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Biodegradation characteristics of high strength municipal wastewater supported by particle size distribution

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ABSTRACT

The objective of this study was to evaluate the biodegradability related chemical oxygen demand (COD) fractionation of selected streams from a municipal wastewater treatment plant (MWWTP). The MWWTP under investigation consisted of an activated sludge process which was fed with domestic sewage and pretreated tannery effluents. Another aim was to use particle size distribution (PSD) analysis as a supportive tool for interpreting the effect of primary settling and biological treatment processes on the partitioning of COD fractions over different size categories. The results of conventional characterization and respirometric analyses revealed the strong character of the primary settling tank influent. The high level of soluble inert COD underlined the necessity of an additional treatment step, since the application of biological treatment alone was not adequate to meet the discharge standards. Primary settling removed 35% of the particulate COD, which corresponded to 70% of the initial total COD content, and exhibited only marginal COD removal (2%) in the soluble and colloidal size ranges. Biological treatment almost completely eliminated the particulate COD portion, translating into 60% contribution within 77% overall COD removal; where the COD decrease in the colloidal range amounted to a reduction efficiency of 12% on an overall basis. PSD-based COD fractionation proved to be a useful tool for evaluating the effect of primary settling and applied biological treatment process. PSD also complemented the results of respirometric analyses and provided supporting information for the interpretation of biodegradation characteristics by yielding the size distribution of major COD fractions.

Keywords: Biological treatment; COD fractionation; Municipal wastewater; Particle size distribution; Primary settling; Respirometry

1. Introduction

Wastewater management is a serious concern in most developing countries, since unplanned urbanization and rapid industrialization usually result in the generation and discharge of growing volumes of wastewater into existing water bodies. In densely populated urban and industrial centers where domestic and pretreated industrial wastewaters are collected by combined sewer systems, the joint treatment may exert operational problems in the municipal wastewater treatment plants (MWWTPs). Especially when the industrial effluents are associated with high levels of organic pollutants, such problems are unavoidable. The mixture of domestic and industrial discharges may reflect characteristics of a strong wastewater with a complex content, indicating the necessity of a comprehensive analysis of both the amount and composition of organic carbon. Hence, special attention should be devoted to the influent streams of MWWTPs that are designed to remove pollutants from domestic and pretreated industrial wastewater mixtures with substantial organic matter contents.

Organic matter based wastewater fractionation, expressed in chemical oxygen demand (COD) units, has been conducted to explore the biodegradation characteristics of organic compounds in domestic sewage [1–3] and industrial wastewaters [4–6]. Recently, the particle size distribution (PSD)-based partitioning of contaminants between particulate, colloidal and soluble size ranges has been introduced as a supportive tool to provide additional insight into the state and fate of the wastewater components. Physical fractionation of COD into different size categories is implemented for a wide range of wastewaters including agricultural [7], food processing [8], municipal [9], olive oil mill [10], pulp and paper mill [11], synthetic sewage [12], tannery [13] and textile [14] wastewaters to determine the exact and/or dominating reaction mechanisms proceeding during the application of a selected treatment process. PSD, although useful for providing COD fingerprints for the investigated samples, cannot differentiate between biodegradable and non-biodegradable organic substances. Accordingly, PSD-based COD fractionation along with biological treatability studies would then offer supporting information for the interpretation of biodegradation characteristics.

In this framework, the objective of this study was to investigate the biodegradability related COD fractionation of primary settling influent and effluent samples from a MWWTP. The MWWTP was composed of an activated sludge facility that received domestic sewage together with pretreated tannery effluents. For this purpose, respirometric tests based on the oxygen uptake rate (OUR) profiles were carried out on the primary settling influent and effluent at the MWWTP, and the respirometric data obtained for both samples were used to determine the COD fractions. Another aim was to use PSD-based fractionation as a supportive tool for evaluating the effect of primary settling and biological treatment processes on concentration fractions of COD in different size intervals. This goal was achieved by performing sequential filtration/ultrafiltration experiments on the influent and effluent of the primary settling tank, as well as on the effluent of the secondary settling tank. The experimental results of physical segregation based PSD together with biodegradability oriented wastewater characterization were integrated for providing supplemental information on size distribution of COD fractions.

