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The evaluation of COD fractionation and modeling as a key factor for appropriate optimization and monitoring of modern cost-effective activated sludge systems

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ABSTRACT

A study was conducted to characterize the raw wastewater entering a modern cost effective municipal WWTP in Poland using two approaches; 1) a combination of modeling and carbonaceous oxygen demand (COD) fractionation using respirometric test coupled with model estimation (RT-ME) and 2) flocculation/filtration COD fractionation method combined with BOD measurements (FF-BOD). It was observed that the particulate fractions of COD obtained using FF-BOD method was higher than those estimated by RT-ME approach. Contrary to the above, the values of inert soluble fraction evaluated by FF-BOD method was significantly lower than RT-ME approach (2.4% and 3.9% respectively). Furthermore, the values for low colloidal and particulate fractions as well as soluble inert fractions were different than expected from a typical municipal wastewater. These observations suggest that even at low load (10% of the total wastewater treatment inflow), the industrial wastewater composition can significantly affect the characteristics of municipal wastewater which could also affect the performance and accuracy of respirometric tests. Therefore, in such cases, comparison of the respirometric tests with flocculation/filtration COD/BOD measurements are recommended. Oxygen uptake rate profile with settled wastewater and/or after coagulation-flocculation, however, could still be recommended as a "rapid" control method for monitoring/optimising modern cost-effective wastewater treatment plants.

Introduction

In the last 15 years, from 2004 onwards, when Poland was still a part of European Union (EU), the Polish National Program for Municipal Wastewater Treatment Plants (MWWTP) have aimed for identifying and solving wastewater treatment and management problems in Poland. This program was conducted with the aim of modernizing or expanding nearly 600 WWTP already identified and also constructing nearly 200 new facilities with a total population equivalent (PE) representing almost 97% of the total PE of the Polish National Program for MWWTP.[1] In large facilities (more than 100,000 PE) such as Gdynia-Debogorze WWTP, in order to achieve the high quality effluent standards defined by the EU regulations, an intense process modification was recommended. However, the main challenge was to develop modern and cost-effective activated sludge (AS) systems. In these circumstances, the appropriate characterization of raw wastewater has been identified as an important aspect and a key factor for the optimization of treatment processes and new reactor design. Operation of a typical MWWTP is usually controlled by parameters such as flow rate, solid retention time, concentration of ammonia and dissolved oxygen etc. It is considered that, together with the chemical and biochemical oxygen demand (COD and BOD), the above parameters indirectly affect the performance of AS processes. In an aerobic AS system the BOD_5: N ratio is recommended to be 100:5 in order to avoid nutrient deficiency.[2,3] A high influent C:N ratio (e.g. 100:10) could negatively affect the nutrient removal efficiencies of the treatment plant, however, depending on the quality of the carbon source it could vary remarkably.[4] Particularly, the BOD indicates the amount of organic pollutants that can be biologically degraded, however, in reality, BOD measurement is inadequate to define the actual biodegradation kinetics of all organic compounds present in wastewater. In contrast, the use of effluent soluble COD for estimating the yield coefficient and decay rate is in practise, however, is not valid under many practical conditions, since the concentration of the influent wastewater is much higher than that of the effluent concentration. Moreover, the particulate COD as slowly biodegradable organics can exhibit a significant effect on the determination of kinetic coefficients, e.g., the specific substrate removal rate for the multiple substrate hydrolysis model and the first-order rate constant. Additionally, particulate compounds can be related to a wide range of physical–chemical and biological phenomena in conventional wastewater treatment systems which demand the need for more research on the proper methods for determination of COD fractionation as a key factor for appropriate modeling and monitoring of activated sludge processes. Thus, among several parameters, COD fractionation has become an important criterion for the development of efficient nutrients removal AS systems in Poland. In such circumstances, special attention has been paid to the slowly biodegradable fractions, essential to design an effective technology for wastewater treatment, mainly denitrification and Enhanced Biological Phosphorus Removal (EBPR).

The Activated Sludge Models[5,6] commonly used by IWA Task Group, are developed based on the COD fractionation, nevertheless, a proper evaluation of COD fractionation, which is crucial for modeling and model predictions, is still under debate. In general, total COD in the wastewater consists of: readily (soluble) biodegradable organic substrates (S_S), slowly (particulate) biodegradable substrates (X_S), inert suspended organic matter (X_I), and inert soluble organic matter (S_I).[6] There are two main approaches for determining the COD fraction in wastewater; 1) based on their physical-chemical properties[7] and 2) microbial growth kinetics, viz., respirometric test based on oxygen uptake rate (OUR) and COD measurements.[8] Respirometric method was first introduced by Ekama et al.[9] in the 70's of the last century and are still being used by many researchers. It is used mainly for determining S_S, whether X_S requires simulation modeling, which is adjusted to the batch experimental data. Additionally, the respirometric approach is highly influenced by experimental conditions and therefore to be reliable, it should be carried out with precision and careful maintenance. Alternatively, physico-chemical method, which is based on physical (particle size) and chemical (coagulation/flocculation) properties of organic matter present in wastewater are used. The disadvantage of this method is connected with imprecise definition of colloidal organic matter, which may contribute to both readily and slowly biodegradable fractions. Thus modification of physico-chemical method was proposed by Roeleveld and Loosdrecht,[10] which combined flocculation and filtration steps with BOD measurements (STOWA protocol).

