

Characterisation and biological treatability of “Izmit industrial and domestic wastewater treatment plant” wastewaters

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Abstract

We investigated the conventional characterisation and biological treatability of wastewaters of the “Izmit Industrial and Domestic Wastewater Treatment Plant”. Respirometric procedures were carried out for the experimental assessment of organic contents of wastewater. The mean value of total COD was 1201 mg·l⁻¹ and varied within a wide range of 580 to 1822 mg·l⁻¹ for the 14 different influents. The soluble COD concentrations were evaluated to vary in the range of 168 to 1061 mg·l⁻¹, with a mean value of 615 mg·l⁻¹. The readily biodegradable organic substance, S_s is between 0.03 to 0.24% of the influent total COD. The BOD₅/total COD ratio in the influent was calculated as 0.20 to be a mean value. The evaluation of this result, wastewater was not suitable for biological treatment. But, the results of COD fractionation studies indicate that the organic content of wastewater is mostly biodegradable (84-92%). Therefore, conventional wastewater characterisation does not enable for a reliable design of biological treatment processes.

Keywords: Conventional characterisation, COD fractionation, biological treatability, oxygen uptake rate.

Nomenclature

COD	chemical oxygen demand (mg·l ⁻¹)
BOD	biological oxygen demand (mg·l ⁻¹)
SS	suspended solids (mg·l ⁻¹)
VSS	volatile suspended solids (mg·l ⁻¹)
TKN	total kjedhal nitrogen (mg·l ⁻¹)
OUR	oxygen uptake rate (mg·l ⁻¹)
ΔO	the difference between total respiration and respiration due to hydrolysed substrate and endogenous metabolism (mgO ₂ l ⁻¹)
C _T	total COD of wastewater (mg·l ⁻¹)
C _S	total biodegradable COD of wastewater (mg·l ⁻¹)
S _I	soluble inert COD of wastewater (mg·l ⁻¹)
S _S	readily biodegradable COD of wastewater (mg·l ⁻¹)
S _H	rapidly hydrolysable COD of wastewater (mg·l ⁻¹)
S _T	total soluble COD of wastewater (mg·l ⁻¹)
X _I	particulate inert COD of wastewater (mg·l ⁻¹)
X _S	slowly biodegradable COD of wastewater (mg·l ⁻¹)
Y _H	heterotrophic yield coefficient [mg cell COD (mg COD) ⁻¹]

Introduction

Characterisation of wastewater and activated sludge has been used for control and optimisation of existing processes, and development of new processes. COD as a basis for organic matter measurements has replaced BOD as the primary parameter in wastewater. The important aspect of organic matter characterisation is the fractionation due to its rate of degradation (Henze, 1992). COD may be used as a direct parameter to yield the stoichiometric equivalent of carbonaceous substrate, with the provision that its biodegradable fraction is ascertained. This fraction reflects the

appropriate electron balance between substrate, biomass and the electron acceptor (Orhon et al., 1999b). COD fractionation involves identification of inert and biodegradable COD together with readily biodegradable and slowly biodegradable fractions. The inert fraction may be further subdivided into soluble inert COD (S_I) and particulate inert COD (X_I). S_I in the influent bypasses the system without affecting the biochemical reactions in the reactor, whereas the X_I is entrapped, accumulates in the activated sludge and leave the system through the sludge wastage stream (Orhon and Ubay Çokgör, 1997).

The experimental assessment of inert soluble and particulate COD of different wastewaters under aerobic and anaerobic conditions has been discussed previously in the literature (Ekama et al., 1986; Germirli et al., 1991; Orhon et al., 1994; Orhon et al., 1999; Ince et al., 1998).

In the literature, various respirometric methods have been proposed for estimating the readily and slowly biodegradable COD fractions. (Ekama et al., 1986; Henze et al., 1987; Xu and Hasselblad, 1996; Kappeler and Gujer, 1992; Mathieu and Etienne, 2000).

Spanjers et al. (1996), indicated that respirometry is a powerful alternative tool for assessing the condition of activated sludge systems because the oxygen utilisation rate can be monitored easily.