2. Materials and methods

2.1. Investigated wastewater treatment plant and samples used

The experimental study was conducted on the wastewater streams of a MWWTP located in Tuzla, Istanbul. The MWWTP treating up to 250,000 $m^3\ d^{-1}$ of mixed domestic sewage and tannery effluents consists of a preliminary treatment (coarse and fine screening followed by aerated grit removal), a primary settling unit and a subsequent activated sludge system. The wastewater samples were collected from three different points of the Tuzla MWWTP; namely (i) influent of the primary settling tank representing the raw wastewater (Sample A), (ii) effluent of the primary settling tank characterizing the biological treatment influent (Sample B), and (iii) effluent of the secondary settling tank demonstrating the outlet of the biological treatment (Sample C). Daily flow proportional composite samples were prepared based on collecting 12 grab samples per day at evenly-spaced intervals of 2 h.

2.2. Conventional characterization

All measurements for conventional characterization were carried out in accordance with the procedures outlined in Standard Methods [15]. COD was determined by closed reflux titrimetric method according to the International Standard ISO 6060 [16]. The total soluble (filtered) COD (S_T) was defined as the filtrate through 450 nm pore size membrane filters. The Millipore AP40 glass fiber filters with an effective pore size of approximately 1200~1600 nm were used for total suspended solids (TSS) and volatile suspended solids (VSS) determinations. Each data point was calculated as the average of three replicate measurements. COD experiments performed on the raw wastewater (Sample A) exhibited a standard deviation of 2.0 mg l^{-1} (4.0%) for 50 mg l^{-1}, 3.5 mg l^{-1} (1.4%) for 250 mg l^{-1} and 6.5 mg l^{-1} (1.3%) for 500 mg l^{-1}.

2.3. Biological treatability oriented characterization

Biological treatability oriented characterization experiments consisted of COD fractionation encompassing not only biodegradable components at different rates of biodegradation, but also non-biodegradable portions of COD of either influent origin or generated during the course of biochemical processes as residual microbial products. Influent soluble inert COD (S_I) and influent particulate inert COD (X_I) fractions were determined according to the direct experimental procedure proposed by Orhon et al. [17]. The method involved three aerated batch reactors of the same volume that were seeded to secure an initial biomass concentration of around 50 mg VSS l^{-1}, previously acclimated to the glucose and wastewater mixture in a lab-scale fill and draw aerobic reactor. The first two reactors were fed with unfiltered and filtered wastewater samples, and the third reactor was run with glucose solution approximately having the same COD concentration as the filtered wastewater reactor. Aliquots were taken periodically from the mixed liquor of the reactors for the determination of total and soluble (filtered) COD (C_T and S_T, respectively). Inert COD experiments were continued until the biodegradable substrates initially fed to the reactors were completely depleted and a stable threshold COD level coupled with no measurable biomass activity was achieved. The concentration of soluble inert microbial products (S_P) was calculated from the data on direct batch-inert COD tests and expressed as a fraction (Y_{SP}) of the influent total biodegradable COD (C_S).

A Manotherm RA-1000 continuous respirometer was used to collect OUR data with a sampling frequency of 1 min [18]. The respirometer, which was specifically designed for a reliable on-line measurement with a 3 l of aerated reactor, consisted of a closed reaction/measurement chamber of 750 ml, in which the dissolved oxygen consumption in the mixed liquor was continuously monitored. Respirometric experiments were operated under room temperature conditions (20 ± 1°C), where pH of the biological reactors was kept in the range of 7.0–8.0, suitable for biological activity. Continuous aeration was supplied to maintain a dissolved oxygen concentration of more than 6 mg l^{-1}. A nitrification inhibitor (Formula 2533™, Hach Company) was added for the prevention of any possible interference induced by simultaneous nitrification. The relative uncertainty of OUR measurements was assessed as 0.1 mg l^{-1} h^{-1}.

Each respirometric test was initiated with the measurement of OUR of the biomass seed added to the reactor to obtain the initial endogenous respiration level. The biomass sampled from the aeration tank of the Tuzla MWWTP was previously acclimated to the influent stream of activated sludge unit for a couple of days in a fill-and-draw reactor. The wastewater samples filtered through a polyamide membrane filter with a pore size of 450 nm were added to the respirometer to achieve an F/M ratio of 0.1 g COD (g VSS)$^{-1}$ when the endogenous decay level stayed constant over a period of about half an hour. The amount of readily biodegradable COD (S_S) fraction present in the wastewater samples was measured respirometrically as described by Ekama et al. [19] and calculated from the area under the OUR curve (ΔO_{SS}) according to the experimental procedure proposed by Ubay Çokgör et al. [20]. When S_S was completely depleted after the first steep incline of OUR profile, the OUR level dropped to a lower level as a result of hydrolysis and subsequent utilization of rapidly hydrolysable COD (S_H). After the depletion of all available external substrate, the OUR profile reached a second threshold level that was similar to that of the endogenous decay, characterizing the outlet of the biological treatment. The total amount of oxygen consumption ($\Delta O_{SS} + \Delta O_{SH}$), obtained from the area under the OUR curve until the endogenous decay level, denoted the soluble biodegradable COD (S_S + S_H) portion. As the S_S fraction was calculated from the area under the OUR curve until the sharp decrease (ΔO_{SS}), the remaining part of the oxygen consumption (ΔO_{SH}) was attributed to the S_H component. The OUR curves were also used for the determination of S_I fraction as defined in the respirometric method proposed by Orhon and Okutman [21]. The S_I fraction may then be calculated by subtracting the sum of S_S and S_H from the total soluble (filtered) COD (S_T). The remaining particulate COD fraction, namely slowly hydrolysable COD (X_S), was calculated by using the mass balance equation, since the total influent particulate COD (X_T) may be further subdivided into X_S and X_I components [22].

