

Effects of UV/Cl₂ and UV/PDS advanced oxidation on chemical characteristics of typical organic matter in reclaimed water

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Abstract. In this research, humic acid was selected as a typical organic substance in reclaimed water, and the effects of higher oxidation of UV/Cl₂ and UV/PDS on its chemical composition, including aromaticity, molecular weight and fluorescence characteristics were investigated. Results showed that under the same oxidation conditions, the UVA₂₅₄ removal rate of UV/Cl₂ was higher than that of UV/PDS, but with the increase of pH, the UVA₂₅₄ removal rate of both decreased. Increasing the oxidant concentration could improve the UVA₂₅₄ removal rate, but UVA₂₅₄ would not continue to decrease after a certain concentration (Cl₂ 0.5mM, PDS 0.75mM). After oxidation, organics whose molecular weight >6520 Da significantly decreased, molecular weight 350-1690 Da significantly increased, with increasing UV dose, the molecular weight of 350-1690 Da decreased in UV/Cl₂, but continued to increase in UV/PDS. The fluorescent regions of fulvic acids under different treatments were effectively degraded after oxidation. The degradation efficiency of UV/Cl₂ and UV/PDS reached 87.6% and 83.3% respectively with 0.75mM oxidant and 1500 mJ/cm² UV light.

Keywords: Ultraviolet/ chlorine, ultraviolet/ persulfate, molecular weight, ultraviolet Absorbance, three-dimensional fluorescence

1. Introduction

Secondary effluent from municipal wastewater treatment plants contains a variety of organic matter that is difficult to be degraded by ordinary physicochemical and microbiological methods, among which humic acid is a representative substance of natural organic matter [1]. Humic acid, which contains a large number of functional groups and has the widest distribution in the earth's water resources, is a yellow-brown substance produced by the natural degradation process of some natural macromolecular organic matter in water [2]. Moreover, humic acid is the main precursor of disinfection by-products. Currently, the ever-strengthening water quality reuse standards and ecological construction goals are placing higher demands on reclaimed water treatment technologies. The application of UV-based advanced oxidation technologies for the removal of trace contaminants from drinking water is steadily growing in recent years [1], which can be broadly categorized into UV/hydrogen peroxide (UV/H₂O₂), UV/chlorine (UV/Cl₂), and UV/peroxidesulfate (UV/PDS). UV/H₂O₂ can effectively decompose a

variety of biologically difficult to degrade organic matter into CO_2 , H_2O and some small molecules, and has been put into practical applications on a small scale. While UV/ Cl_2 and UV/PDS are still in the exploratory stage, there are fewer studies on the oxidative removal of natural organic matter humus in water. However, the treatment of low concentrations of trace organic matter by advanced oxidation is inevitably affected by humic acid analogues [3], so it is important to study the response characteristics of advanced oxidation to humic acid analogues.

UV/ Cl_2 is an advanced oxidation method that combines two of the more common disinfectants, UV and chlorine, both of which have some disinfectant properties. By combining the two, UV light is used to activate the free chlorine, generating $\cdot\text{OH}$ and $\cdot\text{Cl}$, which degrades the dissolved organic matter in the reclaimed water into small molecules. The $\cdot\text{OH}$ and $\cdot\text{Cl}$ produced by UV/ Cl_2 advanced oxidation can in turn react with chlorine ions in water to produce $\text{Cl}\cdot^{2-}$ radicals. By nature, $\cdot\text{OH}$ is a non-selective and highly efficient oxidant, while $\cdot\text{Cl}$ and $\text{Cl}\cdot^{2-}$ radicals are highly reactive with trace pollutants containing electrophilic groups. The standard reduction potentials of $\cdot\text{OH}$, $\cdot\text{Cl}$ and $\text{Cl}\cdot^{2-}$ are 2.7, 2.4 and 2.0 V, respectively, which have strong oxidising properties, so the treatment effect of coupled UV and chlorine techniques is better than the two alone [4]. Persulfate is a strong oxidant, which needs to be activated under UV light, heat, transition metal ions (Fe^{2+} , Co^{2+} , Ag^+ , etc.), and ultrasound to be decomposed to produce the free radical $\text{SO}_4\cdot^-$, which has a strong oxidising ability with a redox potential of 2.5-3.1 V, close to or even exceeding that of 1.8-2.7 V of $\cdot\text{OH}$, and $\text{SO}_4\cdot^-$ and its oxidation product sulfate (SO_4^{2-}) have less effect on microorganisms [5]. The excellent removal of many organics by UV/PDS advanced oxidation has made it popular among researchers. This experiment was conducted (1) to characterize the organic matter by UVA_{254} , relative molecular weight and 3D fluorescence spectroscopy (3D-EEM), (2) to compare and analyze the effect study of two advanced oxidation techniques, UV/ Cl_2 and UV/PDS, on the removal of the chemical composition of typical organic matter (humic acid) from water, and (3) to investigate the effect of UV dose, pH and concentration of oxidant on the oxidation effect, respectively.

