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Respirometric evaluation of a mixture of organic chemicals with different biodegradation kinetics

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ABSTRACT

The study evaluated the biodegradation characteristics of a mixture of organics with different biodegradation characteristics in an integrated chemical plant effluent. The wastewater had a total chemical oxygen demand (COD) content of 12,800 mg/L, mostly soluble and 93% biodegradable. The evaluation was based on respirometry, and mainly consisted on model calibration and interpretation of the oxygen uptake rate data, which exhibited an original and specific profile with a sequence of two peaks and three plateaus. A specific model was defined for this purpose, which identified four different biodegradable COD components with significantly different process kinetics. The major fraction accounting for 57% of the total biodegradable COD in the wastewater had to be hydrolyzed before biodegradation with a low hydrolysis rate of 1.3 day^{-1}. The analysis of the experimental data showed that the oxygen utilization started with a delayed response after substrate addition. The delayed logarithmic phase could be characterized by a *Haldane* type of inhibition kinetics.

1. Introduction

Most industrial activities generate high amount of different pollutants in terms of organic and specific substances. The resulting wastewater contains a vast array of chemicals that have different chemical structures. A part of chemicals used in the process finally end up in the discharge, resulting in concentrated streams including specific pollutants. Moreover, existence of inhibitory and toxic compounds causes severe problems for biological treatment [1,2]. Consequently, treatment of industrial effluents containing a mixture of highly concentrated organic pollutants with unknown biodegradation characteristics poses difficulties in meeting the stringent discharge regulations. Hence, more relevant information on the biodegradability of substrates in wastewater needs to be collected, in a way that is readily adaptable to modeling and design, specifically for each industrial activity.

Assessment of the overall biodegradation characteristics of a substrate mixture in terms of its constituents, i.e. observing the fate of individual organic compounds, while ideally desirable, proves in most cases not meaningful and sometimes misleading for a number of reasons: (i) complete identification of specific organics is too difficult and the process is likely to miss the most significant compounds affecting overall biodegradation; (ii) assessment of biodegradation kinetics in a way that can be incorporated in models requires a series of experiments where each specific substrate serves as a single substrate; (iii) the fate of a compound as a single substrate may be different than in a mixed culture and not representative because of a different microbial composition sustained and different substrate interactions in the system. So far, only a few single substrates such as volatile fatty acids and especially acetate, PHAs, glycogen, with clearly defined specific metabolic function could be differentiated and incorporated into mechanistic models with the corresponding stoichiometry and kinetics. Studies have shown that even simple substrates like starch involve a sequence of complex conversion and utilization mechanisms requiring elaborate experimental evaluation for appropriate modeling [3,4]. In this context, models development primarily relied upon the chemical oxygen demand (COD) as the overall parameter for substrate and biomass. The recognition of COD fractions with different biodegradation characters by Dold et al. [5], served as a milestone in providing significant advances in multi-component modeling, where the basic approach has been to identify groups of substrate – COD fraction – that could be collectively defined in terms of the same biodegradation kinetics.

The significance of the dissolved oxygen was largely ignored in the traditional models for substrate utilization from wastewaters under aerobic conditions. Ekama et al. [6], in their groundbreaking study, promoted the process rate for dissolved oxygen utilization, better known as the oxygen uptake rate (OUR) as the key experimental tool in identifying different biodegradable COD fractions

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Nomenclature

b_H	endogenous decay rate (1/day)
C_{S1}	initial total biodegradable COD (mgCOD/L)
C_{T1}	total influent COD (mgCOD/L)
f_p	inert fractions of biomass (mgCOD/mgCOD)
k_h	maximum hydrolysis rate (1/day)
K_I	inhibition concentration on S_{S1} (mgCOD/L)
K_{S1}	half saturation constant for S_{S1} (mgCOD/L)
K_{S2}	half saturation constant for S_{S2} (mgCOD/L)
K_{S3}	half saturation constant for S_{S3} (mgCOD/L)
K_X	hydrolysis half saturation constant (gCOD/gcellCOD)
OUR	oxygen uptake rate (mg/L/h)
S_{H1}	hydrolysable COD (mgCOD/L)
S_I	soluble inert COD (mgCOD/L)
S_P	soluble residual COD generated as metabolic products (mgCOD/L)
S_{S1}	first readily biodegradable COD (mgCOD/L)
S_{S2}	second readily biodegradable COD (mgCOD/L)
S_{S3}	third readily biodegradable COD (mgCOD/L)
S_{T1}	influent soluble COD (mgCOD/L)
S_{02}	oxygen concentration (mgO_2/L)
X_{H0}	active biomass concentration (mgcellCOD/L)
X_I	particulate inert COD (mgCOD/L)
Y_H	heterotrophic yield coefficient (gcellCOD/gCOD)