2.4. Particle size distribution analyses

An ultrafiltration cell with a volumetric capacity of 400 ml (Millipore, Amicon 8400) was used for the size fractionation experiments to obtain multiple molecular weight range fractions. The wastewater samples were processed with positive pressure in the range of 0.6–2.5 bar as provided by compressed nitrogen gas. Sequential filtration/ultrafiltration tests were performed under room temperature conditions. The filtrates were collected in separated acid-washed flasks and placed in a refrigerator at 4°C to prevent sample decomposition during storage. pH adjustment was not required, since the original pH values of the wastewater samples (as denoted by Table 1) were within the range recommended by the manufacturer. PSD by sequential filtration/ultrafiltration was initiated by passing the samples through the use of conventional disposable filters with pore sizes of 1200~1600 nm (Millipore AP40, glass fiber), 450 nm (Durapores HV, polyvinylidene fluoride [PVDF]), and 220 nm (Durapores GV, PVDF) (Millipore Corp., Bedford, MA 01730). Further ultrafiltration of the permeates obtained from 220 nm membrane filter was performed using membrane discs with nominal molecular weight cut-off (MWCO) values of 100, 30, 10, 3 and 1 kDa (Ultracel PL, regenerated cellulose) (Millipore Corp., Bedford, MA 01730). The stirrer speed in the ultrafiltration cell was adjusted to provide a surface vortex of one-third of the total sample height, thereby reducing premature polarization. The filter materials used for filtration and ultrafiltration were chemically compatible with a number of commonly used solvents and with no adsorptive capacity for soluble organics. Thus, no interference due to interaction between the membrane discs and

Table 1
Characterization of samples

Parameter	Unit	Sample A		Sample B	Sample C
		This study	Sözen et al. [25]		
Total COD (C_T)	mg l^{-1}	1190	1280 ± 352	865	200
Filtered (450 nm) COD (S_T)	mg l^{-1}	290	258 ± 56	280	170
TSS	mg l^{-1}	1435	1605 ± 492	730	20
VSS	mg l^{-1}	620	701 ± 195	360	20
TKN	mg l^{-1}	95	88 ± 16	75	45
NH$_4$-N	mg l^{-1}	55	51 ± 7	50	40
TP	mg l^{-1}	13	14 ± 3	10	4
PO$_4$-P	mg l^{-1}	6	6 ± 2	5	2
pH	–	7.34	7.47 ± 0.25	6.84	6.93
Alkalinity	mg CaCO$_3$ l^{-1}	455	469 ± 109	420	450
Chloride	mg l^{-1}	2635	2754 ± 470	2390	2160

samples was observed. Sequential filtration/ultrafiltration experiments started with an initial volume of 1000 ml to secure enough volume of permeate (approximately 100 ml) for the analytical COD measurements.

The nominal MWCO values of the ultrafiltration membrane discs given in kDa units are most meaningfully expressed when they are approximated to their corresponding particle size values defined in nm. The approach suggested by Cheryan [23] and McGregor [24] circumvented this difficulty simply by achieving a consensus on a uniform format for the presentation of size fractions and allowing a better interpretation of experimental results obtained by filtration and ultrafiltration techniques. In this context, the particulate range was defined as retentates on Millipore AP40 glass fiber filters with an effective pore size of approximately 1600 nm. Since the same filters were also used to assess particulate components on a suspended solids basis, the measurement of TSS included the settleable and most of the supracolloidal substances. The permeate passing through 1 kDa ultrafiltration membrane (<2 nm), thus containing the majority of the truly dissolved components, was designated as the soluble range. As an intermediate phase between the particulate and soluble portions, the colloidal range was addressed as the microparticles and/or macromolecules in the size range of 2 nm (1 kDa membrane) to 1600 nm (AP40 glass fiber filter).