The aim of this study was therefore to evaluate and compare the COD fractionation method for a municipal wastewater treatment plant using respirometric batch tests combined with model estimation (RT-ME approach) and flocculation/filtration COD method combined with BOD measurements (FF-BOD approach). The first method measures biomass activity *in situ* and is expressed by changes in the dissolved oxygen (DO) and the results are compared with COD measurements. In the second method, the characterization of COD into readily, slowly and non-biodegradable fractions is achieved indirectly, which involves physical-chemical and biological processes. The COD fractionation and modeling results obtained were discussed and compared in terms of appropriate prediction of the effectiveness of organic carbon, nitrogen and phosphorus removal in activated sludge processes which forms a key factor for process optimization in modern cost-effective WWTPs.

Material and methods

The wastewater and activated sludge samples were obtained from Gdynia-Debogorze WWTP, which receives mainly municipal wastewater (only 10% of industrial wastewater in the total inflow) with a pollutant load corresponding to 420,000 PE and an average flow rate of Q_{av}= 55 000 m^3/d. Twenty-four-hour composite samples of influent wastewater were taken after fine screening and/or after primary clarifier, while the final effluent samples were collected at the outlet of the secondary sedimentation tanks. Wastewater samples were collected for about 8–9 months for each study period, representing different sessions of the year from September 2009 to May 2010 for RT-ME approach, and from February to September 2015 for FF-BOD approach. The raw wastewater was characterized by total COD value ($COD_{T,influent}$). Additionally, the Gdynia-Debogorze WWTP is equipped with a brand new computer controlled automation system, where, information from field controllers and online probes are directed to the central control room. The computer network includes all the instrumentation system, which consists of 21 field controllers and operator station SCADA 4. Each controller supports one separate area of technology and are located at different points of the plant. More information about process configuration, operational conditions and control system are available from Drewnowski et al.[1]

Evaluation of COD fraction using the flocculation/filtration COD method combined with BOD measurements (FF-BOD approach)

The FF-BOD approach was carried out using a modified STOWA protocol.[10] The total soluble organic fraction (S_T) was determined as COD of raw wastewater after coagulation. The inert (soluble) non-biodegradable organic fraction – S_I was determined as COD of wastewater, biologically treated in WWTP Gdynia-Debogorze – taken from the outlet of the secondary sedimentation tanks, then coagulated and filtrated through 0.45 μm membrane filters. Additionally in raw wastewater, the BOD was measured for a period of 20 days (BOD_{20}). In the case of other COD fractions viz., S_S – readily (soluble) biodegradable, X_S – slowly (particulate) biodegradable, X_T – total particulate organic fraction, X_I – inert (particulate) non-biodegradable and X_B – biomass were calculated according to the conversion formulas set out in the ATV–A113.[11] Briefly, the fractions were calculated as: $S_S = S_T - S_I$, X_S as: $X_S = BOD_{20} - S_S$, X_T as: $X_T = COD_{T,influent} - (S_S + X_S)$ and X_I as: $X_I = COD_{T,influent} - (S_S + X_S + X_B)$. In total, the COD fractions were determined twenty-two times.

Evaluation of COD fraction using the respirometric tests combined with model estimation (RT-ME approach)

The experimental set-up consisted of a computer controlled batch reactor equipped with stirring and aeration systems, thermostatic unit, DO, redox, and pH/temperature probes. In order to eliminate the oxygen consumption via

Table 1. The fractionation procedure of COD in the raw/settled wastewater for the modeling evaluation based on the literature data and measurements carried out at "Gdynia-Debogorze" WWTP.

Measured parameters

Definition	Symbol	Unit	Monthly average value raw/ settled wastewater	Source of data
Influent COD	COD_{in}	$gCOD/m^3$	1078/856	Laboratory analyses at study WWTP
Influent COD in filtered sample	$COD_{f,in}$	$gCOD/m^3$	267/211*	
Volatile fatty acids	VFA	g/m^3	—/167	
Influent BOD_5	$BOD_{5,in}$	$gBOD_5/m^3$	472/319	
Influent biodegradable COD	$BCOD_{in}$	$gCOD/m^3$	806/545	Calculation (Grady et al. 1999) $BCOD_{in} = \frac{BCOD_{5,in}}{f_{BOD}(1-Y_H \cdot f_p)}$
Effluent COD	COD_{out}	$gCOD/m^3$	25.4	Laboratory analyses at study WWTP
Effluent COD in filtered sample	$COD_{f,out}$	$gCOD/m^3$	20.5**	
BOD_5/BOD_U ratio	f_{BOD}	—	0.67	(Grady et al. 1999)
Heterotrophic biomass yield coefficient	Y_H	gCOD/gCOD	0.63	
Unbiodegradable fraction from the biomass decay	f_P	—	0.2	