Greek letters

$\widehat{\mu}_{H1}$	maximum growth rate on S_{S1} (1/day)
$\widehat{\mu}_{H2}$	maximum growth rate on S_{S2} (1/day)
$\widehat{\mu}_{H3}$	maximum growth rate on S_{S3} (1/day)

and rate coefficients. Multi-component models developed for the activated sludge process incorporated this parameter as a major model component [7]. With the significant instrumental support developed for this purpose, respirometry now provides a scientifically reliable procedure for fingerprinting biodegradable substrate, also identifying different biodegradation characteristics [8–10]. In this respect, the oxygen uptake rate profile contains ample information on substrate utilization by heterotrophic biomass. The interpretation of the OUR profile with the aid of a selected biodegradation model allows estimating relevant kinetic and stoichiometric parameters which can be used in the design and operation of biological treatment systems. Moreover, respirometric modeling can also be used for the evaluation of inhibitory and/or toxic effects (i.e.: substrate inhibition, specific toxic compounds, effect of xenobiotics, etc.) on model parameters, giving this way the necessary clues about changes occurring in corresponding metabolic processes [11].

The evaluation of the OUR profile with model calibration has been successfully applied for interpreting the biodegradation characteristics of domestic sewage and most industrial wastewaters. The main problem tackled in this effort was to further explore the single overall substrate parameter (COD) commonly used in wastewater characterization. While COD is quite useful in establishing the electron balance between substrate utilized, biomass generated and dissolved oxygen consumed in aerobic systems, it cannot differentiate biodegradable and inert substrate or substrate fractions which undergo a number of biochemical reactions at different rates. This evaluation is now fairly complete for domestic sewage and the results are well reflected in all mechanistic models which incorporate a wide spectrum of substrate and biomass components, all expressed in terms of COD equivalents [12,13]. Similar respirometric studies have also been conducted on industrial wastewaters, revealing markedly different process rates as compared to domestic sewage [14]. This type of an evaluation based on modeling of the OUR profile, while fairly straight forward for industrial effluents with relatively simpler substrate composition such as confectionary wastes [15], may become quite difficult for more complex wastewaters.

The objective of the paper was to evaluate the biodegradation characteristics of the wastewater generated from a chemical industry producing a wide spectrum of different chemicals, which evidently reflects on the character of the plant effluent. The evaluation mainly relied on model calibration and interpretation of the OUR data exhibiting a very original and specific profile, obtained through aerobic degradation of the complex substrate mixture in the wastewater. A multi-component mechanistic model was developed for this purpose, enabling to define and quantify the main COD fractions and their biodegradation kinetics. The experimental work yielded the essential kinetic information for defining the appropriate biological treatment scheme.

2. Materials and methods

2.1. Investigation site

The study was conducted at an integrated chemical plant located in Tuzla, in the eastern part of Istanbul, manufacturing a wide spectrum of organic chemicals. The production portfolio of the plant mainly includes cleaning/personal care products, nutrition and health, functional products and process chemicals. Nutrition and health products such as soaps, detergents and different pharmaceuticals account for more than 80% of the production. During the study, the wastewater generated from the plant was treated on-site by means of a wastewater treatment plant that was previously built and operated with the following steps and functions: (1) equalization tank, (2) coagulation using $FeCl_3$ and lime, (3) flocculation with polyelectrolyte (3) settling, (4) neutralization and (5) activated sludge treatment. The aerobic activated sludge reactor was operated at a F/M ratio of 0.3 in COD/TSS unit.

