The correlation analysis of TOC, COD_{Cr} and fluorescence characteristics in MPR

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Abstract. Water samples from different biochemical reaction time in one reactor period in Micro-Pressure Inner-Loop Bioreactor (MPR) were measured respectively with adopt Excitation-emission matrix (EEM) fluorescence spectroscopy,Total organic carbon (TOC) and chemical oxygen demand (COD_{Cr}),analyzed the correlation among the fluorescence integrates volume,TOC and COD_{Cr}.Results showed that with the increase of biochemical treatment time, sewage fluorescence integrates volume declined significantly, known fluorescence integrates volume,COD_{Cr} and TOC value better correlation,by fluorescence spectrometry analyzed fluorescence characteristics of sewage to determine the organic wastewater degradation effect, can be simpler and more rapid the judgment of the sewage treatment effect.

1 Introduction

MPR is a new sewage treatment process, which has advantages of small footprint and low energy consumption, can realize the existence of three different oxygen regions(anaerobic region, anoxic region and aerobic region)in the same space at the same time.TOC and COD_{Cr} reflected water organic pollution condition[1-4], but contained in municipal wastewater of organic matter is very complicated, potassium dichromate doesn't oxidize all organic compounds in municipal wastewater, the standard analytical method for COD_{Cr} determination is cumbersome to operate, silver sulfate and sulfuric acid mercury reagent is easy to cause secondary pollution, although the TOC analysis measurements can be more comprehensive reflection of the organic pollutants in municipal wastewater, but compared with Excitation-emission matrix (EEM) fluorescence spectroscopy, the latter sample amount needed for the smaller, shorter measure time.In recent years, EEM fluorescence spectroscopy widely applied in wastewater treatment field, with higher sensitivity, can be fully dissolving organic matter in water identification and resolution, also gets the benefits of high selectivity and high amount of information[5].

This paper is mainly based on FRI analysis method to analyze the DOM of sewage in the process of MPR reactor treatment.Set up the correlation of COD_{Cr}, TOC and DOM content, to broaden the application of three-dimensional fluorescence spectrometry and realize the rapid and accurate monitoring of municipal wastewater, in order to optimize the MPR operation, management, provide the specialized reference and support.

2 Materials and methods

2.1 Samples collections

Water samples are gathered in the MPR. The main body of the MPR is made from the processing of plexiglass, which is divided into two parts.The upper part is open, and the size is 500mm×80mm×60mm. The lower part is the primary reaction zone, with the size of 800mm×600mm×110mm. The perforated aerator is installed at the bottom, and the single point aeration is performed by an air compressor. The effective volume of the reactor is 54L[6].

The activated sludge was inoculated from an aeration tank of a sewage treatment plant in changchun. The sewage was derived from the domestic sewage of a municipal sewage treatment plant in the south of changchun. The operation cycle of MPR is 12h, with restricted aeration, instantaneous water inlet, aeration for 7h, precipitation for 4h, and idling for 1h. Aeration capacity is 3.5mg/L, and the PH is controlled between 8.0-8.5. In the experiment, the water temperature was kept at 11±1℃ in a constant temperature room.

In this study, total of seven samples was collected, including influent water , effluent and five different time water samples.Beginning time of sampling was 8 o 'clock in the morning, and the sampling interval time was two hours. All the measured diachronic water samples were mixed water samples, which were filtered by 0.45μm filter membrane and stored in the refrigerator at 4℃ for use.

2.2 Samples measure methods

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TOC was established by TOC-5000A of Shimadzu Corporation of Japan.The method for detecting COD_{Cr} is the dichromate method (HJ 828-2017).EEM spectra was established by Hitachi F-7000 fluorescence spectrophotometer. PMT voltage:700V,Slit:Ex=5nm, Em=5nm,Response time: auto,EEM spectra scanning excitation wavelength Ex = 200 ~ 450 nm, emission wavelength of Em = 250 ~ 550 nm;scanning speed: 2400 nm/min,the fluorescence EEM of each samplesubtracted the fluorescence EEM of Milli-Q water.