Model components – raw/settled wastewater

Fraction name	Symbol	Unit	Equation	Average % of COD: This procedure	Average % of COD: Calibration of SRT
Inert soluble	S_I	$gCOD/m^3$	$0.95\ COD_{f,out}$	2.8	
Readily biodegradable	S_S	$gCOD/m^3$	$COD_{f,out} - S_I$	22.8/21.8	
Slowly biodegradable	X_S	$gCOD/m^3$	$BCOD_{in} - S_s$	51.9/41.8	47.9/38.8
Inert particulate	X_I	$gCOD/m^3$	$COD_{in} - COD_{f,in} - X_s$	22.5/33.6	26.5/36.6

Note:
*Mesured by coagulation-flocculation method of Mamais et al. (1993) during batch tests.
**Correlated with daily measurements of $COD_{f,out}/COD_{out}$ ratio.

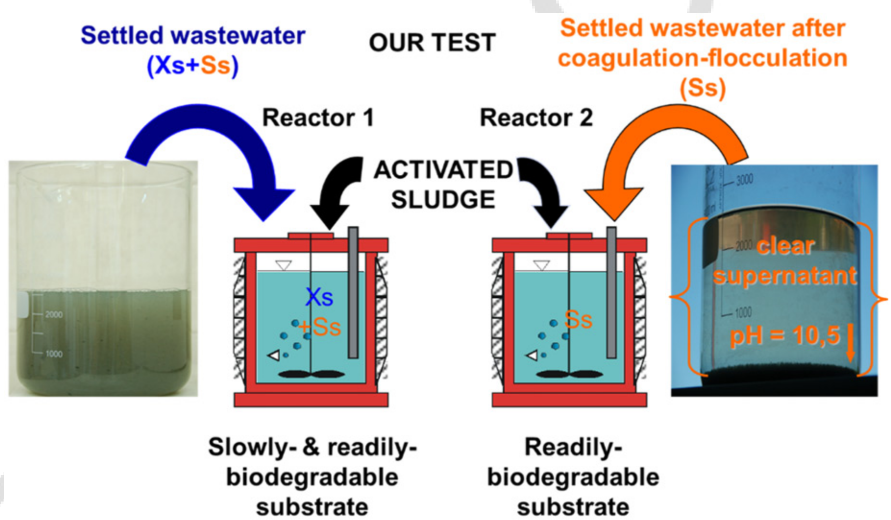

Figure 1. The experimental procedure with the coagulation-flocculation method[15] to evaluate the contribution of $S_S/COD_{T,influent}$ by single respirometric tests.

nitrification, allylthiourea (ATU) was added to the reactor. The pH was kept in the range of 7.0 to 8.0 and the oxygen level in the reactor was controlled with a WTW Oxi-Stirrer 300 (magnetic stirrer) probes.

The oxygen utilization rate (OUR) was measured according to the method described by Kristensen et al.[12] Activated sludge was tested with raw/settled wastewater (SWW), and after coagulation-flocculation in 4 L batch reactors at 15.4–17.2 °C. The OUR was obtained by measuring the decrease in oxygen concentration every 3 min, with a constant oxygen supply every 10 s (6–7 mg/L oxygen was supplied to the system) for 6–7 h. The OUR was further calculated from the linear regression of the slope of the obtained curve. The fractionation of organic matter in the influent wastewater was performed according to the modified method of Grady et al.[3] and Makinia.[13] The procedure was developed based on the Dutch STOWA standard guidelines for wastewater characterization (Table 1) with minor modifications. The standard laboratory analyses at Gdynia-Debogorze WWTP does not include the measurement of soluble COD. However, additional measurements were needed to analyze the contribution of S_S to $COD_{T,influent}$ for the respirometric tests combined with model estimation and the coagulation-flocculation method of Mamais et al.[14] Figure 1 shows the experimental procedure with the coagulation-flocculation method of Mamais et al. (1993) to evaluate the contribution of $S_S/COD_{T,influent}$ by single respirometric tests. Additionally, the actual laboratory measurements of volatile fatty acids (VFA)s (assumed to be equal to S_A – fermentation products) were carried out from the samples of the SWW. The X_S/X_I ratio was estimated by calibrating the sludge retention time (SRT) in

Table 2. Results of the average COD fractionation determined by the flocculation/filtration COD method and respirometric test method in municipal wastewater in Gdynia-Debogorze WWTP.