3. Results and discussion

3.1. Conventional characterization

Conventional characterization results obtained from the studied samples are summarized in Table 1, together with the ranges reported in a previous study [25] where the same wastewater source was monitored for 6 mo. According to the figures presented in Table 1, Sample A could be characterized by a considerable C_T content of 1190 mg l^{-1}, slightly higher than that of an average strong domestic sewage [26]. The analytical survey revealed a relatively low S_T concentration of 290 mg l^{-1}, accounting for only 24% of C_T. The level of TSS detected in Sample A was about seven times as high as a medium strength domestic sewage [26]. The concentration of total Kjeldahl nitrogen (TKN) was assessed as 95 mg l^{-1} with a corresponding N/COD ratio of 0.080, in agreement with previously reported literature data based on studies carried out on the domestic wastewater from important wastewater discharge stations of Istanbul [27] and representative domestic wastewater characteristics for selected countries in Europe [28]. The P/COD ratio was calculated as 0.011 for Sample A, a level not consistent with the range of 0.014–0.019 given for European wastewaters [28]. The high chloride content of 2635 mg l^{-1} indicated the significant effect of discharges from the local tannery industries on the wastewater quality. The interpretation of the values listed in Table 1 revealed that Sample A was quite representative, since all the pollutant concentrations fell within the range of the general characteristics outlined by the above mentioned long-term survey.

Primary settling of Sample A induced a COD decrease of 27%, lowering the C_T content from 1190 to 865 mg l^{-1}. The ratio of S_T over C_T increased from 0.24 to 0.32, as the S_T level remained practically unchanged during settling. Approximately half of the TSS content of Sample A could be removed by primary settling. As expected, the N/COD and P/COD ratios in Sample A were improved to 0.087 and 0.012, respectively. The increase in these ratios was due to a higher COD settling and removal rate compared to TKN and total phosphorus (TP). Conventional characterization results obtained both for Samples B and C demonstrated that the biological treatment reduced the C_T concentration from 865 to 200 mg l^{-1}, achieving a total COD removal efficiency of 77%. The residual ammonium concentration of 40 mg l^{-1} was an indicator of the low nitrification activity, since the adopted sludge age of 3 d was not long enough to allow nitrifiers to reach sufficient numbers to adequately nitrify the amount of ammonia present in Sample B.

3.2. Biological treatability oriented characterization

Samples A and B passed through membrane filters with a pore size of 450 nm were exposed to OUR measurements for the assessment of S_S. The resulting OUR profiles are illustrated in Fig. 1. The S_S fraction was determined for a selected Y_H value of 0.67 g cell COD (g COD)$^{-1}$ generally accepted for domestic wastewaters and verified for Istanbul sewage [22]. The amount of S_S in Sample A was calculated as 51 mg l^{-1} from the part of the OUR curve (ΔO_{SS}). The remaining portion of the oxygen consumption (ΔO_{SH}) was used to estimate the S_H concentration (92 mg l^{-1}). The respirometric test performed on Sample B revealed that the character of the OUR curve was quite similar to the one obtained for Sample A. The area under the OUR curve ($\Delta O_{SS} + \Delta O_{SH}$) derived for Sample B was equivalent to a total oxygen consumption of 45.5 mg O_2 l^{-1}. This level corresponded to a soluble biodegradable COD content of 138 mg l^{-1}, which could be further subdivided into an S_S fraction of 49 mg l^{-1} and an S_H fraction of 89 mg l^{-1}. Evaluation of the OUR profile shown in Fig. 1 indicated that Sample A could be characterized by an S_I concentration of 147 mg l^{-1}. The respirometric assessment of the S_I fraction, bypassing the treatment system without being affected from biochemical reactions, amounted to 142 mg l^{-1} in Sample B. Both values determined for S_I from the respirometric evaluation of the OUR data were also confirmed by applying the direct experimental procedure. The X_I fraction, becoming enmeshed in the activated sludge and leaving the system mainly with sludge wastage, was calculated as 264 mg l^{-1} for Sample A. Primary settling removed about half (138 mg l^{-1}) of the initial X_I, lowering to 126 mg l^{-1}. The concentration of X_S decreased from its initial value of 636 to 459 mg l^{-1}, corresponding to a reduction efficiency of 28%.

