformation process of composting material. The changes of the effective concentration of DOM (DOC as a representative) may be used as simple indexes and measurement of compost maturity [12, 13]. As shown in Fig. 1, the DOC value of the MSWs showed an apparent downward trend with the extension of the composting time, from 59.27 g kg\(^{-1}\) in initial stage, down to 11.90 g kg\(^{-1}\) at the end of the period, decreased by 79.92 percent. The values declined fast at the beginning of composting, and dropped to half at the 8th day, then easily degradable compounds reduced continually. At the same time, complex structured compost materials degraded slowly, and macromolecules humic substances composed continuously, so the values of DOC slowed down at the end of composting.

![Fig. 1 The variation of DOC in the different stages of MSW composting](image)

Bernal et al. [13] regarded DOC value less than 17 g kg\(^{-1}\) as evaluation index of compost maturity, while Hue and Liu [12] established the indicator which was DOC value less than 10 g kg\(^{-1}\). Based on the two indicators, samples in this study became thoroughly mature at the 46th day during composting.

**UV absorption curve of DOM at different stages during composting.** The shape of UV absorption curve was mainly depended on the molecular structure of organic matter, and different
organic compounds have various molecular structure and complexity. Fig. 2 showed that the absorption intensity of DOM increased during compost, and reduced rapidly with the increasing of wavelength. The absorbance under short wavelength was higher than that under the long wavelength significantly. The entire spectrum was clear and simple, as well as there was no elaboration and complex structure. At the same time, the absorbance value of livestock manure was up to 2.0 while that of DOM extracted from MSW was only 0.47 approximately, therefore, the molecular complexity of MSW compost was significantly lower than that of livestock compost [14].

![Fig. 2 UV absorption curve of DOM extracted from different stages of MSW compost](image)

It is notable that a small acromion was formed at the wavelength of 235 nm, which was mainly caused by the $\pi \rightarrow \pi^*$ transition of electrons in $\pi$-$\pi$ molecular with cellular structure (e.g., aromatic). There was an apparent absorption platform in the vicinity of 280 nm. According to previous reports, the absorption platform of about 280 nm wavelength was caused by the optical absorption, which came from the lignin suffocates and its derivatives in the humus material. And the unit mole intensity of UV absorption of humus substance enhanced with the increasing humus aromatic and unsaturated conjugated double bond structure [10, 15].

As described above, variation trend of absorption spectral curve of DOM at different MSW compost stages indicated that DOM contained simple humus substances, and the degrees of aromaticity and unsaturation of humus substances increased during compost process, as well as the degree of humification.

**Study on the changes of characteristic UV absorption parameters.** The characteristic UV absorption parameters were analyzed in detail, which can characterize the changes of DOM extracted from MSW composting and the degree of maturity apparently. The results were listed in Table 1.

<table>
<thead>
<tr>
<th>Composting time</th>
<th>$A_{200-226}$</th>
<th>$A_{226-400}$</th>
<th>SUVA$_{250}$</th>
<th>$E_{255}/E_{203}$</th>
<th>$E_{250}/E_{365}$</th>
<th>$E_{465}/E_{665}$</th>
<th>$S_{275-295}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 d</td>
<td>0.927</td>
<td>1.895</td>
<td>0.8</td>
<td>1.966</td>
<td>5.460</td>
<td>0.672</td>
<td>0.079</td>
</tr>
<tr>
<td>4 d</td>
<td>1.630</td>
<td>2.743</td>
<td>0.9</td>
<td>1.393</td>
<td>2.805</td>
<td>0.718</td>
<td>0.058</td>
</tr>
<tr>
<td>8 d</td>
<td>1.991</td>
<td>4.251</td>
<td>1.6</td>
<td>2.274</td>
<td>2.715</td>
<td>0.632</td>
<td>0.045</td>
</tr>
</tbody>
</table>
The area integral of UV absorption from 200 to 226 nm ($A_{200-226}$) was used to characterize the content of inorganic nitrogen, for nitrate, nitrite and other inorganic ions can produce a strong ultraviolet absorption at low UV wavelength range (200–226 nm).