	Component	FF-BOD (flocculation/filtration COD) approach combined with BOD Average COD (range)		RT-ME approach combined with Dutch STOWA Average COD (range)	
		$g\ O_2/m^3$	%	$g\ O_2/m^3$	%
COD fraction in Gdynia-Debogorze WWTP	S_I	27.0	2.4 (1.1–3.2)	42.0	3.9 (2.8*–4.9)
	X_I	382.3	33.1 (8.3–62.7)	263.6	24.4 (12.8**–36.1)
	S_S	200.0	18.1 (10.1–34.1)	292.1	27.1 (22.8*–31.3)
	X_S	521.7	46.3 (22.0–71.4)	480.8	44.6 (37.3–51.9*)
	Total COD	1130.9	100	1077.9	100

*Combined with the standard Dutch STOWA guidelines.
**Combined with model estimation proposed by Henze et al. (1999) according ASM2d $X_I = 0.128 \times COD_{T,influent}$.

modeling predictions. The results of the respirometric test were simulated by ASM2d to compare predictions in terms of OUR and COD behavior. The biodegradable COD fractionations were directly estimated during OUR batch tests. The soluble inert COD component (S_I) of SWW was determined according to Henze et al.[15] In this approach, the COD fractionations were carried out sixteen times and evaluated by mathematical modeling and computer simulations.

Mathematical modeling and computer simulation

The mathematical modeling and computer simulation procedure were followed as described previously.[1] Briefly, data sets obtained from the full-scale Gdynia-Debogorze WWTP were used for steady-state simulations in the software GPS-x ver. 5.0.2.[16] The mathematical modeling and computer simulations were carried out based on the ASM2d model according to Henze et al.[17] In order to perform accurate calibration, the data sets from both full-scale WWTP and laboratory batch tests were used from our previous study.[1] The stoichiometric and kinetic parameters were determined by numerical optimization using the Nelder-Mead simplex method by Nelder and Mead.[18] The respirometric batch tests (OUR and corresponding COD consumption for estimating fractionation) were carried out and the OUR, biodegradable substrates monitoring and the conditions of activated sludge were also determined. Once calibrated and validated, the model used in this study and the data collected previously during different seasons (Drewnowski et al.[1]) were used to evaluate the performance of Gdynia-Debogorze WWTP as well as to validate the COD fractionation and modeling approach for appropriate optimization and monitoring of modern cost-effective activated sludge system.

Analytical methods

The COD, BOD_{20}, and TSS/VSS were determined according to Standard Methods (APHA, 2005). The total soluble COD fractions (S_T) and the inert (soluble) non-biodegradable organic fraction (S_I) in wastewater were also determined after coagulation with zinc sulfate (10% $ZnSO_4$, at pH = 10.5) followed by filtration through 0.45 μm membrane filters.[14] The detailed procedure can be obtained from Makinia[19] and Drewnowski et al.[20]

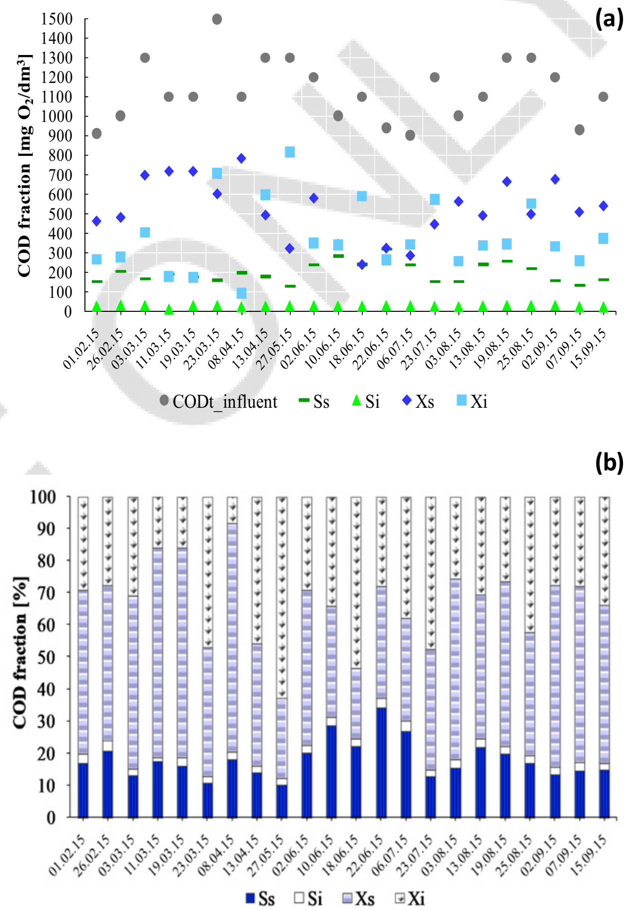

Figure 2. Values (a) and the ratio of COD fractions to $COD_{T,influent}$ (b).