The main practical concern was also to test and evaluate the merit and the need for the present flow scheme and especially the pretreatment steps for system upgrading, if necessary. Both conventional characterization and biodegradation results indicated, as will be elaborated in the following section, that chemical pretreatment had only a minor role and could well be eliminated. Therefore, the study focused on the biodegradation characteristics of the raw wastewater, which was sampled from the equalization basin of the treatment plant.

2.2. Assessment of inert COD fractions

The soluble (S_I), and particulate (X_I), inert COD fractions of the wastewater were determined using the method developed by Orhon et al. [16]. The method involves three aerated batch reactors fed with the unfiltered, filtered wastewaters and the glucose seeded with a very small amount of biomass previously acclimated to the glucose and wastewater mixture. Inert fractions are calculated using final threshold values of the glucose, total and soluble COD in three reactors after a period where all biological activity is practically completed. In parallel to the determination of inert COD fractions, 2 L fill and draw reactor was operated with an initial COD to biomass ratio (S_0/X_0) of approximately 10, to observe the soluble COD removal with time under aerobic conditions. The oxygen in the reactor was kept around 5 mgO_2/L that is sufficient for heterotrophic activity.

2.3. Respirometric biodegradation test

The respirometric tests were conducted with acclimated biomass sampled from activated sludge unit of wastewater treatment plant. Batch respirometric (OUR) experiment was conducted at desired initial food/microorganism (S_0/X_0) ratio. The OUR measurements were performed with Applitek Ra-Combo continuous respirometer. A nitrification inhibitor (Formula 2533™, Hach Company) was added to the reactors to prevent possible interference induced by nitrification. The biomass and wastewater mixture was continuously aerated with compressed air in order to keep the dissolved oxygen level above 5 mgO_2/L in the aeration vessel. The respirometric test was performed with approximately five times diluted wastewater sample. The dilution of wastewater before the batch respirometric test is inherently required mainly because of the actual oxygen limitations within the cell of respirometer and also to sustain the necessary amount of biomass that would establish appropriate F/M ratio that is compatible with the actual biological reactor operation.

After observing the endogenous OUR level, a wastewater sample was added to mixed liquor having a volatile suspended solids (VSS) concentration of 2000 mg/L to maintain an initial substrate to biomass (S_0/X_0) ratio of 0.5 gCOD/gTSS day. The model parameters and initial state variables were estimated in accordance with the method proposed by Insel et al. [10] and Dochain et al. [17]. The SECANT algorithm was selected in order to find the best fit of degradation model on experimental OUR data. Model simulations and parameter estimation works were performed using AQUASIM program [18].

2.4. Analytical procedures

The COD was measured according to ISO6060 method [19]. For soluble COD determination, samples were subjected to vacuum filtration by means of Millipore membrane filters with a pore size of 0.45 μm. Other experiments were performed according to the standard methods [20]. The Millipore AP40 glass fiber filters were used for total suspended solids (TSS) and volatile suspended solids measurements.

3. Results and discussion

3.1. Raw wastewater characterization

Results of conventional raw wastewater characterization in terms of significant parameters, as outlined in Table 1, may be interpreted as follows: (i) the wastewater has a strong character with a total COD of 12,800 mg/L, a total nitrogen concentration of 1160 mgN/L and a total phosphorus concentration of 162 mgP/L; (ii) although high, the ratio of organic carbon (COD) to nitrogen and phosphorus is suitable for biological treatment; (iii) the organic carbon in the wastewater is mainly soluble with a filtered (soluble) COD level of 11,100 mg/L, accounting for more than 85% of the total COD content. Accordingly, the volatile suspended solids concentration, another index for particulate COD is relatively low, with a particulate COD/VSS ratio of around 1.9.

Table 1
Conventional raw wastewater characterization

Parameters	Unit	Concentration
Total COD	mgCOD/L	12,800
Filtered COD (0.45 μm)	mgCOD/L	11,100
Total suspended solids (TSS)	mg/L	1,045
Volatile suspended solids (VSS)	mg/L	895
Total Kjeldahl nitrogen (TKN)	mgN/L	1,160
Ammonia nitrogen (NH_4-N)	mgN/L	1,120
Total phosphorus (TP)	mgP/L	162
Ortho-phosphate (PO_4-P)	mgP/L	66
pH	–	6.3

Aside from the strong and complex character of the influent in terms of organic carbon, the high total nitrogen concentration also requires attention for possible inhibitory effects on nitrification in the presence of complex organic chemicals. The study however was limited at this stage with the biodegradation characteristics of organic carbon, mainly because current effluent discharge regulations do not impose a nitrogen limitation for the plant.