Xie et al. [16] proved that the area integral of low UV wavelength range from 190 to 300 nm and the content of inorganic nitrogen exhibited a linear relationship. Data in Table 1 showed that, the $A_{200-226}$ values increased from 0.927 to 6.127 during composting, indicated that the content of inorganic nitrogen increased, especially nitrate and nitrite included. As is known to all, nitrogen-containing such as proteins degraded continuously, a large quantity of inorganic nitrogen were produced in the form of ammonia. Results obtained in this study were in accordance with Xie et al. [16].

$A_{226-400}$. UV absorption spectrum from 226 to 400 nm can reflect the characteristics of absorption spectra of the organic matter fully. According to previous reports [17, 18], there was usually a strong UV absorption from 200 to 400 nm of DOM extracted from compost which mainly attributed to the presence of aromatic carbon structure. In general, the UV absorbance occurring at wavelengths of 226–250 nm was mainly caused by unsaturated $\pi-\pi^*$ bond. While the absorbance around 260–400 nm was caused by the benzene ring structures with multiple conjugated structures [19, 20].

In order to explore the changes of the aromatic compounds with benzene rings in compost DOM, the UV absorbance wavelength range of 226–400 nm was chose to integrate in this study (Fig. 3). Results in Table 1 showed that the $A_{226-400}$ value of DOM extracted from MSW increased constantly with composting time, indicating that the content of the benzene ring-containing compounds in compost DOM increased. Typically, it degraded more difficult and its stability was stronger, if there were more benzene ring structures in the organic molecules. Therefore, DOM extracted from MSW stabilized gradually during compost.

![Fig. 3 Area integral of the UV absorbance from 226 to 400 nm](image)

SUVA$_{280}$. Studies on organic matter in water showed that the UV absorbance of the organic
matter in the 280 nm wavelength ($\text{SUVA}_{280}$) can provide some information on the molecular size, the degree of DOM humification and aromaticity [9]. The research about the changes of organic matter in MSW compost by researchers [21] also concluded a similar conclusion. It confirmed that $\text{SUVA}_{280}$ was positively correlated to the molecular weight.

Data in Table 1 showed, $\text{SUVA}_{280}$ increased from 0.008 to 0.036 with the increasing compost time, indicated that the molecular weight of the organic matter increased. Li et al. [14] proved that non-humus substances were gradually transformed to humus substances during compost, so the degree of humification and numbers of benzene ring structures increased, which caused the molecular weight of organic matter increasing accordingly. This experiment showed that the molecular weight of the organic matter increased. This result demonstrated that the degree of humification and aromaticity of organic matter increased during composting to some extent.

$E_{253}/E_{203}$. The ratio of absorbance at 253 ($E_{253}$) and 203 ($E_{203}$) nm, corresponding to the electron-transfer band (ET) and the benzenoid band (Bz) of benzene UV light absorption respectively [22], was calculated in this study. As the $E_{203}$ value can be affected by the presence of nitrate in the samples, the equivalent ratios at 253 and 220 nm and, at 253 and 230 nm, (which were not affected by nitrate) were also calculated [22].

According to Peuravuori et al. [10] the absorbance ratio of the ultraviolet spectrum at 253 and 203 nm $E_{253}/E_{203}$ reflected the types and degree of substitution of the aromatic ring. The value decreased when the content of the aliphatic chains in the substituent of aromatic ring increased, while the value increased when the content of C=O, -OH, -COOH and ester in the substituent of aromatic ring increased.

Table 1 showed that, the $E_{253}/E_{203}$ ratio increased gradually during composting, indicating that the number of the non-polar functional groups on the aromatic ring reduced during the process, while the number of substituent such as C=O, -OH, -COOH and ester increased. It inferred that the aliphatic chains on the aromatic ring were oxidized and decomposed continuously during composting, and degraded into small molecules such as C=O, -OH, -COOH and some other functional groups.

$E_{250}/E_{365}$. The parameter $E_{250}/E_{365}$ was commonly used in the characterization of the degree of humification of organic matter in limnology [10, 20]. When using the UV spectra to indicate changes of organic matter of compost, the ratio between two specific wavelength absorbance values was commonly used [14]. This can excluded the influence of the interfering factors under a single specific wavelength.