Results and discussion

In this study, the total influent COD ($COD_{T,influent}$) and COD fractionation of Gdynia-Debogorze MWWTP were determined by RT-ME (September 2009 to May 2010) and FF-BOD (February to September 2015) approaches. During the study period, the $COD_{T,influent}$ values detected in raw wastewater varied from 750 to 1570 mg O_2/dm^3 (average 1077.9 mg O_2/dm^3) and 900 to 1500 mg O_2/dm^3, (av. 1130.9 mg O_2/dm^3), respectively (Table 2 and Figure 2a). These observed values were higher, in comparison to a typical municipal wastewater (av. 750 mg O_2/dm^3).[21] The higher COD value could be due to low water consumption or the influence of industrial wastewater. Though in Gdynia-Debogorze WWTP, the industrial wastewater

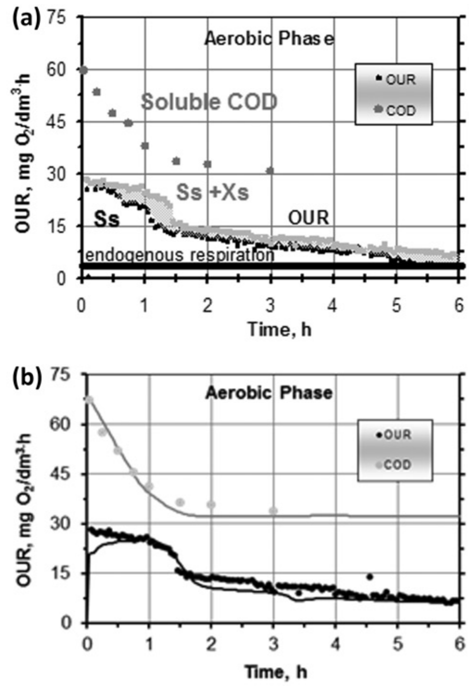

Figure 3. Results of the OUR and COD profiles during the respirometric batch test: a) the settled wastewater without pretreatment ($Ss + Xs$ – gray) and after coagulation-flocculation (only Ss – black) b) data vs. model predictions by ASM2d.

represents only 10% of the raw inflow, it could probably affect the quantity and quality of organic matter entering the plant. In such cases, reliable evaluation of COD fractionation is crucial for process optimization and model predictions.

COD fractionation determined by FF-BOD approach

The data obtained for $COD_{T,influent}$ and the FF-BOD approach are presented in the Figure1a–b and in Table 2. The S_S fraction accounted from 10.1% to 34.1% of the $COD_{T,influent}$, with higher values observed for summer months (>20%; Figure 3a–b). This could be as a result of recreational activities in the studied area or due to the discharge of higher amount of typical domestic wastewater to the sewer during the summer season. In the case of S_I, it appeared to be the most stable fraction in the tested wastewater (1.1% to 3.2% of the $COD_{T,influent}$). The X_S together with X_I constituted the main fraction of total $COD_{T,influent}$ (av. 46.3% and 33.1%, respectively). Using a similar approach, a short term study conducted by Myszograj and Sadecka[22] obtained the following values for COD fractions: $S_S = 23–29\%$, $S_I = 2–3\%$, $X_S = 51–56\%$, $X_I = 7–19\%$ of the $COD_{T,influent}$ which are slightly different from the current observations. It should be noted, however that besides duration, the above study was also differed in the size of the WWTP investigated, volume of wastewater treated and population equivalent (PE). Therefore, to reflect the impact of seasonal changes on wastewater quality and to understand the specificity of both WWTP catchment and sewer systems, a long-term study deem necessary.

COD fractionation determined by RT-ME approach

The measurement of COD by respirometric tests combined with model estimation showed similar differences in the raw and SWW in the amount of soluble COD fractions without pretreatment and also after coagulation-flocculation. However, in the amount of particulate COD fractions, more discrepancy for the X_S/X_I ratio was observed between the raw and SWW. After settling in primary clarifier, low X_S value was measured, which was a key factor for appropriate modeling of short- and long-SRT and monitoring of activated sludge processes. In a study, Ginestet et al.[23] characterized raw wastewater originating from seven WWTPs in French. Respirometric measurements were carried out with samples of the raw, settled and "coagulated" (i.e. settled and precipitated with $FeCl_3$) wastewater. The latter group predominantly consisted of the readily hydrolyzable fractions (37–90%), whereas the readily biodegradable and inert fractions accounted for 2–27% and 2–47% of soluble COD respectively. Koch et al.[24] found a poor correlation between soluble COD (after filtration on a 0.45 μm pore size filter) and S_S readily biodegradable COD (estimated based on aerobic respiration tests) under Swiss conditions, where the biodegradable fraction of wastewater primarily consisted of slowly biodegradable compounds X_S due to short hydraulic retention times in the sewer systems.