The relative magnitudes of individual COD fractions as percentage of C_T before and after primary settling are displayed in Table 2. The C_T concentration of 1190 mg l^{-1} associated with Sample A contained a total inert COD ($S_I + X_I$) fraction of 34%, indicating that only 66% of the C_T content was of biodegradable nature. X_S was observed as the major biodegradable COD fraction in Sample A, constituting 82% of the C_S and 54% of the C_T content. The results of COD fractionation experiments obtained for Sample A revealed that S_H represented 8% of C_T, a relatively low level compared to data given in the literature [22,29,30]. COD fractionation for Sample A yielded an S_S/C_T ratio of only 4%, approximately half the level normally encountered in domestic sewage [22,27,29,30]. S_I in Sample A accounted for 51% of S_T and 12% of C_T, a level significantly higher than the S_I values reported for domestic wastewater in Istanbul [22,27,29,30], but it was in accordance with the range of 9–14% ascertained for tannery effluents [17]. Primary settling reduced the percentage of X_I/C_T from 22% to 15%, accompanied by a negligible increase in the ratio of C_S over C_T from 0.66 to 0.69. The X_S fraction removed by primary settling was up to 15% of C_T and 23% of C_S present in Sample A. As expected, the primary settling process proved relatively inefficient for removing soluble COD (S_S, S_H and S_I), since both the composition and concentration of S_T remained practically unchanged.

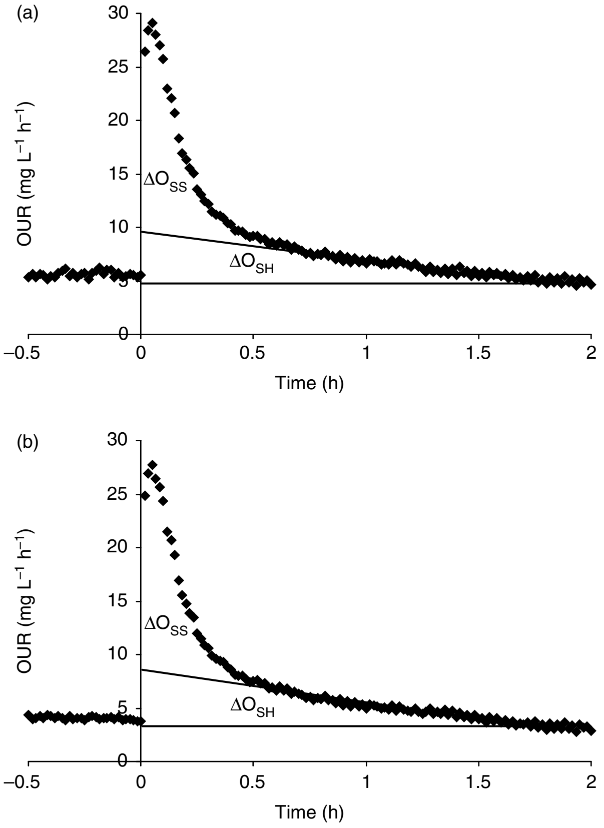

Fig. 1. Respirogram for filtered samples: (a) Sample A and (b) Sample B.

The performance of the biological treatment process primarily depends on S_I of influent origin and S_P generated during the course of metabolic reactions. Evaluation of the experimental survey conducted on Sample B yielded an Y_{SP} value of 0.046, compatible with the range of 0.040–0.047 reported in the literature for plain settled tannery effluents [31,32]. The corresponding level of S_P was assessed as 28 mg l^{-1}. As clearly visualized by the data presented in Table 1, the soluble residual COD ($S_I + S_P$) in Sample B (170 mg l^{-1}) consisted solely of S_I

Table 2
Results of COD fractionation for Samples A and B

COD component	Sample A		Sample B	
	Concentration (mg l^{-1})	Percentage (%)	Concentration (mg l^{-1})	Percentage (%)
S_S	51	4	49	6
S_H	92	8	89	10
S_I	147	12	142	16
S_T	290	24	280	32
X_S	636	54	459	53
X_I	264	22	126	15
X_T	900	76	585	68
C_T	1190	100	865	100

of the wastewater (142 mg l^{-1}) and S_P generated during biological processes (28 mg l^{-1}), since the biodegradable COD portions were expected to be completely depleted in well designed and operated systems. According to the By-Law on Urban Wastewater Treatment [33] set by the Ministry of Environment and Forestry of Turkey, the total effluent COD after treatment must be reduced to under 125 mg l^{-1} prior to discharge into a receiving water body. Due to the high level of biorecalcitrant COD in Sample C, the existing treatment scheme was incapable of complying with the discharge to receiving water standards. This evidence promoted the necessity of applying an additional treatment step such as advanced oxidation or electrochemical process to lower S_I initially present in Sample B.