The “Izmit Industrial and Domestic Wastewater Treatment Plant” (IIDWTP) is a plant where raw domestic wastewaters and pretreated industrial wastewaters of various sectors such as tyre, drug, chemistry, yeast industries which have been discharged to collectors are treated biologically. Design of an activated sludge process has a significant importance with respect to high treatment efficiencies and constructional and operational costs of plants. The purpose of this study was to investigate the conventional characterisation and biological treatability of wastewaters of IIDWTP.

Materials and methods

The respirometric procedure for the assessment of the readily biodegradable COD consisted of running 1.5 l batch reactors. The

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TABLE 1
The characterisation of influents for IIDWTP

Sampling time	pH	COD, mg·l ⁻¹		SS, mg·l ⁻¹	VSS, mg·l ⁻¹	TKN, mg·l ⁻¹	NH ₃ -N, mg·l ⁻¹	Total P, mg·l ⁻¹	BOD ₅ , mg·l ⁻¹	Alkalinity, mg CaCO ₃ ·l ⁻¹
		Total	Soluble							
13.03.2001	8.03	749	422	305	275	151	67	4.25	-	-
26.04.2001	8.20	653	634	345	255	134	52	3.33	-	-
14.05.2001	8.91	1 296	691	580	425	101	95	2.93	320	-
28.05.2001	7.50	864	576	315	285	98	-	-	165	1720
28.06.2001	8.30	1 824	326	910	680	174	-	1.87	275	-
31.07.2001	7.57	1 077	59	2 765	2 470	50	3	8.68	150	-
30.09.2001	7.11	2 736	1 924	727	600	159	111	7.12	470	-
15.10.2001	7.91	1 901	1 002	245	215	160	119	5.32	170	2344
05.11.2001	7.45	1 505	830	256	232	86	78	5.18	545	-
24.12.2001	7.69	385	206	164	113	74	25	3.23	55	-
23.01.2002	8.05	1 241	488	751	631	-	-	-	420	-
24.01.2002	7.80	789	460	324	288	172	83	4.84	235	-
27.02.2002	7.94	1 012	552	220	180	111	103	3.85	172	1720
08.04.2002	7.56	782	434	143	116	68	47	2.43	70	1040
Average	7.86	1 201	614.57	575	483.21	118.31	71.18	4.42	253.92	1706
Std. dev.	0.44	621.28	446.46	674.31	601.07	42.49	36.59	1.97	156.68	532.6
Minimum	7.42	579.72	168.12	99.31	117.85	75.82	34.59	2.45	97.24	1173.4
Maximum	8.30	1 822.28	1 061.03	1 249.31	1 105.71	160.80	107.77	6.39	410.59	2238.6

(-): not analysed

TABLE 2 BOD₅/Total COD ratios of influents	
Sampling time	BOD ₅ /COD
14.05.2001	0.25
28.05.2001	0.19
28.06.2001	0.15
31.07.2001	0.14
30.09.2001	0.17
15.10.2001	0.09
05.11.2001	0.36
24.12.2001	0.14
23.01.2002	0.34
24.01.2002	0.30
27.02.2002	0.17
08.04.2002	0.09
Average	0.20

TABLE 3 Results of inert COD experiment for the Study A				
Time	Reactor 1 Fed with raw wastewater (COD, mg·l ⁻¹)		Reactor 2 Fed with filtered wastewater (COD, mg·l ⁻¹)	
	C _T	S _T	C _T	S _T
Start of experiment	5 068	1971	1549	1267
End of experiment	683	580	271	252
Duration, h	576	576	576	576

nitrification inhibitor (AQUALYTIC Nitrifikationshemmer B) was used in the OUR test. The reactor was constantly aerated to maintain a dissolved oxygen concentration of 6 to 8 mg·l⁻¹. The biomass was previously acclimated to the wastewater and glucose in a fill and draw reactor operated in an aerobic condition at a sludge age of 9 to 11 d. Aliquots were removed from reactors every 5 to 10 min for OUR measurements. OUR measurements were conducted with a WTW OXI 3000 oxygenmeter and P500 recorder. In the experiments, the pH value of samples was not adjusted because the pH value of influents was 7 to 8. The tests were carried out at room temperature.

In the study of conventional characterisation; the grab samples, which have been taken monthly during a year, were used. The

biological treatability of wastewaters was performed on three different samples, which were characterised November 2001 (Study A), February 2002 (Study B) and April 2002 (Study C).