The aerobic batch respirometric test monitors the oxygen uptake rate (OUR), which indicates the oxygen consumption rate resulting from the microbial activity. In the current study, the total duration of each OUR test was about 6–7 h, however, approximately after 1 h, a sudden change in OUR plot was observed. Once the readily biodegradable compounds (S_S) were consumed, the OUR stabilized due to the switch to slowly biodegradable substrate (X_S) and endogenous respiration products (Figure 3a). In the experiments with the SWW, the observed OUR was found to be associated with the utilization of S_S in soluble form as well as colloidal and particulate organic compounds (X_S). By taking the VSS into account (average value 256 mg/L), the specific OUR for a particular activated sludge was obtained. The maximum OUR values with the SWW varied within the range of 19.0–24.2 g O_2/(kg VSS·h) respectively, in the studied WWTP. In comparison with the values reported for the OUR experiments[25] with real wastewater and activated sludge from a pilot-scale plant, the results from this study varied around the level of 20 mg O_2/gVSS·h. When the pretreated samples of wastewater were used in the experiments, the observed OUR was found to be associated with the utilization of S_S and the remaining colloidal organic fraction (part of X_S). Consequently, the values of OUR from studied plant were lower (11.8–17.8 g O_2/(kg VSS·h) in comparison with the parallel tests with the SWW. The average difference of OUR profiles observed between the parallel reactors with the SWW without and with pretreatment were between 30 and 50% in comparison to the most extreme cases.

The results of OUR and COD during the respirometric batch test vs. model predictions by ASM2d are shown in Figure 3a–b. Additional profiles of pH and ORP during the respirometric batch test are presented in Figure 3a–b. Based

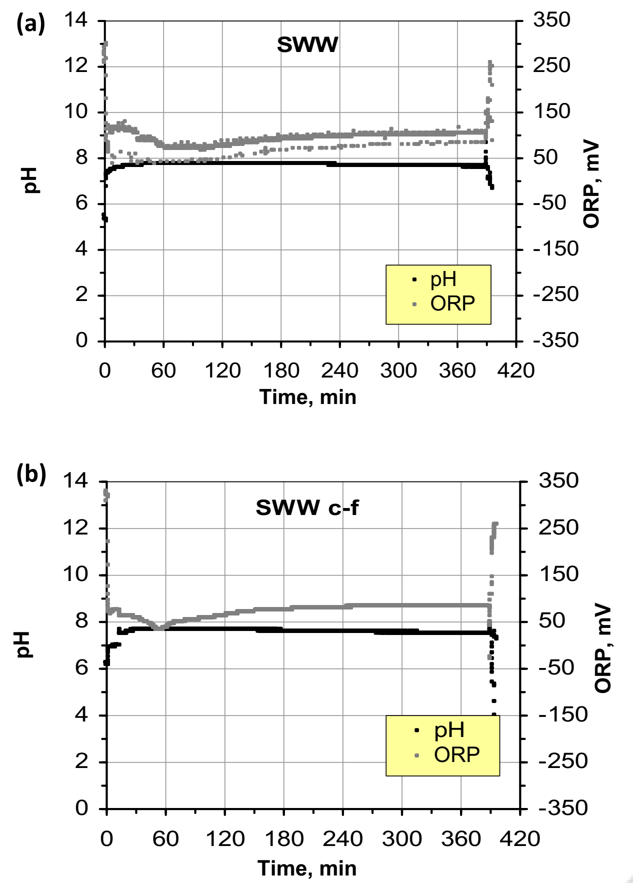

Figure 4. Profiles of pH and ORP during the respirometric batch test: a) the settled wastewater without pretreatment, b) the settled wastewater after coagulation-flocculation.

on the results obtained, it can be observed that duration of OUR tests (6–7 h in total) in some cases could be extended, so that the biodegradation of slowly hydrolyzable fraction as well as other form of COD continues. Describing the ORP and pH values during the respirometric batch test, it should be noted that the pH remained stable for about 7.8–7.9 for both investigated samples, i.e., the SWW without pretreatment and after coagulation-flocculation. However, the ORP values decreased from 100 mV to 50 mV in the initial feeding hour due to the rapid degradation of readily biodegradable substrates. Once the readily biodegradable COD fractions (mostly S_S and partly X_S after hydrolysis process conversion) were utilized, conditions were reestablished and the ORP increased from 50 mV to 100 mV reaching a steady-state, which is similar to the value obtained during the initial-stage tests.

