Monitoring of COD as an organic indicator in waste water and treated effluent by fluorescence excitation-emission (FEEM) matrix characterization

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Abstract The fluorescence excitation-emission matrices (FEEM) of domestic waste water, treated effluent of a waste water treatment plant and receiving river water were analyzed to select wavelengths for the monitoring of organic contents as COD.

Excitation/emission wavelengths of 220/350 nm and 270/350 nm for protein-like fluorescence and 240/450 nm and 340/450 nm for humic-like fluorescence were suggested as fluorescence peak emitting wavelength pairs, respectively. Without any pre-treatment, the protein-like fluorescence peaks showed better correlation between COD values and fluorescence intensities than the humic-like fluorescence peaks. No enhanced correlation was observed by removing the suspended solids from the samples using filtration. However, statistical multiple regression methods, using the fluorescence intensities from each peak and the light scattering intensity at 633 nm as variables, resulted in an enhanced correlation, with $r^2 > 0.9$ for the measured and predicted COD values.

Keywords COD; fluorescence; quality monitoring; SS; waste water

Introduction

To protect and manage the quality of the water environment, monitoring strategies are essential. Successful monitoring of water quality can be achieved by reliable analysis methods. Recently, real-time monitoring has gained greater attention for the prevention of water pollution accidents and in the protection of aqueous ecosystems. It is also important to implement real-time on-line monitoring technology in water pollution control facilities, such as waste water treatment plants, for the optimization of process performance.

For the purpose of water quality management, a series of indicators have been developed and applied. The chemical and biological oxygen demands (COD and BOD, respectively) have been widely accepted as surrogate indicators of organic contaminants in water. Wet chemical methods as standard procedures for the determination of values for indicators have been established. However, the procedures are tedious and time consuming, and cannot be applied to real-time quality monitoring of natural and waste water. The BOD test needs 5 days for a result to be obtained. The COD values of collected samples can be obtained by a series of steps, including 1–2 hours of chemical digestion, but this also leads to the production of chemical waste.

To resolve these problems, optical sensing technologies, based on the UV absorption properties of natural water and wastewater at 200–350 nm, have been suggested (Dobbs *et al*., 1972; Mrkva, 1975, 1983; Edwards and Cresser, 1987; Galvin *et al*., 1994; Khorassani *et al*., 1999). Instruments using the correlation between wet chemical results and the absorbance at 254 nm are commercially available. The major drawback of this technology is the requirement for frequent cleaning of the optical components and re-calibration of the correlation curves.

Recently, optical sensing technology, using fluorescence, has been explored for environmental monitoring. Synchronous fluorescence spectroscopy (SFS) was applied to

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selected major peaks related to biodegradable and non-biodegradable components in sewage samples (Reynolds and Ahmad, 1995, 1997), and to differentiate sewage-originated organic components from organic matters in natural water samples (Ritchelita *et al*., 1998). NAD(P)H fluorescence has been used to monitor biological treatment processes (Isaacs and Henze, 1994; Ju *et al*., 1995; Tartakovsky *et al*., 1996; Li and Ju, 1999).

In the present study, the fluorescence excitation-emission matrices (FEEM) of a domestic waste water, treated effluents of the waste water and the receiving river water were analyzed to select the most appropriate wavelengths for the monitoring of organic contents, such as the COD. Enhancement of the correlation was also suggested by statistical multiple regression using the light scattering intensity.

Materials and methods

Tested samples

Influents (Inf), treated effluents (T1–4) from a domestic waste water treatment plant (WWTP) and the receiving river waters of the effluents (RW) were collected for a 3 month period, and used for the present study. The WWTP was operated to treat domestic waste water using an activated sludge type biological treatment process. The WWTP consisted of three treatment process lines and one pilot scale experimental set-up; therefore, collected samples were labeled as T1, T2, T3 and T4, respectively. Collected samples were analyzed for their FEEM using a luminescence spectrometer, and the COD and SS by wet chemical methods. Table 1 summarizes the characteristics of the tested samples.

Analytical methods

The fluorescence and light scattering were analyzed using a luminescence spectrometer (LS-50B, Perkin Elmer), with FEEM analysis excitation and emission wavelength varying from 200 to 400 nm and from 200 to 500 nm, respectively. The slit width was set to obtain the FEEM at 5 nm intervals. Figure 1 shows a typical image from the FEEM analysis of the tested samples.