All analyses were performed as defined in *Standard Methods* (1995). The soluble COD was defined as the filtrate through Millipore AP40 filters, also used in the determination of VSS and SS. The activated sludge was supplied from the IIDWTP and used after adaptation for laboratory conditions.

Experimental results

Results of conventional characterisation

The results of characterisation experiments are given in Table 1. The total COD concentration was 580 to 1822 mg·l⁻¹, with a soluble fraction of 161 to 1061 mg·l⁻¹. The BOD₅/total COD ratios of influents are shown in Table 2.

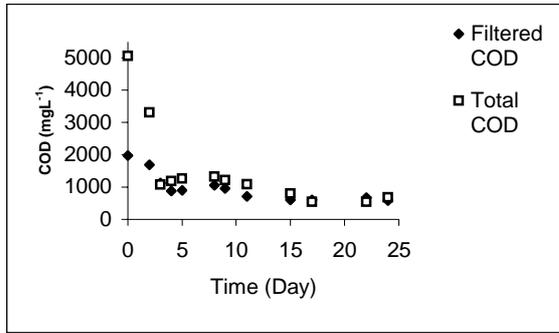


Figure 1
COD profile in reactor 1

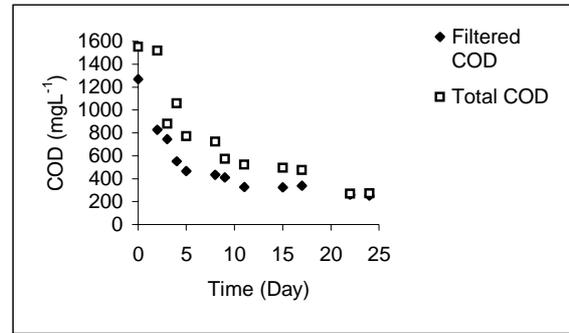


Figure 2
COD profile in reactor 2

Results of experiments carried out on COD fractionation

The inert COD fraction of the Study A was determined using the procedure proposed by Orhon et al. (1994). Both soluble and particulate inert microbial products, S_p and X_p can be expressed as a constant fraction of the influent biodegradable COD in that procedure. The experiment requires two aerated batch reactors, one started up with the unfiltered wastewater (C_T) and the other with the filtered wastewater (S_T). In each reactor, total and soluble COD are monitored for a period long enough to ensure the depletion of all biodegradable substrate and the mineralisation of all biomass, so that the measured C_T and S_T values reach their constant threshold levels containing only initial inert COD and residual products. Both reactors are initially seeded by a minimal amount of biomass previously acclimated to the wastewater to avoid the interference of residual COD released through the decay of the initial inoculation. It is suggested that the acclimatisation be carried out in fill and draw systems operated at F/M ratios over $1.0 \text{ g COD (g VSS)}^{-1} \text{ day}$ to ensure a highly viable biomass, and the amount of seed is adjusted between 10 to $50 \text{ mg}\cdot\text{l}^{-1}$, depending on the nature of the wastewater to be tested. This method for the assessment of inert COD fraction is applicable to wastewater samples with a reasonably large particulate COD fraction. The results of inert COD experiment for Study A are given in Table 3 and illustrated in Figs. 1 and 2.

The evaluation of the inert COD experiment for Study A is summarised in Table 4.

Because the particulate COD fractions of influent were not large enough in Study B and Study C, the soluble inert COD was determined by the procedure proposed by Germirli et al. (1991). The method depends on the measurement of soluble COD of two aerobic reactors (glucose and filtered wastewater reactors) seeded with the same amount of biomass previously acclimated to the glucose-wastewater mixture. At the end of the experiment when all biodegradable substrates in the two reactors are depleted, the soluble inert fraction can be calculated from the difference between the COD values of the wastewater and glucose reactors.

In Study B, the filtered wastewater sample had an initial soluble COD of $570 \text{ mg}\cdot\text{l}^{-1}$ in the first batch reactor. The second reactor was supplemented by glucose with the same COD concentration. The test was continued for 600 h. And in Study C, the filtered wastewater sample had an initial soluble COD of $325 \text{ mg}\cdot\text{l}^{-1}$ in the first batch reactor. The second reactor was supplemented by glucose with the same COD concentration. The test was continued for 696 h. The results are illustrated in Figs. 3 and 4.