The effect of primary clarifiers and precipitation on COD removal in the SWW and after coagulation-flocculation (c-f) using the method of Mamais et al.[14] are shown in Figure 5a–b. The soluble fraction in the 24-h wastewater samples used in the experiments accounted for 23 to 46% of $COD_{T,influent}$ in the tested (16 samples) SWW. The average values of total and soluble COD in SWW determined (c-f) from the annual routine operational data were slightly different from the raw wastewater concentrations, i.e. 751 and 168 g COD/m^3 (2009) vs. 788 and 167 g COD/m^3 (2010). In an earlier modeling study,[13] the estimated ratio of

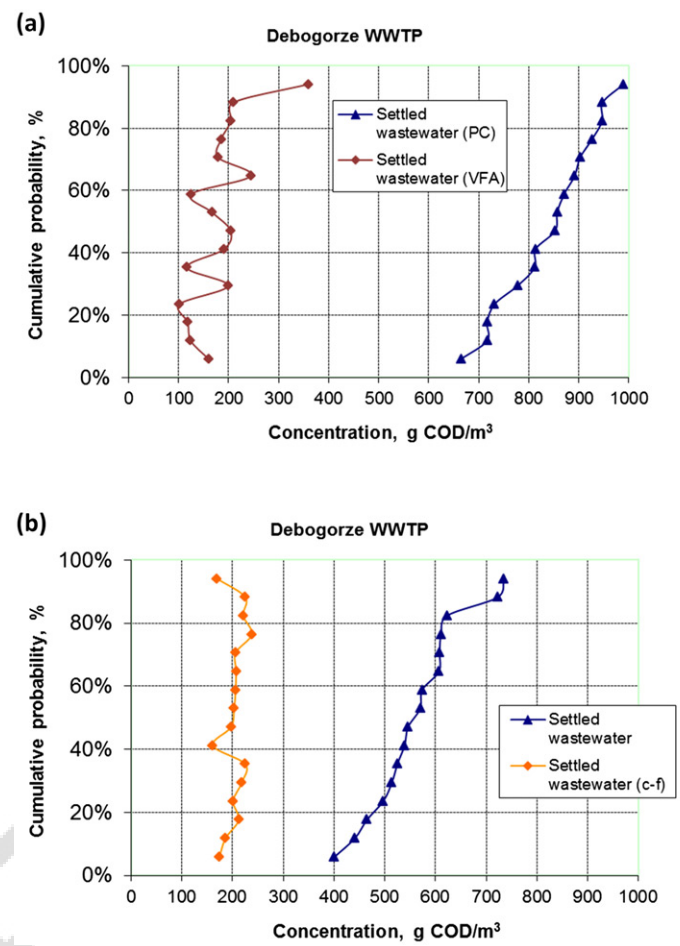

Figure 5. The effect of (a) primary clarifiers (PC) with volatile fatty acid (VFA) release and (b) precipitation on COD removal in the settled wastewater and after coagulation-flocculation (c–f).

biodegradable to non-biodegradable particulate (and colloidal) organic fractions varied in the range of 1.4–1.5 to fit the waste activated sludge (WAS) production. As a consequence, the ratios of ($S_S/(S_S+X_S)$) at the Gdynia-Debogorze WWTP (0.50–0.54) slightly exceeded a typical range of 0.3–0.5. Specifically, in a WWTP the successful settling has been described to be highly dependent on floc density, size and chemical composition.[26] These characteristics are in turn dependent on factors such as the retention time of solids,[27,28] oxygen concentration,[29] predator grazing effects,[30] levels of filamentous bacteria[31] and floc size.[32]

From a practical point of view, it should be noted that the conventional chemical precipitation with $FeCl_3$ has very similar effects as the method of Mamais et al.[14] In a full-scale WWTP using $FeCl_3$ to precipitate SWW, Xu and Hultman[33] found no difference in COD determined in the samples of SWW (untreated and treated with $ZnSO_4$). Due to sedimentation in the primary clarifiers, the ratio of particulate (and colloidal) COD (XCOD) to volatile suspended solids (VSS) increased from 1.67–2.58 g COD/g (raw wastewater) to 1.83–2.68 g COD/g (SWW). This indicates that a VSS fraction with a low COD/VSS ratio, such as particulate carbohydrates[34] was removed in the primary clarifiers (Figure 4b). The clarifiers are operated with a high sludge blanket level to hydrolyze settleable organic particulates to

VFAs for enhancing denitrification and Enhanced Biological Phosphorus Removal (EBPR) in the bioreactor (Figure 5a). The above observations indicate that particulate compounds in wastewater may be related to a wide range of physical–-chemical and biological phenomenon in conventional wastewater treatment systems. This warrants a pressing need for further research on the development of accurate methods for COD fractionation as a key factor for modeling and monitoring of activated sludge processes. Figure 5a–b is a typical example showing potential differences in precipitation on COD removal in the SWW and after coagulation-flocculation (c-f) representing conventional chemical precipitation in comparison to the effect of primary clarifiers (PC) with VFA in real conditions of WWTP operation strategy.

Comparison of FF-BOD and RT-ME approaches in determination of COD fractionation

COD fractionation has been described as a major challenge in conventional activated sludge systems: in solid and liquid separation in clarifiers,[35] in nitrogen removal[36] and in assessing the kinetics of NUR, PUR, AUR in biological reactors with different internal and external COD composition.[19] The average values of COD fractions estimated during this study for Gdynia-Debogorze WWTP are presented in the Table 1.