2. Materials and methods

2.1. Experimental reagents and Experimental water

Potassium iodide, sodium bicarbonate, potassium iodate, sodium borate, humic acid (humic acid FA $\geq 90\%$), sodium dihydrogen phosphate, sodium hydrogen phosphate, sodium persulphate, sodium sulfite, potassium dihydrogen phosphate, potassium hydrogen phosphate, sodium chloride, hydrochloric acid, sodium hydroxide, sodium hypochlorite, all chemical reagents were analytically pure. High-purity water was used as the solvent in the test.

The water used in the experiment was a mixture of humic acid solution at a concentration of 1 g/L and buffer solutions at pH=6, pH=7, and pH=8, which were prepared to have an initial UVA_{254} of approximately 0.3 and an organic carbon concentration of approximately 10 mg/L.

2.2. Experimental Methods

The light intensity of UV used in this experiment (0.623 mJ/cm^2) was first measured by iodometric method (KI/KIO_3), and the irradiation dose of different UV was determined according to the time of UV irradiation as a means of investigating the effects of different pH time doses on the properties of UVA_{254} , molecular weight distribution, and three-dimensional fluorescence, etc. The results were averaged. When studying the effects of other factors such as oxidant concentration, ion concentration, etc., the time of UV irradiation was controlled to be unchanged, and parallel experiments were set up for all experimental groups, and the results were averaged.

2.3. Methods of analysis

Determination of UVA_{254} : The water samples were filtered through a $0.45 \mu\text{m}$ membrane to remove non-dissolved particulate matter prior to the determination. UVA_{254} refers to the ultraviolet absorbance of the water samples at a wavelength of 254 nm in cm^{-1} , which was determined using an ultraviolet spectrophotometer (UV2200);

Determination of residual oxidant concentration: (1) sodium persulfate: take a small amount of sample in the test solution prepared by sodium bicarbonate and potassium iodide reagent, leave to react for fifteen minutes, through the determination of iodide ion absorbance at 352 nm to deduce the residual concentration of oxidants [6]. (2) Sodium hypochlorite: The residual chlorine detector can be used to indirectly determine the concentration of sodium hypochlorite remaining in the sample, take a small amount of the sample in the test bottle, pure water dilution of the appropriate number of times (10 times diluted in this experiment) to ensure that the residual chlorine detector within the range of accurate measurement.

Determination of molecular weight: The molecular weight was measured by liquid chromatography using 0.5 mM phosphate and sodium chloride as mobile phases at an injection flow rate of 0.8 mL/min; the injection volume was 100 μ L, and the programmed run time was kept at 22 min. The standards sodium polystyrene sulfonate 6520 and 1690 MW were used as molecular weight scales. The elution times were 12.06 min and 13.52 min, respectively, and the molecular weight plots of the working solutions under different conditions were compared to analyze the changes before and after treatment.

3D-EEM analysis: 3D-EEM were determined by a fluorescence spectrophotometer (Hitachi F-4600) using a 1 cm quartz cuvette, ultrapure water as a blank, a slit width of 5 nm for the excitation light Ex and the emission light Em, excitation wavelengths 220-450 nm in steps of 5 nm, and emission wavelengths 240-600 nm in steps of 1 nm. The scanning intervals were all 5 nm. The EEM fluorescence spectra were plotted by Matlab for data processing and Origin2020 for curve contour plotting.