TABLE 4
Evaluation of the inert COD experiment for the Study A

$$C_{T1} - S_{T1} = X_{P1} + X_I = 103.15 \text{ mg}\cdot\text{l}^{-1}$$

$$C_{T2} - S_{T2} = X_{P2} = 19 \text{ mg}\cdot\text{l}^{-1}$$

$$\Delta C_{T1} = C_{T0} - C_{T1} = C_{S0} - S_{P1} - X_{P1} = 4384.62 \text{ mg}\cdot\text{l}^{-1}$$

$$\Delta C_{T2} = S_{T0} - C_{T2} = 1277.8 \text{ mg}\cdot\text{l}^{-1}$$

$$X_{P1} = X_{P2} (\Delta C_{T1} / \Delta C_{T2}) = 65.19 \text{ mg}\cdot\text{l}^{-1}$$

$$X_I = (C_{T1} - S_{T1}) - X_{P1} = 37.96 \text{ mg}\cdot\text{l}^{-1}$$

$$S_{T1} - S_{T2} = S_{P1} - S_{P2} = 328.23 \text{ mg}\cdot\text{l}^{-1}$$

$$S_{P1} = (S_{T1} - S_{T2}) / [1 - (\Delta C_{T2} / \Delta C_{T1})] = 463 \text{ mg}\cdot\text{l}^{-1}$$

$$S_I = S_{T1} - S_{P1} = 117 \text{ mg}\cdot\text{l}^{-1}$$

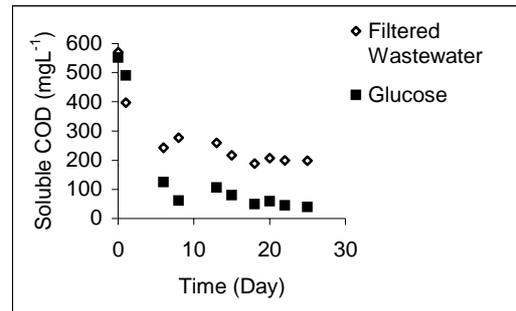


Figure 3
COD profiles of filtered wastewater and glucose reactor (Study B)

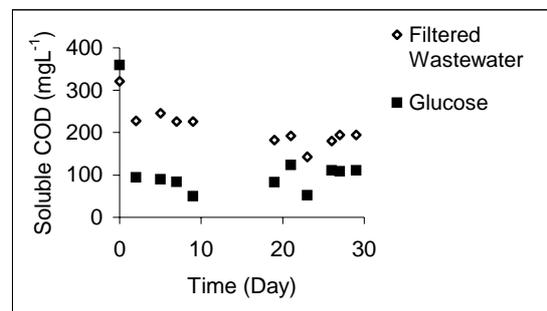


Figure 4
COD profiles of filtered wastewater and glucose reactor (Study C)

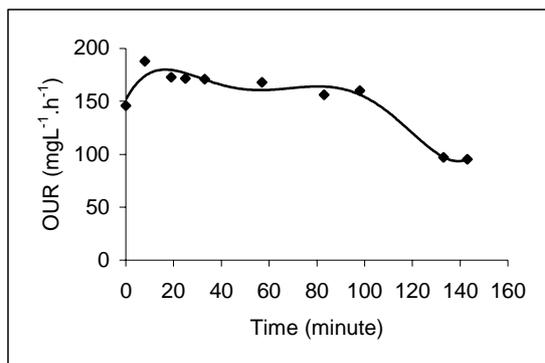


Figure 5
OUR profile for Study A ($F/M=0.45 \text{ mgCOD}\cdot\text{mg}^{-1}\text{VSS}$)

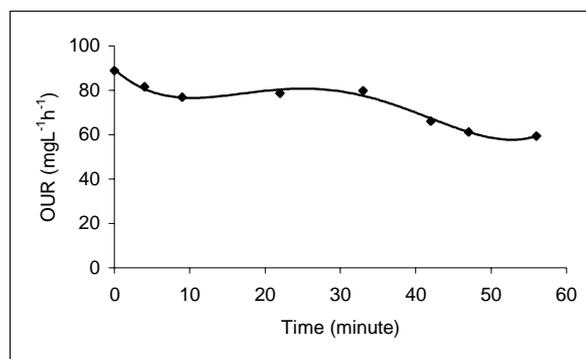


Figure 7
OUR profile for Study C ($F/M=0.44 \text{ mgCOD}\cdot\text{mg}^{-1}\text{VSS}$)