As listed in Table 1, the $E_{250}/E_{365}$ value of DOM extracted from MSW compost increased during the course of composting. Based on previous conclusions, the results inferred that the molecular weight of compost organic matter increased gradually during composting, which was consistent with the results of the analysis of $\text{SUVA}_{280}$.

$E_{465}/E_{665}$. The ratio of UV absorbance occurring at the wavelength 465 and 665 nm (namely $E_{465}/E_{665}$) has been widely used for the characterization of humic substances [8, 23, 24]. It was an important indicator to evaluate the quality, condensation degree and aromatization degree of compost [25]. It was also the most commonly characterization constant to study the stabilization of compost [26]. The $E_{465}/E_{665}$ ratio can provide information on the molecular structure; it produced a direct effect on the extent of polymerization of skeleton C in the benzene rings of compost organic matter. The lower the $E_{465}/E_{665}$ value was, the higher the degree of polymerization and aromatization in compost DOM were, and the higher the molecular weight was [7, 21, 27].
During compost, the $E_{465}/E_{665}$ values increased first and then down. This result indicated that organic matter with high molecular weight such as protein substances mineralized and degraded continually during the first fermentation process, then generated organic matter with low molecular weight and reduced the degree of polymerization. The degree of polymerization and aromatization of DOM molecules increased significantly during the secondary fermentation stage. In contrast to the $E_{465}/E_{665}$ values in previous studies on livestock manure compost, the $E_{465}/E_{665}$ values in this study were significantly lower than that in livestock manure compost. This indicated that the degree of polymerization of the DOM molecules in MSW compost was higher than in the livestock manure compost.

$S_{275-295}$. Spectral slopes provide additional insights into the average characteristics of DOM than absorption values alone, and have been widely used as indicators of molecular weight, composition, and source. According to previous studies [8, 28], at lower UV wavelength (200~226 nm), NO$_3^-$, NO$_2^-$ and inorganic ions can produce a strong UV absorption, which could influence the analysis results. Therefore, based on previous researches, slope of far ultraviolet wavelength at the range of 275~295 nm ($S_{275-295}$) was selected to explore the content of aromatic carbon in DOM extracted from different stages MSW compost. Helms et al. [29] successfully described the changes in chromophoric dissolved organic matter composition brought by photodegradation using the $S_{275-295}$. This result suggested that the spectral slope at lower wavelengths may be a better index for the aromaticity of compost DOM. Result from this study was consistent with the findings of Helms et al. [29], but was contrary to those of Hur et al. [30]. The different results may be explained by the structural complexity and the difference in source of organic matter.

As shown in Table 1, the $S_{275-295}$ values decreased during compost, and presented a clear downward trend. Based on previous research reports [31], the content of aromatic carbon in organic matter and its molecular weight was positively correlated to the absorption spectrum value of DOM, and negatively correlated to the slope of absorption curve. Results of this experiment showed that, content of aromatic carbon and molecular weight in organic matter increased along with MSW composting. It was in accordance with the analysis result of UV absorption parameters and other characteristics described above, and also in accordance with the result of Shao et al [32], who proved the regulation of DOM exacted from garbage in simulated aerobic compost.

Correlation between ultraviolet absorbance parameters and DOC. In order to further explain the relationship of different UV absorption parameters, the relationship between these parameters and the degree of compost maturity during composting, SPSS version 17.0 was used to analyze the correlation of each characteristic parameters of UV absorption and the indicators of maturity (DOC). The results were listed in Table 2.

