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Biological treatment by activated sludge of petroleum refinery wastewaters

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ABSTRACT

This paper reports on biological treatment by activated sludge of petroleum refinery wastewaters, in a lab-scale reactor constituted by an aeration tank and clarifier provided with sludge recycle system. The main objective of the work includes the optimization of the process efficiency in terms of chemical oxygen demand (COD), total organic carbon (TOC), and total suspended solids (TSS), and modeling of the biological treatment by activated sludge and determination of the main stoichiometry and kinetic parameters for the process, such as, synthesis and decay of biomass, oxygen consumption related to organics oxidation, and endogenous respiration with and without sludge recycle. Laboratory-scale experiments successfully showed high removal efficiencies for COD (94–95%), TOC (85–87%), and TSS (98–99%). The removal of organic matter was well described by a pseudo-first-order kinetic model, with rate constant (k) values of 0.055 and 0.059 L mg^{-1} VSS day^{-1}, with and without biomass recirculation, respectively. The consumption of oxygen in the biological reactor was calculated according to parameters a' (0.071/0.069 mg O$_2$ mg^{-1} COD) and b' (0.012/0.024 mg O$_2$ mg^{-1} VSS day^{-1}), experimentally obtained by operating the reactor with and without sludge recycle. The parameters related to the production and destruction of biomass were also determined: $a = 0.33/0.32$ mg VSS mg^{-1} COD; $b = 0.07/0.03$ mg VSS mg^{-1} VSS day^{-1}, respectively, for the systems with and without sludge recycle.

Keywords: Petroleum refinery wastewater; Activated sludge process; Kinetics; Oxygen consumption; Biomass production

1. Introduction

Petroleum refinery wastewaters composition depends on the refinery and on the units that are in operation at any specific time. Normally, it contains many different chemicals at different concentrations, such as, ammonia, sulphides, phenols, and hydrocarbons, which constitute a major source of aquatic environmental pollution [1]. The treatment of petroleum refinery wastewater involves normally a three-stage process, including: primary (elimination of free oil and gross solids by gravity separation, e.g. American Petroleum Institute separators, parallel plate interceptors, tank separation, etc.), secondary (elimination of dispersed oil and fine solids by flocculation,

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flotation, sedimentation, filtration, etc.), and tertiary treatment (elimination of dissolved oil and other dissolved organic contaminants by biological treatment, e.g. bio-filters, activated sludge, aerated ponds, etc.) [2]. According to CONCAVE report number 2/11 [3], in 2008, 111 of 125 refineries apply a biological treatment to their wastewaters before discharge, for which 103 sites apply a three-stage biological system. The majority of refineries (78) have an aerated activated sludge reactor as the biological unit.

The functional activity of the activated sludge is dependent on the existence of a microbial culture comprising of bacteria, fungi, protozoa, and various other micro-organisms that degrade particulate and dissolved organic matter. The bacteria and fungi are the primary producers and decomposers that obtain energy directly from the dissolved organic matter. The general arrangement of activated sludge system consists of a biological reactor (or the aeration tank), in which the air or oxygen is injected into the mixed liquor, and a clarifier (secondary settling tank), where the biological flocs settle down. Aeration is necessary to meet oxygen demand of chemo-heterotrophic bacteria which convert the organic substrates, present in the mixed liquor, to carbon dioxide (CO_2), water, and other oxidized compounds and cell biomass. The chemo-autotrophic nitrifying bacteria also require oxygen as they obtain energy through oxidation of ammoniacal nitrogen (NH_4^+/NH_3) to nitrate (NO_3^-) or nitrite (NO_2^-). The carbon source for the autotrophic bacteria is bicarbonate (HCO_3^-) or carbon dioxide (CO_2). Oxygen is also important to the protozoa and metazoa [4].

The hydrocarbons present in the effluents of the petroleum refinery wastewater can be selectively biodegraded by micro-organisms under optimized conditions of temperature [5–7]. The degradation process can occur under aerobic or anaerobic conditions [8–11]. The removal of organic compounds from the biological sludge takes place by a series of complex physical and chemical mechanisms, and depends on several parameters such as the reactor operating conditions, characteristics of the effluent, and reactor configuration [12].

For the correct design of a continuous aerated activated sludge reactor, it is necessary to obtain kinetic and stoichiometric parameters concerning the oxidation of organic matter, synthesis and decay of biomass, oxygen consumption related to organics oxidation and endogenous respiration, which can be obtained by applying a mathematical model that incorporates kinetics mass balances for oxygen utilization and net yield of biomass, and an appropriate mass load factor for optimum sludge settling conditions [13].