2.3 Fluorescence data analyses

To avoid second-order Rayleigh scattering on the EEM spectra, a cutoff filter of 295nm was inserted on the side of the fluorescence emission. EEM spectra before parsing, first through the reduction of blank and interpolation method,then emission wavelength is greater than or equal to 1 times the excitation wavelength in the region and its adjacent area (plus or minus 20 nm) zero,the result of the modified EEM spectra is a Rayleigh scattering and the area of Raman scattering effects, then used the fluorescent area integral (FRI) for quantitative analysis of EEM spectra. EEM spectra was divided into 5 regions, in which the regions I and II were Ex/Em=(200~250)nm/(280~330)nm and Ex/Em=(200~250)nm/(330~380)nm. The areas of region III and IV are Ex/Em=(200~250)nm/(380~550)nm and Ex/Em=(250~450)nm/(280~380)nm, respectively. The range of region V is Ex/Em=(250~450)nm/(380~550)nm[7]. Fluorescent area integral volume Φ_i calculated by Origin9.1,calculate accumulation fluorescence intensity of fluorescence region I,II,III,IV,V, then the integral of the five region area volume for standardization, get the area volume integral standardized $\Phi_{i,n}$, said fluorescent area in a specific structure relative content of organic matter. SPSS22.0 was utilized to test the correlation levels between COD_{Cr} and TOC of water samples and the fluorescence integral volumes of each fluorescence region.

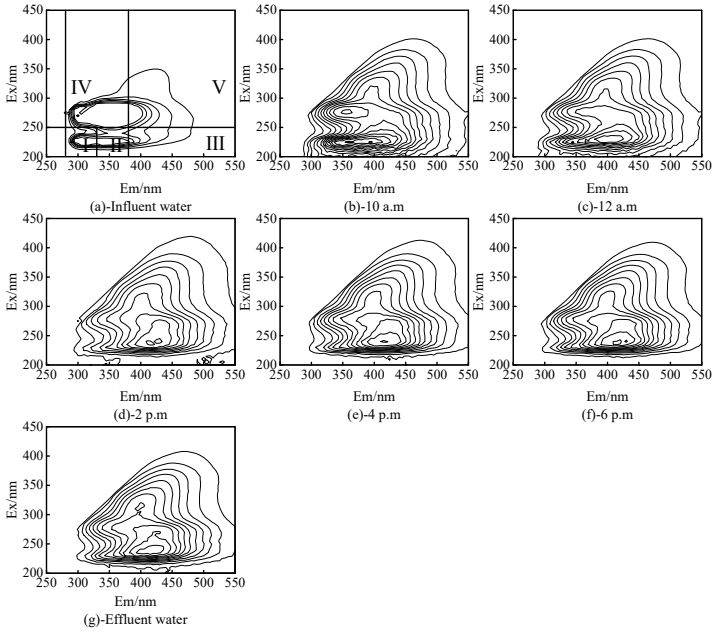

Fig.1. EEMs of the DOM in MPR with different time

3 Results and discussion

3.1 Integral analyses of fluorescence region in MPR

Depending on FRI calculation method, get the EEM spectra of five regional volume integral standard $\Phi_{i,n}$ (table 1). The Figure 1 showed that the region I fluorescent signal is mainly composed of tyrosine protein such as organic produce,region II mainly associated with aromatic proteins,the fluorescence signal of region III is mainly generated by substances such as fulvic acid, phenols and quinones in the ultraviolet region, region IV is mainly composed of microbial metabolites produced fluorescence in the process of sewage treatment, such as protein, coenzyme, small molecule organic acids, pigment, etc. Region V is related to the organics with large molecular weight and high degree of aromatization, such as fulvic acid, humic acid and polycyclic aromatic hydrocarbon in visible light region.Every region is integral standardized volume $\Phi_{i,n}$ indirectly characterize the five fluorescent areas represent the relative content of soluble organic matter.