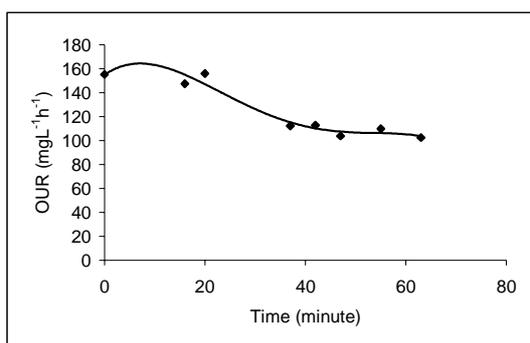


Figure 6
OUR profile for Study B ($F/M=0.17 \text{ mgCOD}\cdot\text{mg}^{-1}\text{VSS}$)

In all studies, the readily biodegradable COD was determined by the procedure proposed by Ekama et al. (1986). The method used in the determination of readily biodegradable COD was based on respirometric measurements conducted under aerobic conditions in the batch reactor. The selection of an appropriate initial F/M ratio provides a clear differentiation between OUR, induced by S_s and X_s . The initial OUR stays constant over a period where the maximum growth rate is sustained. After the depletion of S_s , it drops to a lower level only correlated with the hydrolysis of X_s and the endogenous respiration. The readily biodegradable substrate, S_s , may be calculated from the following relationship:

$$S_s = \frac{\Delta O}{1 - Y_H}$$

The heterotrophic yield was evaluated by comparing the OUR and COD profiles obtained on the same sample in accordance with the method proposed by Ubay Çokgör (1997).

The OUR profiles which were used to determine the readily biodegradable COD concentrations for Study A, Study B and Study C are shown in Figs. 5, 6 and 7 respectively.

The results obtained from OUR profiles and evaluations related to readily biodegradable COD fractions are outlined in Table 5.

The soluble and particulate slowly biodegradable organic fractions were determined from mass balance. S_H and X_s were calculated from the equations below.

$$\begin{aligned} S_T &= S_s + S_H + S_I \\ C_T &= S_T + X_s + X_I \end{aligned}$$

	F/M	Y_H [mg cell COD (mg COD) ⁻¹]	S_s (mg·l ⁻¹)
Study A	0.45	0.40	355
Study B	0.17	0.68	172.4
Study C	0.44	0.52	15

Results of experimental studies, carried out on COD fractionation are given in Table 6, and the evaluation of experimental studies is shown in Table 7.

Results and discussion

In Study A, the wastewater could be characterised with a total COD of $1\,505 \text{ mg}\cdot\text{l}^{-1}$, with a biodegradable fraction of 90%; including only 24% of readily biodegradable COD, while the remaining 66% was classified as slowly biodegradable COD, composed of predominantly particulate portions.

In Study B, the wastewater could be characterised with a total COD of $1\,012 \text{ mg}\cdot\text{l}^{-1}$, with a biodegradable fraction of 84%; including only 17% of readily biodegradable COD, while the remaining 67% was classified as slowly biodegradable COD, composed of predominantly particulate portions.

In Study C, the total COD value is $562 \text{ mg}\cdot\text{l}^{-1}$, with a biodegradable fraction of 85%; including only 3% of readily biodegradable COD, while the remaining 82% was classified as slowly biodegradable COD which is composed of predominantly soluble portions.

The particulate inert COD components are negligible for practical purposes in Study B and Study C.

The BOD_5/COD ratio may be conceived as an acceptable index of biological treatability, or more accurately a rough proportion of easily and slowly biodegradable organic matter (Orhon et al., 1997). The results indicate that wastewater has relatively low $BOD_5/\text{total COD}$ ratios of 0.09 to 0.36. Thus, wastewater was not suitable for biological treatment. However, the results of COD fractionation studies indicate that the organic content of wastewater is mostly biodegradable (84% to 92%). So, conventional wastewater characterisation does not enable a reliable design of biological treatment processes.