3.2. Determination of inert COD fractions

The results of COD profiles obtained from inert COD experiments are illustrated in Fig. 1. Total inert COD concentration was found to be 845 mg/L, which covers 7% of total COD. The soluble and particulate inert COD fractions were calculated as 5% and 2%, respectively. The assessment of inert components showed that organic content of the chemical industry wastewaters was mostly soluble and biodegradable. Thus, the total COD in raw wastewater was found to be 93% biodegradable (Fig. 2).

3.3. Biological treatability study

The results of filtered COD profile obtained from batch reactor operation shows that the COD concentration is leveled off after

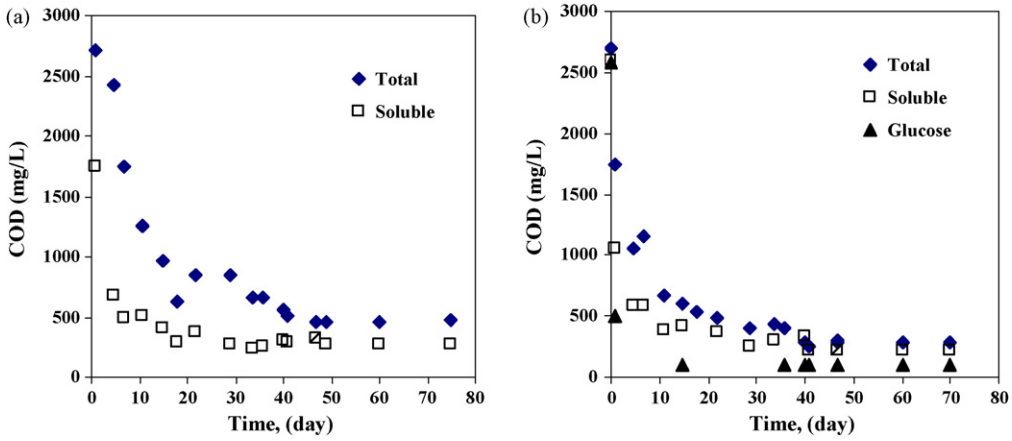

Fig. 1. COD profiles for the determination of inert COD fractions (a) total wastewater reactor and (b) filtered wastewater reactor.

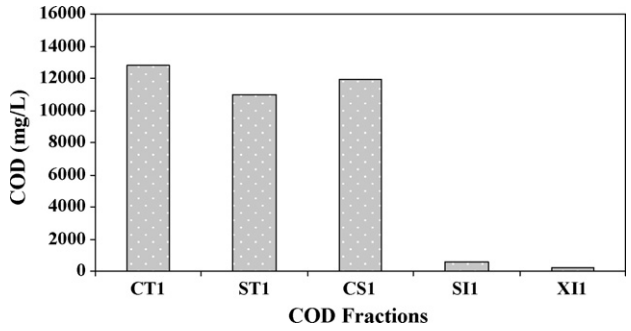

Fig. 2. Schematic representation of different COD fractions in the wastewater.

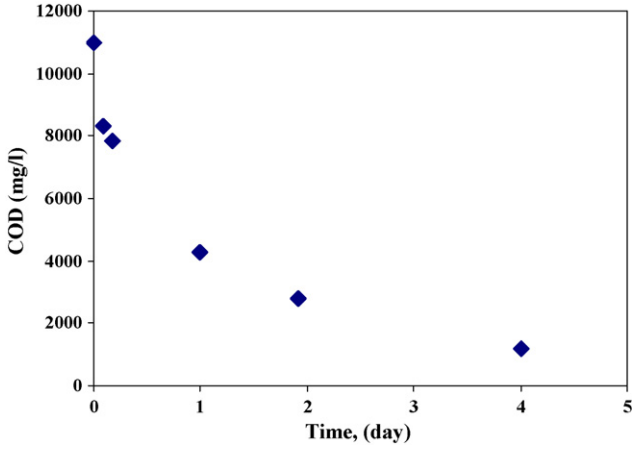

Fig. 3. Soluble (filtered) COD concentrations vs. time in batch reactor.