3.3. Particle size distribution analyses

3.3.1. PSD-based COD fractionation of Sample A

A physical fractionation of Sample A in terms of COD was performed by means of sequential filtration and ultrafiltration. The results obtained for the PSD-based COD fractionation experiments are summarized in Table 3. The COD values measured in the permeates obtained after each filtration/ultrafiltration step were expressed as cumulative values, as each of them defined the C_T content below the designated filter size. The difference of the two relevant absolute COD values was calculated to obtain the differential value between the two subsequent size categories. No quiescent settling was carried out prior to sequential filtration/ultrafiltration tests.

Table 3
Cumulative and differential COD values of Sample A

Separation technique	Particle size (nm)	Cumulative COD (mg l^{-1})			Size category (nm)	Differential COD (mg l^{-1})		
		This study	Previous studies			This study	Previous studies	
		Sample A	Domestic Sewage [36]	Tannery Wastewater [13]		Sample A	Domestic Sewage [36]	Tannery Wastewater [13]
Total		1190	440	3100				
Filtration								
AP40 filter	1200~1600	360	155	1240	>1600	830	285	1860
HV filter	450	290	115	1195	450–1600	70	40	45
GV filter	220	260	85	1190	220–450	30	30	5
Ultrafiltration								
100 kDa	13	240	85	970	13–220	20	0	220
30 kDa	8	225	75	965	8–13	15	10	5
10 kDa	5	210	65	870	5–8	15	10	95
3 kDa	3	205	65	845	3–5	5	0	25
1 kDa	2	195	60	780	2–3	10	5	65
					<2	195	60	780

Consequently, the initial C_T concentration of Sample A (1190 mg l^{-1}) comprised of the sum of settleable, supracolloidal, colloidal, and soluble portions. As outlined in Table 3, a complete size distribution was executed for the physical separation of the COD fractions into nine sequential size intervals ranging from 2 to 1600 nm. Percent distribution values of COD fractions, obtained by normalizing the differential COD values to the initial C_T level of 1190 mg l^{-1}, revealed a bimodal size distribution for Sample A. Both ends of the entire size spectrum, that is COD fractions at the particle size intervals of >1600 nm (particulate range, 70%) and <2 nm (soluble range, 16%), were identified as the two main contributors to the C_T content. The upper colloidal size range (450–1600 nm) constituted 6% of the C_T concentration as another significant component in Sample A. The remaining 8% was evenly distributed among other particle size intervals throughout the colloidal range (2–450 nm). This COD fingerprint is comparable with the values presented in the literature [34,35], summarizing several studies on fractionation of organic matter in raw municipal wastewater.

Table 3 also outlines the PSD-based COD fractionations of domestic sewage and tannery wastewaters [13,36]. Review of the data displayed in Table 3 pointed out that the percent distribution of COD fractions for Sample A exhibited similar characteristics as those for domestic sewage [36] and tannery wastewater [13], especially the latter reflecting a clearly bimodal COD distribution with two distinct peaks at the particulate and soluble ranges. Comparative evaluation of the results revealed that the PSD-based differential COD values of Sample A were found experimentally to lie between those of domestic sewage and tannery wastewater, denoting the presence of tannery wastewater discharges into the Tuzla MWWTP.

3.3.2. Effect of primary settling

A similar PSD analysis was employed for Sample B to provide essential information on the fate of COD fractions subjected to settling. The differential COD profiles of Samples A and B are plotted in Fig. 2. Primary settling, aside from a considerable COD removal efficiency of 27% that was in accordance with the literature data [37], generated a COD distribution comparable to that of its non-treated counterpart. Evaluation of the differential COD profile obtained for Sample B revealed that the particulate size range (>1600 nm) with a value of 540 mg l^{-1} was identified as the predominant fraction, corresponding to 62% of the initial C_T concentration after settling. The soluble portion (<2 nm) represented the second remarkable fraction which accounted for 22% of the initial C_T value for Sample B. The residual 14% of the C_T content appeared to be well partitioned among particle size intervals throughout the entire colloidal size range (2–1600 nm). The decrease in COD fraction achieved at the particle size interval of >1600 nm (particulate range) corresponded to 25% within 27% overall removal efficiency. Primary settling reduced the COD level at the upper colloidal size range (450–1600 nm) from its initial value of 70 to 45 mg l^{-1}, translating into only 2% contribution to the overall COD removal performance. The percent distribution values before and after primary settling appeared to be the same in the remaining size spectrum of the colloidal range (2–450 nm). Primary settling remained relatively inefficient for the lowest particle size range (<2 nm), as no appreciable COD removal was observed in the soluble range.