Results and discussion

From the FEEM analysis shown in Figure 1, the emission peaks at the excitation/emission wavelength pairs of 220/350 nm, 270/350 nm, 240/450 nm and 340/450 nm were selected. It has been reported that natural water shows a humic-like fluorescence emission peak at 420–450 nm by excitation at 230–260 nm, and a protein- or amino acid-like emission peak at 340–350 nm by excitation at 220 and 275 nm (Smart *et al*., 1976). All the samples in the present study showed strong excitation/emission intensities at around 220/350 nm and 240/450 nm. These two peaks were assigned as a protein-like fluorescence peak 1 (PF1) and humic-like peak 1 (HF1), respectively. Two weak peaks, at 270/350 nm and 340/450 nm, were also labeled as PF2 and HF2, respectively.

Table 1 Characteristics of tested samples for the present study

		COD, mg/l (average)	SS, mg/l (average)
Raw wastewater	(Inf)	132.4	65.1
Treated effluents	(T1)*	33.2	15.6
	(T2)*	38.7	11.8
	(T3)*	43.1	13.2
	(T4)**	17.3	7.5
Receiving river water	(RW)	19.2	37.4

* T1–T3 :Treated secondary effluents by full scale activated sludge processes

** T4 : Treated secondary effluent from pilot scale experimental set-up

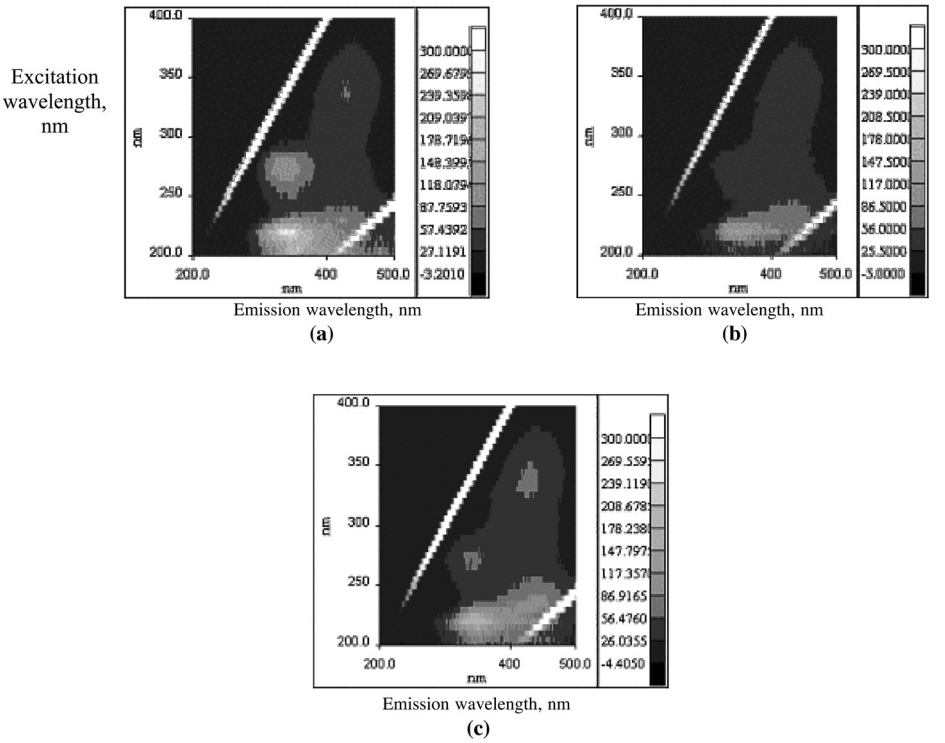

Figure 1 Contour presentation examples of the FEEM analysis for (a) raw waste water (Inf), (b) treated effluent (T2), and (c) receiving river water (RW)

Intensity ratios of the raw waste water to that of the treated effluent at each peak varied, as shown in Table 2. The ratios at the PF peaks were larger than unity, suggesting the reduction in the bio-degradable contents, like protein- or amino acid-like components, by the biological treatment process. The ratios varied with the different process lines due to their differing performances. The PF peak reduction by the T4 process was the most significant among the process lines, showing good consistency with the COD removal performance. This result proposes a close link between the COD removal by biological domestic waste water treatment and the reduction of the PF peaks. Conversely, none of the HF peaks were decreased by the waste water treatment. Rather, in the case of HF1, slight increases in the intensities for the T2 and T3 process lines were observed. Therefore, the HF1 peak has the potential to be used as a tentative indicator of non-biodegradable humic-like organic compounds. Figure 2 shows the plot of the fluorescence intensity ratios of the tested samples at PF2 vs. HF1, which were suggested as indicator peaks of biodegradable and non-biodegradable organics, respectively.