4 days and reached down to 1160 mg/L starting from an initial COD of 11,000 mg/L (Fig. 3). In particular, the achievable minimum COD concentration with this batch test was found to be around 1160 mg/L which is greater than inert COD (S_I) of 610 mg/L as shown in Fig. 2. So, the difference of 550 mgCOD/L can be attributed to the generation soluble microbial products (S_P) during the utilization of biodegradable organics that might be of inert or very slowly biodegradable nature, which may be considered residual for the experimental conditions of the study.

3.4. Respirometric evaluation of biodegradation kinetics

The experimental OUR profile may provide a preliminary, qualitative information on the sequence of biochemical reactions taking place in the OUR reactor. The shape of the profile primarily depends on the amount of substrate available for biochemical reactions, or in other terms, on the initial substrate to biomass (S_0/X_0) ratio [2]. With a properly selected (S_0/X_0) ratio, the initial peak in the OUR curve, as illustrated in Fig. 4(a), is due to microbial growth on readily biodegradable COD. The following gradual decrease is commonly interpreted by the hydrolysis and subsequent utilization of the slowly biodegradable COD. This pattern is quite typical for domestic sewage [8] and most industrial wastewaters [2]. Calibration of the OUR data with a model that incorporates readily and slowly biodegradable COD as model components and heterotrophic growth and hydrolysis as biochemical processes responsible for substrate utilization may then be used to quantify these COD fractions and respective process kinetics.

Depending on the complexity of substrate, the OUR curve may deviate from its typical pattern. The observed OUR perturbations are commonly explained with the existence of other COD fractions and/or an additional biochemical processes with different kinetics.

The OUR experiment was started with diluted wastewater down to around 3000 mg/L COD to obtain the optimum initial S_0/X_0 ratio for the test. The OUR profile obtained in the experiment is given in Fig. 4(b). It is quite different from a typical OUR curve associated for simpler substrates, as exemplified in the previous figure. Observations on significant features of the profile may be outlined as follows: (i) The initial OUR increase was markedly different as compared to typical OUR curves illustrated in Fig. 4(b). After the wastewater spike into biomass with the aerated endogenous phase at the beginning of the experiment, the initial OUR increase gradually developed, spreading over 300 min to reach a peak of 140 mgO_2/L h, as opposed to a common sharp growth increase. This delayed increase has been observed before and attributed to the presence of inhibitory substances in the wastewater [21] and (ii) After the first 300 min, a smooth decrease associated with a single hydrolysable substrate did not occur; instead, the OUR dropped to sequential three plateau levels at 100, 80 and 40 mgO_2/L h, respectively, with a subsequent decrease to endogenous respiration level after 800 min.

The smaller second peak after the first OUR drop was also observed and attributed to the utilization of a secondary substrate in similar studies: Fig. 5 displays an OUR profile derived tannery wastewater containing a significant level of acetate. Consequently the second peak in the OUR curve could be interpreted by the utilization of polyhyroxybutyrate (PHB), a commonly observed intracellular compound generated through storage of acetate. The figure also shows the inadequacy of model simulation if the existence of a secondary substrate is not properly accounted for [22]. Another interesting example reported in the literature is the OUR profile associated with the utilization of glucose by *Escherichia coli*. The second peak in this curve, as shown in Fig. 6, was explained by the utilization of acetate as a secondary substrate, generated by an overflow mechanism during the metabolism of excess glucose consumption [23].