Study name	Sampling time	C_T ($\text{mg}\cdot\text{l}^{-1}$)	S_T ($\text{mg}\cdot\text{l}^{-1}$)	S_S ($\text{mg}\cdot\text{l}^{-1}$)	S_I ($\text{mg}\cdot\text{l}^{-1}$)	X_I ($\text{mg}\cdot\text{l}^{-1}$)	S_H ($\text{mg}\cdot\text{l}^{-1}$)	X_S ($\text{mg}\cdot\text{l}^{-1}$)
Study A	November 2001	1505	830	355	117	38	358	637
Study B	February 2002	1012	552	172	159	*	221	460
Study C	April 2002	562	434	15	83	*	336	128

(*): Practically negligible

Study name	Sampling time	S_T/C_T	S_S/C_T	S_S/S_T	S_I/C_T	S_I/S_T	S_H/C_T	S_H/S_T	X_S/C_T	X_I/C_T
Study A	November 2001	0.55	0.24	0.42	0.08	0.14	0.24	0.43	0.42	0.02
Study B	February 2002	0.55	0.17	0.31	0.16	0.29	0.22	0.40	0.45	-
Study C	April 2002	0.77	0.03	0.03	0.15	0.19	0.59	0.77	0.23	-

	S_T/C_T	S_S/C_T	S_S/S_T	S_I/C_T	S_H/C_T	X_S/C_T	X_I/C_T	References
Domestic sewage Raw	0.39	0.10		0.03	0.27	0.53	0.07	Orhon et al., 1994
Settled	0.57	0.14		0.04	0.39	0.38	0.05	
Domestic sewage Switzerland I		0.11		0.20		0.53	0.09	Kappeler and Gujer, 1992
Switzerland II		0.07		0.10		0.60	0.08	
Switzerland III		0.08		0.12		0.55	0.10	
Textile Industrial Organised District (Predominantly textile)	0.60	0.17	0.28	0.02	0.42	0.26	0.13	Orhon and Ubay Çokgör, 1997
Textile denim processing	0.71	0.14	0.19	0.04	0.53	0.29	-	Germirli et al., 1998
Dairy integrated dairy processing	0.76	0.28	0.37	-	0.48	0.16	0.08	Orhon and Ubay Çokgör, 1997
Wastewaters of IIDWTP Study A	0.55	0.24	0.42	0.08	0.24	0.42	0.02	This study
Study B	0.55	0.17	0.31	0.16	0.22	0.45	-	
Study C	0.77	0.03	0.03	0.15	0.59	0.23	-	

On the other hand, the slowly biodegradable COD (S_H+X_S) is 66% to 82% of the influent total COD. Therefore, the slowly biodegradable COD of wastewater has been accepted as the major rate limiting process component for heterotrophic growth in the IIDWTP. As clearly shown in this study, the initial readily biodegradable COD is a small fraction of the total COD content of wastewater (3% to 24%). Therefore, the IIDWTP is not controlled by the depletion of the readily biodegradable organics, but by

hydrolysis of slowly biodegradable organics, a much slower process compared to heterotrophic growth.

A comparison between the COD fractions obtained in this study and the COD fractions of different wastewaters given in the literature is shown in Table 8.

The soluble COD/total COD ratios (S_T/C_T) vary from 0.55 to 0.77 for this study. These ratios are higher than the value of raw domestic sewage (39%), reported by Orhon et al. (1994).

Conclusions

In the studies of conventional characterisation, the total COD values were $1201 \pm 621 \text{ mg} \cdot \text{l}^{-1}$ (580 to $1822 \text{ mg} \cdot \text{l}^{-1}$). The main reason of this variability is the absence of a continuous control system, although there are limit values for the wastewaters to be treated in IIDWTP. Discharging the uncontrolled wastewaters to the IIDWTP collector leads to the variability of operational conditions.

The results of conventional characterisations and biological treatability evaluations together show that the organic content of influents of IIDWTP is mostly soluble and biodegradable.

Inspection of the results given in Table 6 and Table 7 shows that, S_s was found to vary in the range of 15 to $355 \text{ mg} \cdot \text{l}^{-1}$, corresponding to S_s/C_T ratios between 0.03 and 0.24. Because of the removal of biodegradable fraction of the industrial wastewaters by pre-treatment prior to discharge, the initial readily biodegradable COD is a small fraction of total COD of wastewater (3% to 24%). We suggest that the readily biodegradable fraction of total COD originated from raw domestic wastewater.

The results of COD fractionation also indicate that the slowly biodegradable COD is an important parameter for this plant.

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