In the present study, the biological treatment was conducted by activated sludge process using as raw wastewater, the influent after primary settling, sulphur oxidation/chemical coagulation and dissolved air flotation of the wastewater treatment plant (WWTP) of the oil refinery in Oporto, Portugal. The main objective of this study was to evaluate the removal of biodegradable compounds, and to determine the stoichiometry and kinetic parameters for the process.

2. Materials and methods

2.1. Analytical determinations

The methods and equipments used for the determination of pH, total organic carbon (TOC), chemical oxygen demand (COD), total suspended solids (TSS), volatile suspended solids (VSS), TOC, biochemical oxygen demand after five days (BOD_5), dissolved oxygen (DO), oil and grease, total petroleum hydrocarbon (TPH), sulphides, phenols, chlorides, and electric conductivity are presented in Table 1. The oxygen uptake rate was determined by using a portable oxygen meter from HANNA Instruments (HI 9,143 model). The analytical determinations were carried out according to the standard methods for the examination of water and wastewater [14].

2.2. Samples collection

Wastewater samples from the oil refinery WWTP, in Oporto, Portugal, were collected at the inlet of the activated sludge bioreactor, after primary settling, sulphur oxidation/chemical coagulation, and dissolved air flotation. The wastewater samples collected on different days, during the period of the biological tests at lab-scale system, were always kept under refrigeration until use. The inoculum required for starting-up the experimental work was obtained from the same biological reactor. Table 2 presents the physicochemical properties of the refinery wastewaters at different treatment phases.

2.3. Experimental set-up

The lab-scale system used for the biological treatment study comprised of a feed tank containing the wastewater to be treated; an aerated biological reactor (internal diameter (ID) = 19 cm; height (H) = 33 cm, working volume (V) = 6 L) equipped with air diffusers at the bottom, for the oxygen supply and mixing (the air flow rate was about $5\,\mathrm{L\,min^{-1}}$); and a

Table 1
Analytical methods and equipment's used in the present study

Parameter	Method	Apparatus	Range	Make/model	References
pH	Electrometric	pH Meter	—	Hanna Instruments	Standard methods [14] APHA 4,500-H
DO	Electrometric	DO meter	0–45 mg O_2 L^{-1}	Crison instruments (model IXI 45)	
TSS	Gravimetric	Balance	0.5 mg L^{-1}	…	Standard Methods [14] APHA 2,540-D
VSS	Gravimetric	Balance	0.5 mg L^{-1}	…	Standard methods APHA 2,540-E
TPH	Partition-infrared	Spectrophotometer	0.1 mg L^{-1}	Bomem Arid-ZoneTM 540	Standard methods [14] APHA 5,520-F
Oil & grease		Partition—infrared		Spectrophotometer	0.1 mg L^{-1}
	…	Standard methods [14]		balance	
				Partition—gravimetric	0.5 mg L^{-1}
APHA 5,520-D					
COD	Open reflux	Digester	10 mg O_2 L^{-1}	G. Vittadini	Standard methods [14] APHA 5,520-B
BOD_5	Dilutions	DO electrode	<1.0 mg O_2 L^{-1}	Orion 97–08-00	Standard methods [14] APHA 5,210-B
TOC	Catalytic Oxidation	Total organic Carbon analyzer	0–25 mg L^{-1} 25–100 mg L^{-1}	Shimadzu 5,000 A	Standard methods [14] APHA 5,310-A
Sulphide	Iodometric	—	0.01 mg L^{-1}	—	Standard methods [14] APHA 4,520-F
Total nitrogen	Persulfate/ brucine	Spectrophotometer	1 mg NO_3^- L^{-1}	Pye Unicam PU 8,600 UV/VIS	Standard methods [14] APHA 4,500-N
Phenols	Extraction with chloroform	Spectrophotometer	0.5 mg L^{-1}	Pye Unicam PU 8,600 UV/VIS	Standard Methods [14]
Chlorides	Argentometry	—	0.5 mg Cl^- L^{-1}	—	Standard methods [14] APHA 4,500-Cl^- B
Electric conductivity	Conductimetry	Conductivimeter	0.1 µS cm^{-1}	Hanna instruments	Standard methods [14]

clarification conical tank (ID = 19 cm; $H_{\text{Cylinder}} = 31$ cm; $H_{\text{Conic}} = 15$ cm working volume (V) = 6 L) equipped with a sludge recycle system (the treated wastewater was discharged into the sewer) (Fig. 1(a)). The system also contains two peristaltic pumps (to pump the feed wastewater into the reactor and sludge recycle) of variable flow rate (VITTADINI, model BIO KONTROLL MARK 2) (Fig. 1(b)).