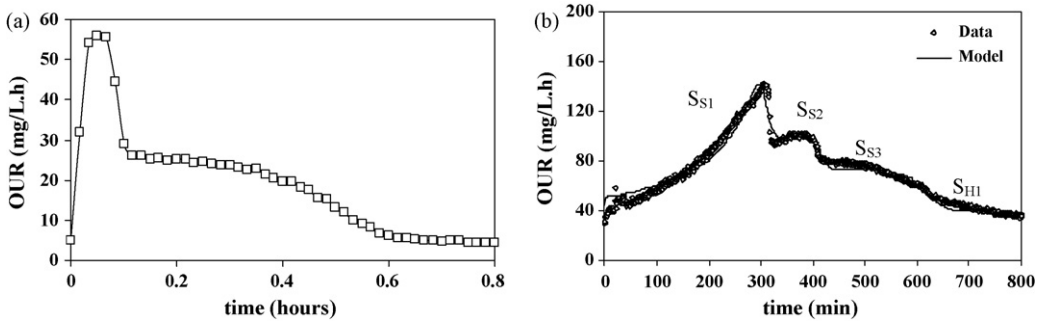

Fig. 4. The OUR profile (a) for a typical domestic sewage [4] and (b) experimental obtained for the wastewater studied together with model calibration.

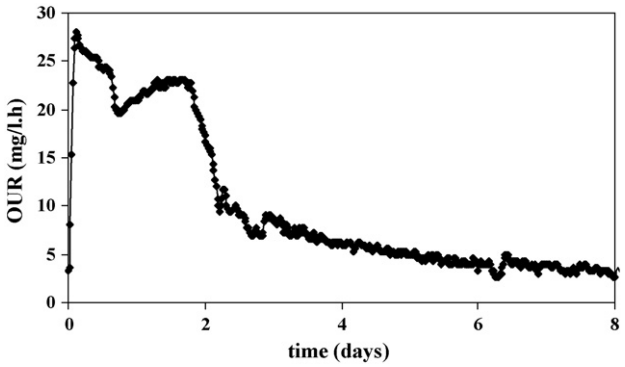

Fig. 5. The OUR curve indicating secondary substrate utilization for tannery wastewater.

3.5. Structure of the mechanistic model

The validity of the selected mechanistic model is essential for an appropriate evaluation. Therefore, it should be structured on the basis of information derived from the OUR profile, which gives clear indication, as outlined before, on the need to differentiate at least four types of biodegradable substrate. Accordingly, the model used in the study incorporated four COD fractions as model components, namely, three readily biodegradable fractions, S_{S1}, S_{S2}, S_{S3} and a slowly biodegradable fraction, S_{H1}. In this context, the model may be regarded as the modified version of ASM1 [7] for organic carbon removal with a more elaborate differentiation of the readily biodegradable COD, S_S. Similarly, the process rates of all three S_S components were defined in terms of a commonly adopted Monod-type of biodegradation kinetics for direct microbial growth, where the rate equation is controlled by the maximum growth rate ($\widehat{\mu}_{H1}$) and half saturation constant (K_S) parameters. The only difference in the process rate of S_{S1} degradation is that an inhibition parameter (K_I) was added in order to model the tampered logarithmic OUR increase within 300 min at initial high biomass concentration. The rate expressions include the switch functions that would ensure simulating sequential substrate utilization observed in the OUR profile. Utilization of secondary substrate after the depletion of the primary substrate is frequently reported in the literature. The work of Karahan-Gül et al. [24] provides a convincing evidence of this phenomenon with a similar OUR interpretation of the sequential removal of a mixture of two simple substrates, acetate and glucose.

The final phase of the OUR profile, much lower than the preceding plateaus and gradually declining towards the endogenous decay level indicated a typical hydrolysis process, a rate limiting step for a much lower biodegradation rate as compared to other COD fractions [10]. Accordingly, it was associated with the final COD fraction, soluble hydrolysable substrate, S_H. The validity of this COD fraction was evaluated and justified through the course of model calibration which provides relevant information on COD mass balance at different stages of the test and related process kinetics. In fact, the OUR profile in Fig. 4(b) indicated that the biodegradation of the slowly biodegradable (hydrolysable) COD, S_{H1}, could be differentiated after approximately 12 h (700 min) from the start of the test. At this time, the remaining filtered COD was measured to be around 650 mg/L which is much higher than the inert soluble COD level of 225 mg/L for the applied S_0/X_0 ratio at the start of respirometric test. This indicated that there was still COD available for the biodegradation process which was characterized by the hydrolysis mechanism. Accordingly, the model was structured to include the four biodegradable components, S_{S1}, S_{S2}, S_{S3} and S_H, together with active heterotrophic biomass, X_H, residual particulate microbial products, X_P and dissolved oxygen, S_O. In the model, the rate of S_O utilization basically yields the OUR profile evaluated in the study. The model, shown in the commonly accepted matrix format in Table 2, has the basic ASM1 structure for organic carbon removal, except for the sequential removal of three biodegradable model components and endogenous decay conveniently utilized in many similar modeling studies for industrial wastewaters [2,25].