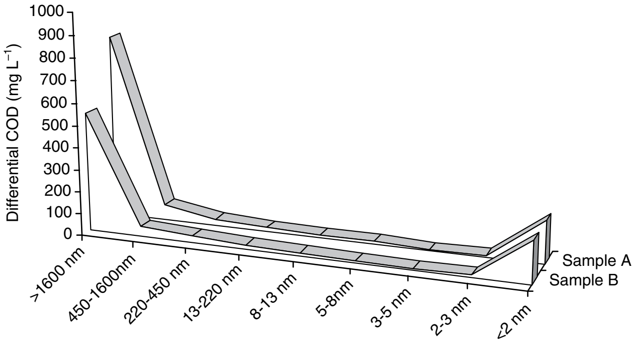

Fig. 2. Differential COD profiles before and after primary settling.

3.3.3. Effect of biological treatment

Sequential filtration/ultrafiltration experiments were also performed not only on Sample B, but also on Sample C to interpret the effect of biological treatment on the partitioning of COD fractions over different size categories. The COD distribution profiles of Samples B and C obtained through PSD-based COD fractionation are illustrated in Fig. 3. In contrast with the one for

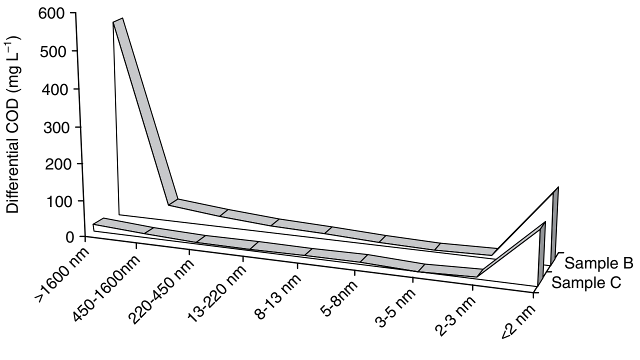

Fig. 3. Differential COD profiles before and after biological treatment.

Table 4
Size distribution of the COD fractions

Sample	COD concentration (mg l^{-1})				COD concentration (mg l^{-1})		
	Component			Size interval	Component		Size interval
	S_S	S_I	$S_S + S_I$	<2 nm	S_H	S_P	2–450 nm
A	51	147	198	195	92	–	95
B	49	142	191	190	89	–	90
C	0[a]	142	142	145	0[1]	28	25

[a] Respriometric measurements were also conducted on Sample C (data not presented). No appreciable biodegradable substrate could be detected in the resulting OUR profile, indicating that all C_S was depleted and that the effluent COD contained only S_I of influent origin and S_P generated through the course of the biological process.

Sample B, Sample C exhibited a single peak structure in the COD distribution profile. The soluble size portion (<2 nm) constituted the bulk (73%) of the COD in Sample C. Evaluation of the COD profile yielded a particulate COD fraction of 20 mg l^{-1} for Sample C, indicating that only 10% of the C_T content was in the highest size range (>1600 nm). The low particulate COD in Sample C may be attributed to the efficient settling of the activated sludge. The rest of C_T was determined to be distributed over the entire colloidal range (2–1600 nm).

The most pronounced effect of biological treatment on the effluent characteristics was observed in the particulate size range (>1600 nm), with a 60% contribution to the overall COD reduction of 77%. Biological treatment lowered the colloidal COD content from 135 to 35 mg l^{-1}, amounting to a COD removal efficiency of 12% on an overall basis. The lowest COD removal efficiency was obtained in the soluble size range (<2 nm), by exerting a 5% contribution to the overall COD removal efficiency. The PSD-based COD fractionation profile for Sample C was quite comparable to those reported for the biological treatment effluents of two different knit fabric finishing textile plants [36,38], with the soluble range (<2 nm) being the only dominant COD fraction. The similarity between the current and previous findings underlined the significance of the soluble portion in optimizing the performance of biological treatment systems and emphasized the necessity for exploration of the nature and composition of organics at the lowest size range (<2 nm).

3.3.4. Joint evaluation of biological treatability-based and PSD-based COD fractionation

The results obtained for both biodegradability based COD fractionation via respirometric analyses and PSD of COD by means of sequential filtration/ultrafiltration experiments were integrated to explore the relationship between physical segregation and biological treatability of organic constituents. In this context, the data on COD fractions of the studied samples presented in Table 2 and the differential COD contents illustrated in Figs. 2 and 3 were used to establish the values given in Table 4. The table provides comprehensive information for the assessment of size distribution of major COD fractions and thus highlights the transformation mechanisms involved in primary settling and biological treatment processes.