3. Results and discussion

3.1. Effect of UV dose on oxidant concentration

With 0.5 mM oxidant added, the UV dose gradients of 0, 500, 1000, 1500 and 2000 mJ/cm^2 were designed at the same pH to study the effect of UV dose on the concentration of residual oxidant. As can be seen from Figure 1, the oxidant concentration decreases as the UV dose increases. At the same UV dose and different pH, the lowest concentration of residual oxidant was pH 6, and the concentration of residual oxidant increased with the increase of pH. As shown in Figure 1(a), the concentration of sodium hypochlorite is reduced by 30%-40% at 500 mJ/cm^2 , and when the light is 1500 mJ/cm^2 , the concentration changes are more than 60%, especially when pH=6, nearly 80% of the oxidizing agent is consumed, which is mainly due to the faster photolysis rate of chlorine. On the other hand, the rapid reaction between chlorine and humic acid consumes a large amount of free chlorine. As shown in Figure 1(b), the only changes in sodium persulfate concentration of more than 10% were at pH=6 and UV dose $\geq 1000 \text{ mJ}/\text{cm}^2$ and at pH=7 and UV dose $\geq 2000 \text{ mJ}/\text{cm}^2$, with most of the oxidant concentrations varying by less than 10%, suggesting that only a small amount of sodium persulfate activates to sulfate radicals, which are involved in the organic matter degradation reaction.

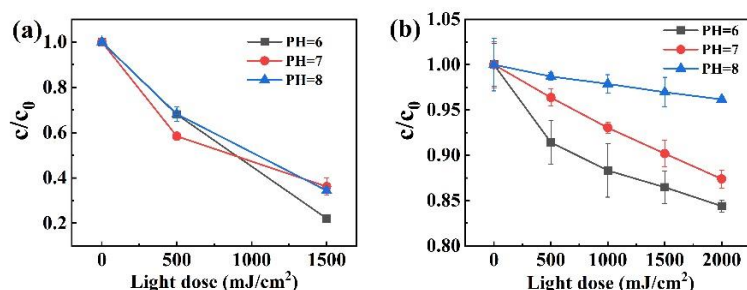


Figure 1. Residual oxidant concentration with UV fluence at different pH (a)UV/Cl₂;(b) UV/PDS

3.2. Effect of UV dose on the aromaticity of organic matter

Ultraviolet-visible spectroscopy can characterize the aromaticity of water by absorbance of specific wavelengths, and can also characterize the hair color group characteristics of molecular structures [7]. The designed UV dose was 500 mJ/cm^2 and 1500 mJ/cm^2 , and the pH gradient of the working liquid

was 6, 7 and 8. After being placed in a glass dish and stirred while being illuminated, a small number of samples were taken to a UV spectrophotometer to measure UVA₂₅₄. The results are shown in Table 1.

Table 1. The removal rate of UV/Cl₂ and UV/PDS to Humic acid UVA₂₅₄

UV dose \ pH	6		7		8	
	NaOCl	PDS	NaOCl	PDS	NaOCl	PDS
500 mJ/cm ²	50.23±9.60	10.23±0.23	53.97±0.41	6.11±0.82	46.74±0.48	1.50±0.25
1500mJ/cm ²	62.84±5.50	16.50±0.52	69.49±1.48	18.22±1.16	65.64±0.97	7.48±0.19

As can be seen from Table 1, both UV/Cl₂ and UV/PDS methods can increase the removal rate of UVA₂₅₄ under the same conditions and within a certain range by increasing the UV dose. For UV/Cl₂, under the same illumination, the removal rate of UVA₂₅₄ at the three pH values of 6, 7 and 8 shows the overall rule: when pH=7, pH=6 and 8 are the best conditions for removal effect. For sodium persulfate, the removal rate of UVA₂₅₄ at the three pH values of 6, 7 and 8 shows the overall rule: the best removal effect is pH=6, and the treatment effect decreases with the increase of pH value. When the light dose is 1500 mJ/cm², the removal effect of pH=6 is slightly less than that of pH=7. Considering the removal rate of UVA₂₅₄ by other treatments, it is found that it may be caused by some experimental errors. In contrast, when the best pH is 6 and the light dose is 1500 mJ/cm², the removal rate of UVA₂₅₄ by UV/PDS is only 16.5%, while that of UV/Cl₂ is as high as 62.84%. This is mainly due to the more active reaction between chlorine and organic matter, and chlorine alone can also oxidize organic matter. In particular, the reaction with conjugated double bonds and benzene rings and other aromatic organic compounds is more intense, reducing its aromatics.