3.6. Model calibration with OUR profile

The selected model provided, as displayed in Fig. 4(b), a good calibration of the experimental OUR profile, estimating the magnitude of different biodegradable COD components and the corresponding rate coefficients. The calibration was started with an endogenous decay coefficient, b_H of 0.15 day^{-1} and a residual endogenous fraction, f_E of 0.2 adopted as default values and the total biodegradable COD consumption was verified with an heterotrophic yield coefficient, Y_H of 0.64 gcellCOD/gCOD, a commonly accepted value in similar model applications [7]. The OUR experiment was started with a diluted sample with an initial COD, C_T of around 3000 mg/L to ensure an F/M ratio of 1.3 mgCOD/mgVSS. The estimation identified S_H as the main COD component, with S_H = 1620 mg/L, corresponding to around 54% of the total COD. The other COD components were estimated as S_{S1} = 510 mg/L; S_{S2} = 200 mg/L and S_{S3} = 495 mg/L, that is, 17%, 7% and 16% of the wastewater total COD, respectively. The maximum growth rate $\widehat{\mu}_{H1}$ for S_{S1} degradation was found to be 5.1 day^{-1}, a level compatible with the utilization of the readily biodegradable COD in domestic sewage suggested in the range of 3.5–6.5 day^{-1} [26,27]. On the other hand, the initial logarithmic OUR increase could be modeled with substrate inhibition which was defined in terms of an inhibition coefficient, K_I of 150 mgCOD/L at high active biomass concentration at 1300 mgcellCOD/L. The

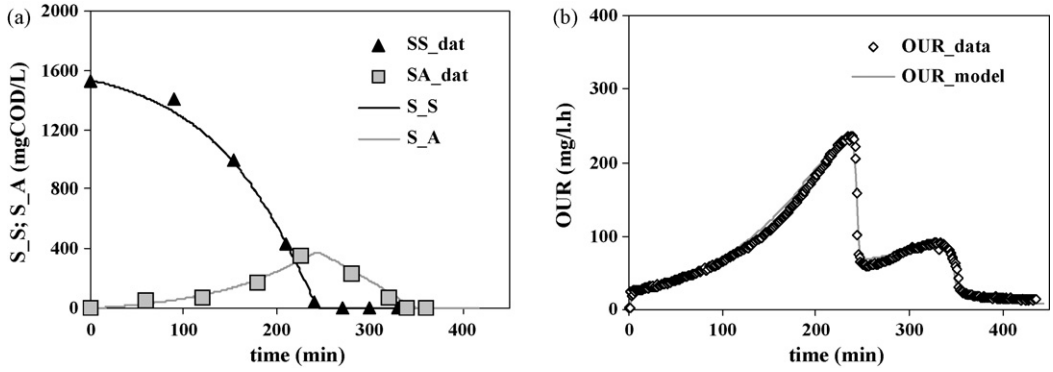

Fig. 6. The profiles of (a) substrate (glucose-S_S, acetate-S_A) utilization and (b) OUR profile during the growth of *Escherichia coli* under aerobic condition [21].

Table 2
Matrix representation of the mechanistic model

Processes	S_{O2}	S_{S1}	S_{S2}	S_{S3}	S_H	X_H	X_P	Rate
Growth on S_{S1}	$-\frac{1-Y_H}{Y_H}$	$-\frac{1}{Y_H}$				1		$\widehat{\mu}_{H1}\frac{S_{S1}}{(K_{S1}+(S_{S1}^2/K_I))+S_{S1}}X_H$
Growth on S_{S2}	$-\frac{1-Y_H}{Y_H}$	1	$-\frac{1}{Y_H}$			1		$\widehat{\mu}_{H2}\frac{S_{S2}}{K_{S2}+S_{S2}}\frac{K_{S1}}{K_{S1}+S_{S1}}X_H$
Growth on S_{S3}	$-\frac{1-Y_H}{Y_H}$			$-\frac{1}{Y_H}$		1		$\widehat{\mu}_{H3}\frac{S_{S3}}{K_{S3}+S_{S3}}\frac{K_{S1}}{K_{S1}+S_{S1}}\frac{K_{S2}}{K_{S2}+S_{S2}}X_H$
Hydrolysis of S_H		1			−1			$k_h\frac{S_H/X_H}{K_X+S_H/X_H}X_H$
Biomass decay	$1-f_p$					−1	f_P	$b_H X_H$