Based on the results obtained, the particulate fractions of COD (X_S and X_I) in FF-BOD were higher than those estimated by RT-ME approach. Contrary to the above, the values of inert soluble fraction (S_I) evaluated by FF-BOD were significantly lower than in RT-ME approach (2.4% and 3.9% of $COD_{T,influent}$, respectively), suggesting that the evaluation of the inert COD amount in wastewater is significantly dependent on the method used for wastewater characterization. Similarly, S_S determined by the FF-BOD and RT-ME approaches differed, and accounted for 18.1% (10.1%–34.1%) and 27.1% (22.8%–31.3%) of $COD_{T,influent}$, respectively.

All COD fractions obtained in this study by RT-ME and FF-BOD approaches for raw wastewater corresponds to the ranges presented in literature of other European countries (S_S: 3.0%–35%; S_I: 2.0%–8.5%; X_S: 28%–66.2%, X_I: 10%–39%).[10,37–42] However, the main challenge is the lack of standardized definition and methodology for COD fractionation. Inconsistency in the adopted methods by various researchers made the available literature results uncomparable. In this study, the discrepancies between the physico-chemical method and respirometric measurements could also be related to the essential content of industrial wastewater in municipal wastewater stream[43] and the presence of soluble COD fractions with different degradation kinetics. For industrial wastewater, the truly soluble COD can be a sum of three fractions: inert (S_I), readily biodegradable (S_S) as well as rapidly (S_{RH}) and slowly (S_{SH}) hydrolyzable fraction.[44]

In this study, the COD fractions obtained for Gdynia-Debogorze WWTP using the FF-BOD approach can be regarded as a close to real value. Due to the longer HRT (which is long enough for the degradation of slowly hydrolyzable fractions) as well as application of coagulation/filtration procedure, it can be expected that both S_I and S_T fractions were determined with acceptable accuracy. Accordingly, other fractions (S_S, X_S, X_I) calculated on this basis of S_I and S_T fractions and BOD_{20}, are also expected to be properly estimated.

RT-ME approach is suitable to determine the adequate COD fractionation profile of a particular wastewater. However, when dealing with the industrial wastewater, special attention needs to be given for the proper estimation of S_I value as well as the low colloidal and particulate fraction as it can pass through the filter even after the coagulation. For the estimation of biodegradability, S_S results might be overestimated, as it probably happened in this study, since only coagulation-floculation procedure was used. As both inert and easily biodegradable COD are essential for the prediction of wastewater treatment processes, for municipal wastewater that are influenced by industrial wastewater, a comparison of respirometric tests with results obtained from a long-term flocculation/filtration COD/BOD measurements can be made for better characterization. To confirm or exclude the presence of slowly hydrolyzable fraction, soluble and/or particulate, as well as the presence of biodegradable, low colloidal/particulate fraction, the RT-ME approach for raw wastewater, after coagulation/filtration can be considered for better profiling. Such data sets together with biological treatment efficiency and precise evaluation of industrial/municipal wastewater ratios may facilitate to maintain a constant high level of phosphorus and nitrogen removal from wastewater treatment plants and to develop efficient and cost effective wastewater treatment systems.

Conclusions

The discrepancies in results obtained between the physico-chemical method and respirometric measurements in determination of COD fractions in this study is suggested to be related to the contribution of the industrial wastewater load in municipal wastewater stream. Mainly, the low colloidal and particulate fractions as well as the soluble inert fraction related to a wide range of physical–chemical and biological phenomena may be present at different concentrations in the municipal wastewater. Thus as presented in this study more research on the proper methods for determination of COD fractionation as a key factor for appropriate modeling and monitoring of activated sludge processes deem necessary. As presented in this study, the comparison of the respirometric tests with the results obtained during flocculation/filtration COD/BOD measurements shown potential in proper fractionation of COD in municipal wastewater with industrial load. Such data sets and different methodology overview in comparison to traditional COD fractionation procedures together with the phosphorus release and denitrification efficiency may facilitate efficient optimization of the treatment processes at full scale level for better nutrient removal. Additionally, kinetic/stoichiometric coefficients in mathematical modeling and computer simulations might also play an important role in general estimation and proposing a cost-effective global solution for worldwide "positive-energy" trends in municipal WWTPs.

Nowadays, carbon (C) extraction is achieved at a rate of 30% in the primary settler and have to be appropriately balanced between biogas production and efficiency of biochemical processes such as denitrification and EBPR in the activated sludge bioreactor. Therefore, the physico-chemical and biological characterization methods of COD fractionation compared in this study might be useful for the modeling approach as well as for monitoring and operating (e.g. short- and/or long- SRT activated sludge) modern WWTP. The wastewater characteristic (soluble, colloidal and particulate fractions) and loading of biodegradable organic compounds could affect the performance of conventional respirometric tests. However evaluation of the OUR profile with SWW and/or after coagulation-flocculation could still be recommended as a "rapid" control method for monitoring/optimising modern cost-effective WWTP.

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