3.3. Effect of oxidiser concentration on UVA₂₅₄

The concentration gradient of the designed oxidizer is 0, 0.25, 0.50, 0.75, 1.00 mmol/L (mM), and the reaction is carried out in about 80 mL glass dish at room temperature. The oxidizer is added to the working liquid prepared by humic acid and buffer solution with pH=7. The ultraviolet light dose is 1500 mJ/cm². A small sample was taken to determine UVA₂₅₄.

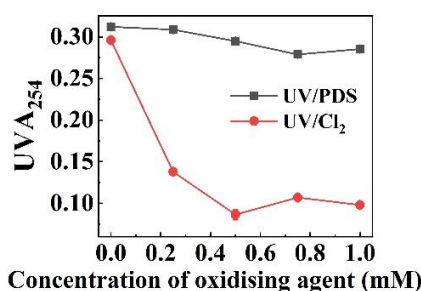


Figure 2. Effect of oxidant concentration on UVA₂₅₄

It can be seen from Figure 2. that with the increase of oxidizer concentration, the influence on organic matter content showed a trend of decreasing at first and then slightly increasing steadily. When the concentration of sodium hypochlorite increased from 0 to 0.50mM, the concentration of aromatic organic compounds decreased sharply, and the removal rate of UVA₂₅₄ reached about 70% at 0.50mM, but when the concentration of sodium hypochlorite increased to 0.75mM, the degradation of organic compounds was slightly weakened, and then tended to be stable, with little change. In contrast, in the range of 0-0.75mM PDS concentration, the concentration of benzene ring aromatic substances decreased with the increase of the concentration of oxidant; in the range of 0.75mM to 1.00mM, the concentration of benzene ring aromatic substances increased slowly with the increase of the concentration of oxidant, but the removal rate of UVA₂₅₄ was only 10.1% at 0.75mm. This is mainly due to the increased

concentration of oxidants, the oxidant itself reacts with free radicals, weakening the reaction between free radicals and humic acid.

3.4. Effect of UV dose on molecular weight distribution of organics

The distribution of molecular weight can reflect the change of the content of different organic substances to a certain extent. The organic matter with higher molecular weight flows out first, and the organic matter with lower molecular weight flows out later. The treated water sample is injected into the liquid chromatograph, and the results obtained are shown in Figure 3.