Table 3
Estimated model parameters and state variables

Model component	Unit	Value
Stoichiometry		
Heterotrophic yield coefficient, Y_H	gcellCOD/gCOD	0.64
Kinetics		
Maximum growth rate on S_{S1} ($\widehat{\mu}_{H1}$)	day^{-1}	5.10
Maximum growth rate on S_{S2} ($\widehat{\mu}_{H2}$)	day^{-1}	0.70
Maximum growth rate on S_{S3} ($\widehat{\mu}_{H3}$)	day^{-1}	0.69
Half saturation constant for S_{S1}, K_{S1}	mgCOD/L	60
Half saturation constant for S_{S2}, K_{S2}	mgCOD/L	10
Half saturation constant for S_{S3}, K_{S3}	mgCOD/L	25
Inhibition concentration on S_{S1}, K_I	mgCOD/L	150
Maximum hydrolysis rate, k_h	day^{-1}	1.3
Hydrolysis half saturation constant, K_X	gCOD/gcellCOD	0.3
Model initial states		
Active biomass concentration, X_{H0}	mgcellCOD/L	1300
Initial total biodegradable COD, C_{S1}	mgCOD/L	2824
First readily biodegradable COD	mgCOD/L	510
Second readily biodegradable COD	mgCOD/L	200
Third readily biodegradable COD	mgCOD/L	495
Hydrolysable COD, S_H	mgCOD/L	1619

Default parameters: $b_H = 0.15\ day^{-1}$, $f_P = 0.2$.

values for half saturation affinity constant, K_S exhibited high variations for different COD components. The K_{S2} and K_{S3} values are in agreement with the range of 5–20 mgCOD/L suggested for readily biodegradable COD for the activated sludge systems treating domestic wastewater. In this model evaluation, only K_{S1} of 60 mg/L was comparably higher, which indicates that the affinity of biomass to this substrate was lower than others. In addition, the maximum hydrolysis rate (k_h) and half saturation coefficient (K_X) for S_H hydrolysis were estimated to be 1.3 day^{-1} and 0.3 gCOD/gcellCOD, respectively. These values, when compared with their counterparts for domestic sewage ($k_h = 3.0\ day^{-1}$ and $K_X = 0.03$ gCOD/gcellCOD), indicate a much lower rate for the hydrolysis and the following biodegradation rate of S_H in this particular wastewater. The magnitude of major COD components together with their corresponding kinetics derived from model simulation of the OUR profile are listed in Table 3.

4. Conclusions

This paper aims model-based evaluation of aerobic biodegradation characteristics of the wastewater generated from a chemical industry producing a wide spectrum of different organic chemicals.

The organic compounds in complex chemical industry wastewater were found to have soluble nature. Respirometry-based model evaluation of biodegradation of organic matters in raw wastewater indicated the existence of multiple COD fractions having different degradation rates during the activated sludge treatment under aerobic conditions. In total, four types of biodegradable COD fractions were experimentally determined in the raw wastewater of complex chemical industry.

Multi-component modeling showed that the highest portion of COD has the lowest degradation rate, which can pass through the treatment system with reduced removal efficiency. In addition, the initial substrate concentration was found to have an inhibition effect on the growth of heterotrophic biomass, which was modeled with Haldane type degradation kinetics. The initial logarithmic growth phase followed by consecutive degradation steps of other substrates were successfully depicted by multi-component modeling.

In activated sludge treatment of industrial wastewaters, respirometric biodegradation tests should be applied on wastewaters that have specific characteristics for each industry. Finally, model-based evaluation of degradation kinetics and determination of influent COD fractions will serve as a basis for the appropriate selection and operation of activated sludge reactor for the optimal removal of organic matters.

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