Figure 3 show the correlation relationship between the fluorescence intensities at each

Table 2 Change of fluorescent intensity ratio

Peak	FL(Inf)*/FL(Eff)**			
	T1	T2	T3	T4
PF1	1.2–1.7	0.8–12.8	0.8–1.1	6.8–15.1
PF2	1.5–2.4	1.0–2.4	1.1–1.7	2.8–5.1
HF1	1.0–1.4	0.7–0.8	0.6–0.8	1.0–1.4
HF2	1.0–2.2	0.8–1.4	0.8–1.6	1.0–1.9

* FL(Inf): fluorescent intensity of raw wastewater
** FL(Eff): fluorescent intensity of treated secondary effluents (T1–4)

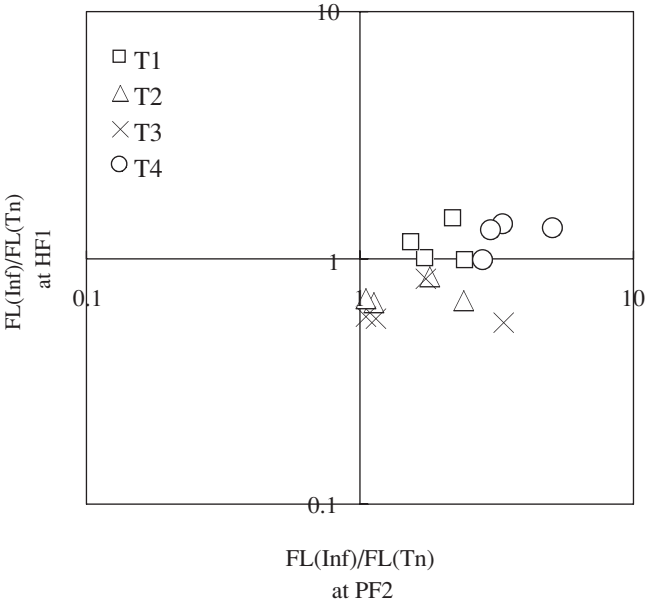

Figure 2 Fluorescence intensity ratio (raw waste water/treated effluents) plot: protein-like fluorescence peak 2 (PF2) vs. humic acid-like fluorescence peak 1 (HF1)

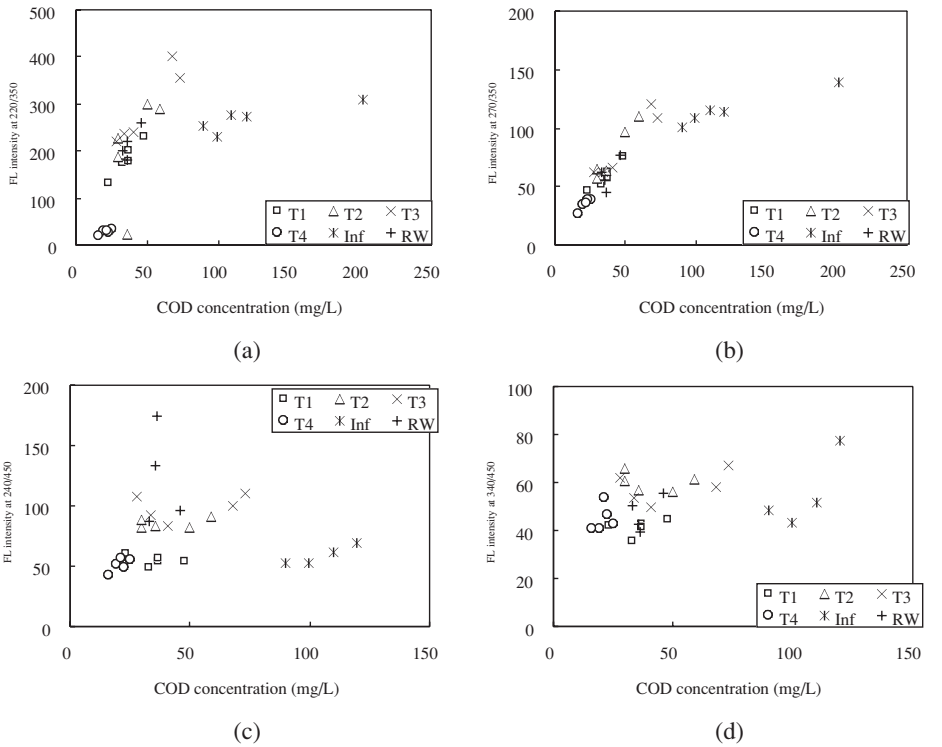

Figure 3 COD vs. fluorescence intensity at (a) 220/350 nm (PF1), (b) 270/350 nm (PF2), (c) 240/450 nm (HF1) and (d) 340/450 nm (HF2) (T1, T2, T3: treated effluents from C WWTP using a typical activated sludge process, T4: treated effluent from advanced waste treatment process, Inf: raw waste water to C WWTP, RW: river water receiving the treated effluents)