<table>
<thead>
<tr>
<th>Characteristic parameters</th>
<th>$A_{200-226}$</th>
<th>$A_{226-400}$</th>
<th>SUVA$_{280}$</th>
<th>$E_{253}/E_{203}$</th>
<th>$E_{250}/E_{365}$</th>
<th>$E_{465}/E_{665}$</th>
<th>$S_{275-295}$</th>
<th>DOC</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{200-226}$</td>
<td>1</td>
<td>-0.827*</td>
<td>-0.804</td>
<td>-0.567</td>
<td>0.950**</td>
<td>0.779</td>
<td>0.974**</td>
<td>-0.976**</td>
</tr>
<tr>
<td>$A_{226-400}$</td>
<td>1</td>
<td>0.877*</td>
<td>0.771</td>
<td>-0.738</td>
<td>-0.909*</td>
<td>-0.929**</td>
<td>-0.856*</td>
<td>-0.908*</td>
</tr>
<tr>
<td>SUVA$_{280}$</td>
<td>1</td>
<td>0.419</td>
<td>-0.657</td>
<td>-0.892*</td>
<td>-0.848*</td>
<td>-0.840*</td>
<td>-0.880*</td>
<td>-0.840*</td>
</tr>
<tr>
<td>$E_{253}/E_{203}$</td>
<td>1</td>
<td>-0.518</td>
<td>-0.702</td>
<td>-0.678</td>
<td>-0.505</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_{250}/E_{365}$</td>
<td>1</td>
<td>0.647</td>
<td>0.922**</td>
<td></td>
<td>0.880*</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$E_{465}/E_{665}$</td>
<td>1</td>
<td></td>
<td>0.844*</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>
Correlation analysis of each parameter showed that, correlations between two specific UV absorption parameters of DOM extracted from different stages MSW compost, SUVA280 and A226~400 reached a significant level. The correlation suggested that it may be mainly caused by several absorption bands at wavelength 250~280 nm of compounds with phenyl in DOM. Take aniline for example, there was a strong absorption at 280 nm, resulting in a high correlation. However, correlation between these two UV absorption parameters and DOC reached a significant negative level. The order of the correlation was A226~400>SUVA280. That meant the two parameters can reflect the degree of decomposition of the compost to some extent, but there were some small differences. A226~400 represented the integral area of UV absorption within the range of 226~400 nm, contained part of the information that the SUVA280 represented. So it was the best indicator which reflected the information of absorption spectrum of the change of compost maturity. As shown in Table 2, correlations between A200~226 E250/E365, S275~295 and DOC were significant at the 0.01 level, which proved that A200~226 was a suitable parameter to represent maturity of compost from the aspect on content of nitrogen.

Data in Table 1 showed that the S275~295 value was significantly positive with the DOC content. This was the same to the section of S275~295 discussed above. So as composting proceeded, the content of aromatic carbon in DOM extracted from MSW compost increased continuously, and the degree of compost maturity improved.

E465/E665 was not only significantly positively related to the above-mentioned UV absorption parameters, but also to the DOC value. This result indicated that the E465/E665 value can reflect the degree of maturity of DOM to a certain extent. From the aspect of molecular structure, it can also provide some information related to maturity. The higher the extent of polymerization was, the higher humification of DOM was. E253/E203 did not reach a significant level with all the UV absorption parameters and DOC. The correlation between E250/E365 both S275~295 and DOC reached a significant level. Both of these two parameters can reflect the changes of DOM molecular weight during composting. This meant the molecular weight of DOM increased with the extension of the composting time. At the same time, correlation with DOC also reached a significant level. It reflected the degree of compost maturity from another angle. After compost, the extent of humification and stability increased accordingly. These conclusions were different from previous conclusions to some extent, perhaps due to some other conditions or parameters, such as the impact of pH, C and O elements, -COOH, C=O in organic matter and the total acidity. In addition, the differences among kinds of compost materials can also put an effect on the results to some extent.

In this study, MSW was used as compost samples, compared with researchers who used livestock manure as compost samples, the result was different on the UV absorption characteristics [14].

Conclusions

DOM extracted from MSW during different stages of compost was characterized by UV-Vis absorption spectroscopy. Each characteristic ultraviolet absorbance parameter and its correlations were studied in detail.
(1) The parameters indicated that non-humus substances of organic fractions transformed into humus substances gradually during composting, while its molecular weight, aromaticity, degree of unsaturation, humification, polymerization, and stability were increased accordingly.

(2) After composting, the aliphatic chains in aromatic ring of organic matter transformed into some kind of functional groups constantly, such as C=O, -OH, -COOH, and so on.

(3) Among all of characteristic ultraviolet absorbance parameters, correlations among $A_{200-226}$, $A_{226-400}$ and $S_{275-295}$ with DOC reached a significant level, these three were the most optimal absorption parameters to represent maturity of compost.

Acknowledgements

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References