Comparative evaluation of the values experimentally determined for Sample A clearly revealed that the soluble size range (<2 nm) consisted of S_S and S_I fractions. The COD portion of Sample A addressed as S_H appeared to be distributed over the entire colloidal range, except in the 450–1600 nm size interval. Closer inspection of the table indicated that the S_I content of Sample C corresponded to the COD in the soluble range (<2 nm). S_P generated through the course of biochemical reactions were located at the colloidal range, representing a group of organics with sizes below 450 nm. The size distribution characteristics of S_S and S_I fractions agree with the ones reported by literature that investigated PSD-based COD fractionation of a textile wastewater before and after biological treatment [36].

4. Conclusions

In the light of the experimental results presented and discussed in the preceding sections, the following issues may be outlined as the concluding remarks of this study:

1. The primary settling tank influent represented a relatively strong municipal sewage with a total COD concentration of around 1200 mg l^{-1}, a considerable amount of TSS and an excessive chloride content, indicating the effect of discharges from the local tanneries.
2. The COD fractionation data demonstrated that the primary influent involved 66% C_S, with a composition

of an S_S of only 4%, an S_H of 8% and a X_S fraction of 54%. The S_I fraction constituted 12% of the C_T, a value quite higher than the level normally given for domestic sewage, but in accordance with high S_I/C_T ratios obtained for plain settled tannery effluents.

3. The PSD analysis defined a specific COD fingerprint for the primary influent and exhibited a bimodal distribution with 70% of the C_T content above 1600 nm (particulate range) and 16% below 2 nm (soluble range).
4. PSD-based fractionation proved to be a useful tool for evaluating the effect of primary settling and biological treatment on the fate of COD components. As expected, the most pronounced effect of primary settling was observed in the particulate size range (>1600 nm), with 25% contribution to the overall COD removal efficiency of 27%. Similarly, biological treatment almost completely removed the COD content at the size interval of >1600 nm (particulate range), corresponding to 60% within 77% overall removal efficiency. The decrease in the COD concentration observed in the colloidal range (2–1600 nm) reflected a contribution of 12% to the overall COD removal performance, where only a slight decline was observed in the soluble range (<2 nm).
5. Joint evaluation of biological treatability-based characterization and PSD-based COD fractionation indicated that S_S and S_I fractions were totally accumulated in the soluble size range (<2 nm). The S_H fraction was determined to be distributed throughout the entire colloidal range, except in the 450–1600 nm size interval. S_P generated during the course of biological treatment fell within the colloidal range, representing a group of organics having particle sizes less than 450 nm.
6. The considerable amount of biorecalcitrant organics promoted the necessity of performing an additional treatment step such as advanced oxidation or electrochemical process along with biological treatment. In this context, it is recommended for future studies to extend the current research by generating supplementary data on both the type and COD removal potential of the additional treatment unit via performing PSD-based fractionation.

Symbols

COD — chemical oxygen demand, mg COD l^{-1}
C_S — total biodegradable COD, mg COD l^{-1}
C_T — total COD, mg COD l^{-1}
F/M — food/microorganism ratio, g COD (g VSS)$^{-1}$
MWCO — molecular weight cut-off
MWWTP — municipal wastewater treatment plant
OUR — oxygen uptake rate, mg l^{-1} h^{-1}
PSD — particle size distribution
S_H — rapidly hydrolysable COD, mg COD l^{-1}
S_I — soluble inert COD, mg COD l^{-1}
S_P — soluble inert microbial products, mg COD l^{-1}
S_S — readily biodegradable COD, mg COD l^{-1}
S_T — total soluble (filtered) COD, mg COD l^{-1}
TKN — total Kjeldahl nitrogen, mg N l^{-1}
TP — total phosphorus, mg P l^{-1}
TSS — total suspended solids, mg TSS l^{-1}
VSS — volatile suspended solids, mg VSS l^{-1}
X_I — particulate inert COD, mg COD l^{-1}
X_S — slowly hydrolysable COD, mg COD l^{-1}
X_T — total particulate COD, mg COD l^{-1}
Y_H — heterotrophic yield coefficient, g cell COD (g COD)$^{-1}$
Y_{SP} — ratio between the soluble inert microbial products and total biodegradable COD
ΔO_{SH} — amount of oxygen consumption for the utilization of the rapidly hydrolysable COD per unit volume, mg O_2 l^{-1}
ΔO_{SS} — amount of oxygen consumption for the utilization of the readily biodegradable COD per unit volume, mg O_2 l^{-1}

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