peak and the COD values of the tested samples. The PF peaks showed good correlation between the fluorescence intensities and the measured COD values. Monitoring of the fluorescence intensity at the 270/350nm excitation/emission wavelength pair (PF2) appeared to give a reliable linear correlation for the determination of the COD at each sampling point. However, a noticeable discrepancy was observed between the raw waste waters (Inf) and the treated effluents (T1–4) from a single linear regression line. For the HF peaks, no significant correlation was observed.

A group of test samples were filtered with 0.45 micrometre MF disk filters, to prevent the influence of suspended particles, prior to measuring the fluorescence intensities at each peak. These results are shown in Figure 4, with the plots being very similar for those of the non-filtered samples (Figure 3), leading to the conclusion that the peak intensities were free from the influence of suspended particles. However, water samples contain a reasonable amount of insoluble organics. Table 3 shows that the treated effluent samples in the present

Table 3 Total COD and soluble COD in secondary effluents

	T-COD, mg/L	S-COD, mg/L	S-COD/T-COD, %	SS, mg/L
T1	23	15	65	7.0
T2	30	21	70	8.3
T3	28	20.5	73	6.7
T4	21.5	12	56	10.5

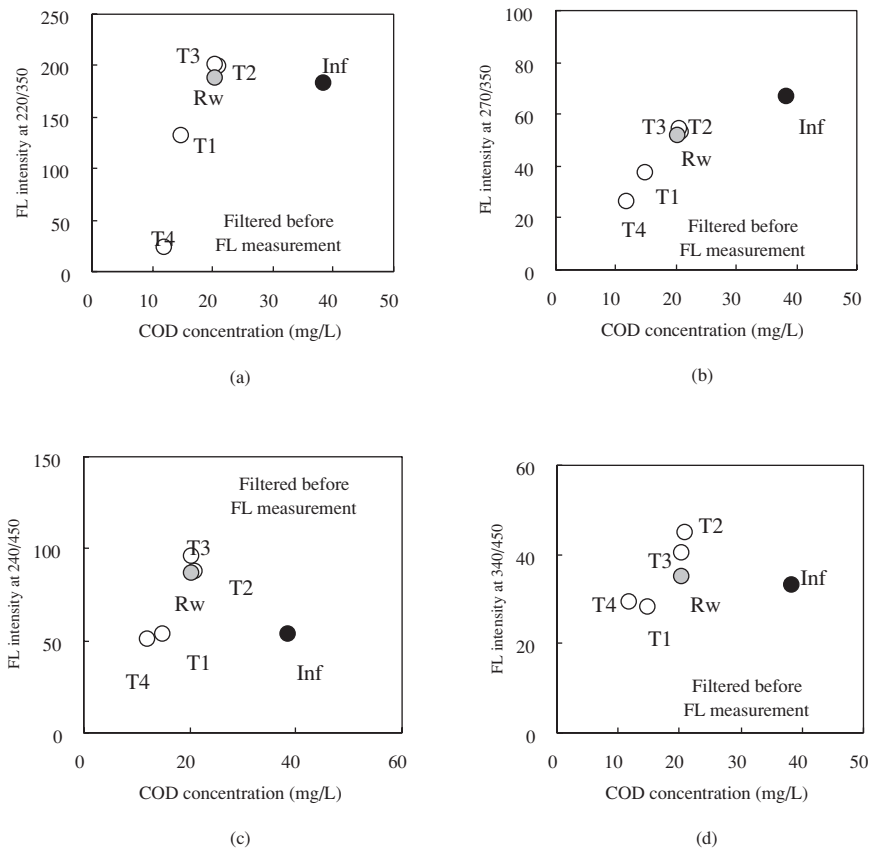

Figure 4 COD vs. fluorescence intensity at (a) 220/350 nm(PF1), (b) 270/350 nm(PF2), (c) 240/450 nm (HF1) and (d) 340/450 nm (HF2) (samples were analyzed for COD and fluorescence intensity after 0.45 µm MF filtration)

study had only 56–73% soluble form organic contents, as expressed by the COD. Raw waste waters and river waters also have suspended solids (SS), which include a certain amount of organic compounds. Therefore, it is clear that the presence of suspended organics in the samples should be taken into consideration in the calculation to obtain a better correlation relationship between the optical and wet chemical measurements.