It can be seen from table 1 that the fluorescence characteristics of samples are different with the separate

treatment time.With the reduction of TOC, COD_{Cr},each region integral standardized volume $\Phi_{i,n}$ also decreases.It showed that the fluorescence spectrum of sewage can reflect the organic pollution degree of sewage correctly, and the advantages and disadvantages of sewage treatment effect can be preliminaries judged. After biochemical treatment, TOC decreased significantly, that the integral volume sum of five regional conveniently reduces, dropped of 77.3%.

Table 1. $\Phi_{i,n}$ of wastewater samples at different time point

	Influent water	10 a.m	12 a.m	2 p.m	4 p.m	6 p.m	Effluent water
TOC(mg/L)	188.73	7.672	4.744	4.406	5.573	5.576	5.441
CODcr(mg/L)	505.7	46.65	25.58	18.06	16.55	19.56	12.04
$\Phi_{I,n}$（$\times10^{-5}$）	2167.7	606.4	356.7	98.8	123.5	93.3	90.6
$\Phi_{II,n}$（$\times10^{-5}$）	2251.1	1246.4	860.4	378.8	443.7	355.3	349.9
$\Phi_{III,n}$（$\times10^{-5}$）	790.4	1171.3	970.9	545.3	623.4	509.5	509.5
$\Phi_{IV,n}$（$\times10^{-5}$）	2160.6	586.5	494.9	419.7	438.9	416.3	390.8
$\Phi_{V,n}$（$\times10^{-5}$）	760.3	587.7	572.2	530.4	561.1	518.6	507.1
$\sum\Phi_{i,n}$（$\times10^{-5}$）	8130.2	4198.3	3255.1	1972.9	2190.6	1892.9	1847.9

3.2 Correlation between fluorescence index and COD_{Cr} and TOC

TOC reflects the total content of soluble organic compounds in wastewater, and the integral standardized volume $\Phi_{i,n}$ represents the different types of fluorescent substances content in the wastewater. Linear regression analysis was carried out between the fluorescence integral volume in water samples and the measured CODcr and TOC values.The table 2 showed that water samples of $\Phi_{i,n}$ and CODcr, TOC value can be set up in good correlation. $\Phi_{i,n}$ of Regional I, II,IV,V in EEM and TOC Pearson index above 0.9, including regional I and IV reached 0.970 and 0.996 respectively.

In 11℃ temperature environment,after biochemical treatment, water samples of TOC and CODcr of Pearson correlation coefficient of 0.999, CODcr and $\Phi_{V,n}$ Pearson correlation coefficient is 0.999, it showed that the COD_{Cr} and TOC data in wastewater can be preliminaries obtained by three-dimensional fluorescence spectroscopy, so as to judge the organic pollution of wastewater.

Table 2. Analysis of correlation between COD_{Cr}、TOC and different fluorescence indices

	TOC	CODcr	$\Phi_{I,n}$	$\Phi_{II,n}$	$\Phi_{IV,n}$	$\Phi_{V,n}$	$\sum\Phi_{i,n}$
Pearson Correlation Coefficient	1	0.999**	0.970**	0.884**	0.996**	0.943**	0.927**
	0.999**	1	0.980**	0.905**	0.999**	0.955**	0.944**

Note :** indicates that the significance level is 0.01, that is, the $P < 0.01$ level.

4 Conclusion

In the biochemical process,organic pollutants in sewage mainly come from dissolved organic matter, which is the main object of MPR.The results showed that the water samples of integral standardized volume $\Phi_{i,n}$ with the sewage COD_{Cr}, TOC has strong linear relationship,between the TOC and COD_{Cr} of Pearson correlation coefficient of 0.999, COD_{Cr} and $\Phi_{IV,n}$ Pearson correlation coefficient is 0.999, which has good linear correlation. At the same time, the three-dimensional fluorescence method has the characteristic of a short analysis time, which indicates that direct analysis of the integral standardized volume of corresponding water samples can quickly obtain the relevant information of organic pollutants. Therefore, during the operation of MPR , the three-dimensional fluorescence method can be utilized to analyze the sewage water samples in MPR , so as to quickly evaluate the pollution situation and treatment effect of sewage.

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