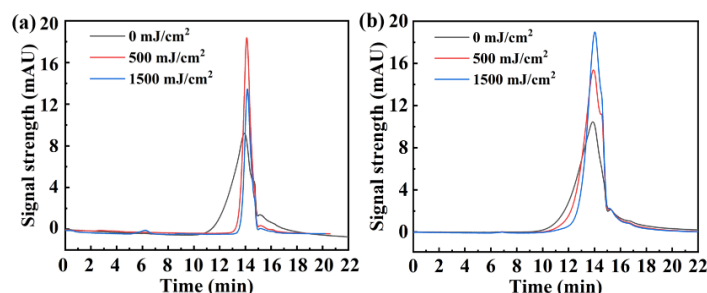


Figure 3. Molecular weight signal diagram (a) UV/Cl₂ pH=6; (b)UV/PDS pH=6

As can be seen from Figure 3(a), before UV/Cl₂ advanced oxidation, the organic matter with molecular weight greater than 1690 Da accounted for about 40%, which decreased sharply after light, and the content was close to 0, indicating a significant degradation effect. The proportion of humic organic matter with molecular weight between 350-1690 Da is nearly half. The content of humic organic matter with molecular weight between 500 mJ/cm² increases sharply, while that with molecular weight <350 Da decreases. The light dose was increased to 1500 mJ/cm², and a small amount of organic matter with molecular weight between 350 and 1690 Da was degraded. These results indicate that UV/Cl₂ mainly acts on humus with molecular weight >1690 Da and degrades it into humus with fewer functional groups and smaller molecular weight. As can be seen from Figure 3(b), after UV/PDS advanced oxidation light of 500 mJ/cm², the content of organic matter with molecular weight >1690 Da decreased, the organic matter with molecular weight <1690 Da increased significantly, and the low molecular weight organic matter decreased. When the light dose increased to 1500 mJ/cm², the organic matter with molecular weight between 1690 and 6520 Da decreased again, and the organic matter with molecular weight less than 1690 Da increased again. After 500 mJ/cm² illumination, UV/Cl₂ has a significant effect on organic matter with molecular weight >1690 Da, and the degradation efficiency exceeds 90%. At the same time, it can fully degrade organic matter with elution time of 15-18min and molecular weight <<1690 Da. UV/PDS mainly acts on organic substances with molecular weight >6520 Da. At 1500 mJ/cm², UV/Cl₂ continues to degrade the products of 500 mJ/cm² light (molecular weight slightly less than 1690 Da), and at the same time degrades a very small amount of the original organic matter with molecular weight <1690 Da into small molecules. At this time, the effect range of UV/PDS is still in the organic matter with molecular weight >6520 Da. It was degraded into organic matter with molecular weight slightly less than 1690 Da and elute time of 13.5-15min. This indicated that there is a certain rule of UV/Cl₂ and UV/PDS on molecular weight: they first oxidize organic matter with larger molecules, and then concentrate on oxidizing organic matter with medium molecular weight after increasing light. UV/Cl₂ can achieve a good effect under a small amount of light, showing a strong reaction activity, while the degradation effect of sulfate radical depends on the gradual increase of light dose.

3.5. Fluorescence spectra under different treatments

Most of the organic matter in the water contains fluorophores, which will produce emission light of characteristic wavelength under the irradiation of specific wavelength excitation light. When the sample concentration is low, the fluorescence intensity is proportional to the luminous substance concentration [8]. Due to the overlap and masking of fluorescence peaks in the atlas, three-dimensional fluorescence

spectroscopy combined with fluorescence region integral method was used to analyze the variation law of dissolved organic matter (DOM) during data processing. DOM was divided into five regions according to differences in structure and composition: Region I, tyrosine aromatic proteins; Region II, tryptophan aromatic proteins; Region III, fulvic acid humus; Zone IV, dissolved microbial metabolites; Zone V, humic acid humus. 3D-EEM technology was used to explore the change rule of typical organic matter in water [8]. After diluting the water sample three times, the water sample was scanned, and ultra-pure water was used as a blank, and the obtained fluorescence data was pretreated, as shown in Figure 4.

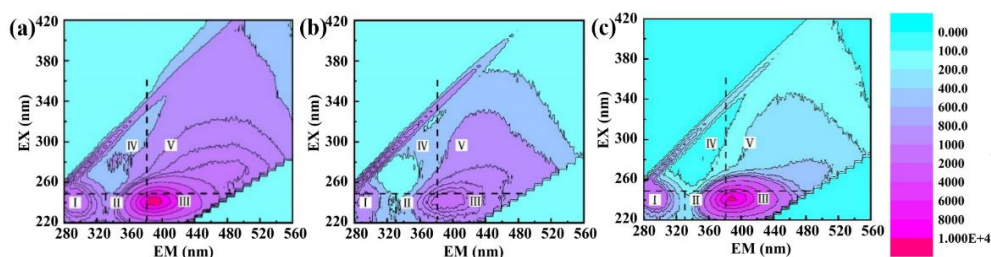


Figure 4. 3D-EEM of representative samples (a) raw water; (b) pH = 7, 500 mJ/cm², sodium hypochlorite concentration of 0.5 mM; (c) pH = 7, 500 mJ/cm², PDS concentration of 0.5 mM

It can be seen from Figure 4 that the overall trend of fluorescence spectra in the five regions is consistent in terms of peak location and concentration differences, indicating that organic matter composition and substance structure are basically the same. The high-concentration fluorescence peaks of the experimental water mainly existed in the region II, III and V, which were typical fulvic humic acids. The integral value of fluorescence intensity in each region and its changes can be seen in Figure 5.