2.4. Experimental procedure

For the first set of experiments, wastewater samples were collected periodically at the refinery WWTP, during a period extending from April to May 2008. The biological oxidation tests in the lab-scale system were carried out by varying the flow rate between 0.3 and 1.2 L h^{-1} at the entrance of the biological reactor, maintaining constant sludge recycle flow rate (0.5 L h^{-1}). The reactor was running at a given flow rate until achieving pseudo-steady state conditions, which usually took about one week. The removal efficiencies of COD, TOC, and TSS, and the rate of oxygen consumption and biomass production were determined during the experiments. Further biological tests in the lab-scale system at flow rates between 0.3 and 2.0 L h^{-1}, without sludge recycle, were performed using wastewaters samples collected periodically from the same location at the refinery WWTP from May to June 2008.

Table 2
Physical/chemical characteristics of the refinery wastewater obtained at different treatment stages (average values from five monitoring campaigns performed during one year)

Parameters	AD	AT	SD	AB
pH	6.7	6.5	6.6	7.1
TSS (mg L^{-1})	461	241	107	49
VSS (mg L^{-1})	255	106	53	15
THP (mg L^{-1})	156	76	29	9
Oil and grease (mg L^{-1})	291	144	61	14
COD (mg L^{-1})	373	287	167	109
BOD_5 (mg L^{-1})	165	124	65	37
Sulfides (mg L^{-1})	10.2	5.5	3.2	1.3
Total nitrogen (mg L^{-1})	26.1	37.7	21.2	13.8
Phenols (mg L^{-1})	0.64	0.33	0.16	0.09
Chlorides (mg L^{-1})	167	177	156	146
Electrical conductivity (mS cm^{-1})	1,382	1,688	1,234	967

AD—treated wastewater from dissolved air flotation unit; AT - Treated wastewater from aeration tank unit; SD—treated wastewater after secondary sedimentation; AB—treated wastewater from the aeration basin unit.

3. Mathematical modeling

For the mathematical modeling of an activated sludge process, the following hypotheses were assumed [15,16]:

- The reactor is perfectly mixed, i.e. the substrate and biomass concentrations are constant all over the reactor;
- Substrate removal takes place only in the bioreactor, i.e. in the clarification tank only a physical separation of biomass takes place;
- The amount of biomass in the clarification tank is negligible when compared to the amount in the reactor, thus, the volume used in the calculation of the mean cell retention time (θ_c) is only the volume of the aerated reactor; Recirculation of biomass from the bottom of the clarifier tank to the aerated reactor is continuous.

Fig. 1(a) and (b) represents the flow diagram and the experimental setup of the activated sludge biological treatment process, where: Q_a—influent flow rate (L day^{-1}); Q_r—sludge recycle flow rate (L day^{-1}); r—recycle ratio ($r = Q_r/Q_a$); Q—combined feed flow rate [$Q = Q_a + Q_r = Q_a(1 + r)$] (L day^{-1}); Q''—excess sludge flow rate ($Q_a = Q' + Q''$) (L day^{-1}); Q_u—clarifier discharge flow rate ($Q_u = Q'' + Q_r = Q'' + rQ_a$) (L day^{-1}); S_i—soluble substrate concentration in stream i (mg COD L^{-1}); $X_{v,i}$—volatile suspended solids concentration in stream i (mg VSS L^{-1}); $X_{nv,i}$—nonvolatile suspended solids concentration in stream i (mg NVSS L^{-1}); ΔX_v—excess of VSS to be removed from the system (mg VSS day^{-1}); ΔX_{nv}—excess of NVMS to be removed from the system (mg NVSS day^{-1}); ΔX_t—excess of total sludge to be removed from the system ($\Delta X_t = \Delta X_v + \Delta X_{nv} + Q_a X_{v,a}$) (mg VSS day^{-1}); V—biological reactor volume (L). Here, index i in the symbols represent: a—influent (feed: wastewater to be treated); o—combined feed; r—biological reactor effluent; e—final effluent; u—sludge line of the clarifier.