To resolve the problem of the suspended contents, the light scattering intensity at 633nm, based on the previous study, was selected and measured as an indicator of suspended organic particles in the tested samples (Figure 5). This value and the fluorescence intensities at the PF2 peak were then used as independent variables for a multiple linear regression, and the COD values as a dependent variable.

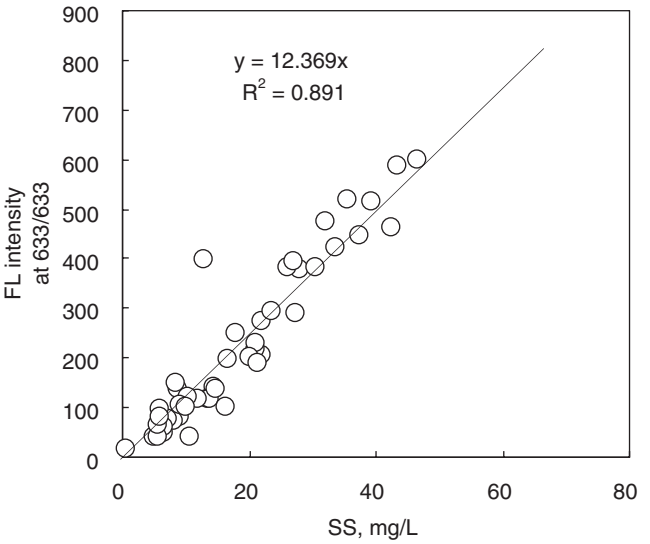

Figure 5 Light scattering intensity measured at 633nm vs. SS concentration for all tested samples

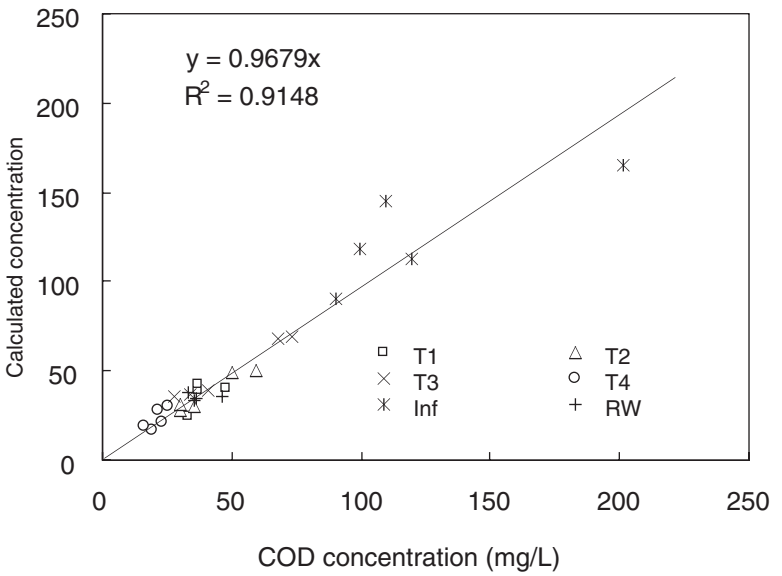

Figure 6 Correlation between measured COD values by wet method and calculated COD values by multiple regression method using fluorescent intensity at 240/450 nm (PF2) and light scattering intensity at 633 nm, respectively

Figure 6 plots the measured COD value by the wet chemical method vs. that of the calculated COD values. Compared to the result of Figure 4, an enhanced prediction model for COD monitoring was calculated ($r^2 > 0.9$) for all the samples irrespective of the sampling point.

Conclusions

From the present study, the following conclusions can be summarized. 1) From the fluorescence excitation/emission matrix analyses for domestic waste water, treated effluents and receiving river water, the 220/350 nm and 270/350 nm excitation/emission wavelengths for protein-like fluorescence and 240/450 nm and 340/450 nm for humic-like fluorescence were selected as fluorescence peak emitting wavelength pairs, respectively. 2) The protein-like fluorescence intensity at 270/350 nm showed the best correlation with the COD values obtained by the wet chemical method. 3) The light scattering intensity at 633nm, as an indicator of suspended organic content, can be used to enhance the correlation using a multiple regression model.

Acknowledgement

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