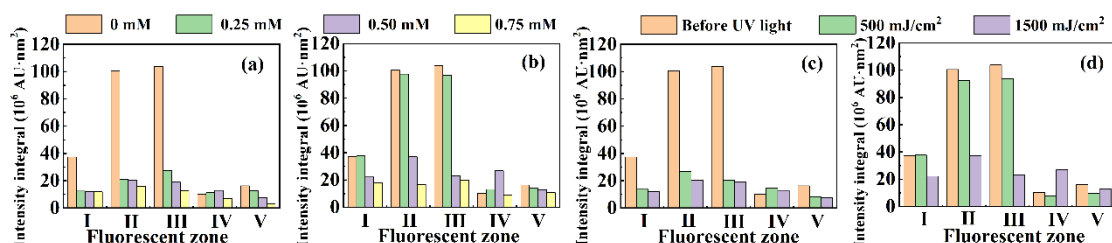


Figure 5. Intensity integral of fluorescence region (a) Different dosages of sodium hypochlorite (b) Different dosage of sodium persulfate (c) different light dose of UV/Cl₂ at pH=7 (d) Different light dose of UV/PDS at pH=7

The light dose of 1500 mJ/cm² was used to investigate the effect of oxidant concentration. As can be seen from Figure 5(a), with the increase of sodium hypochlorite concentration, the integral values of zone II decreased by 78.9%, 79.6% and 84.3%, respectively. Zone III decreased by 73.4%, 81.7% and 87.6%, and zone V changed by 22.5%, 53.4% and 82.4%, respectively. In Figure 5(b), increasing the concentration of sodium persulfate reduced the integral values of zone II by 2.8%, 63.1% and 83.3%, respectively. Zone III decreased by 7.0%, 77.8% and 81.0%, and zone V changed by 12.3%, 20.4% and 34.8%, respectively. In Figure 5(c), after 500 mJ/cm² illumination, the degradation efficiency of zone II reached 73.5%, 80.3% of fluorescent substances in zone III were degraded, and the concentration of zone V was reduced by 50.6%. In Figure 5(d), the degradation efficiency of zone II and zone III reached 7.9% and 9.8% respectively under 500 mJ/cm² light.

As can be seen from Figure 5(a and b), the intensity of the above fluorescence peaks showed a downward trend with the increase of the concentration of oxidant added, especially in region III. These results indicate that free radicals can significantly degrade fulvic acids during UV irradiation. As can be seen from Figure 5 (c and d), UV light activation of free radicals can effectively degrade fluorescent

substances in regions I, II and III. UV/Cl₂, in particular, requires only a small amount of light, the effect is very significant.

4. Conclusion

The concentration of oxidizer decreases with the increase of UV dose, and the concentration of residual oxidizer is the lowest when pH is 6, UV/Cl₂ and UV/PDS consume about 80 per cent and 15 per cent of the oxidant, respectively. Ultraviolet dose can greatly affect the aromaticity of organic matter, and the increase of pH will reduce the removal rate of UVA₂₅₄ and weaken the reaction between free radicals and organic matter. The UVA₂₅₄ removal rate of UV/Cl₂ was significantly higher than that of UV/PDS, about 4 times that of UV/PDS. Increasing the concentration of oxidant can improve the removal rate of UVA₂₅₄, but beyond a certain concentration (Cl₂ 0.5mM, PDS 0.75mM), UVA₂₅₄ no longer decreases, showing a trend of increasing first and then stabilizing. UV/Cl₂ and UV/PDS first degrade organic matter with molecular weight >6520 Da, and dramatically increase the content of organic matter with molecular weight less than 1690 Da. After increasing the light, the oxidation of organic matter with medium molecular weight is concentrated. After illumination, the fulvic acid humus of different samples were effectively degraded. In a certain range, the degradation efficiency increases with the increase of oxidant concentration. The greater the UV dose, the better the degradation effect.

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