The mean hydraulic retention time of mixed liquor in the system can be calculated by the expressions:

$$\theta_a = \frac{V}{Q_a} \tag{1}$$

$$\theta = \frac{V}{Q} \tag{2}$$

The mean cell retention time, or age of the biological sludge, is given by:

$$\theta_c = \frac{X_{v,r} V}{Q'' X_{v,u} + Q' X_{v,e}} \tag{3}$$

Expressing the biomass in terms of volatile suspended matter, it must be taken into account that the VSS present in the feed ($X_{v,a}$) (mg VSS L^{-1}) go through the biological reactor without undergoing significant degradation. In this case, Eq. (3) should be written as follows:

$$\theta_c = \frac{X_{v,r} V}{Q'' X_{v,u} + Q' X_{v,e} - Q_a X_{v,a}} \tag{4}$$

In a particular case where $X_{v,e} = X_{v,a} = 0$ mg VSS L^{-1}:

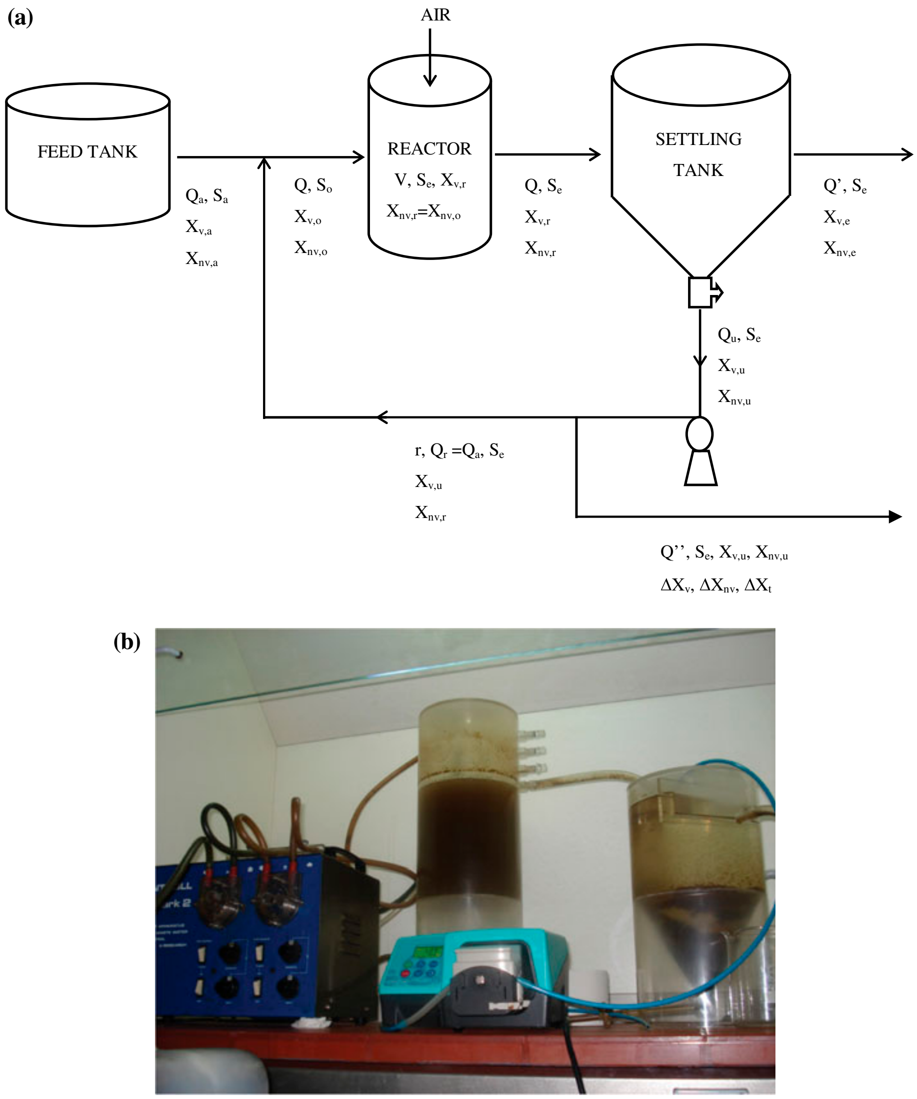

Fig. 1. Flow diagram (a) and the experimental setup (b) of the activated sludge biological process.

$$\theta_c = \frac{X_{v,r}V}{Q''X_{v,u}} = \frac{X_{v,r}V}{\Delta X_v} \tag{5}$$

The mass balance for the VSS can be given by:

$$\frac{dX_{v,r}}{dt}V = Q_a X_{v,a} - (Q''X_{v,u} + Q'X_{v,e}) + r_g V \tag{6}$$

where r_g is the net biomass production rate (mg VSS L^{-1} day^{-1}), i.e. the difference between the biomass specific growth (μ, mg VSS mg^{-1} VSS day^{-1}) and decay (b, mg VSS mg^{-1} VSS day^{-1}) rates.

At steady state, and given that $r_g = (\mu—b)X_{v,u}$, we obtain:

$$Q_a X_{v,a} = Q''X_{v,u} + Q'X_{v,e} - (\mu - b)X_{v,r}V \tag{7}$$

or

$$\frac{1}{\theta_c} = (\mu - b) \tag{8}$$

Bearing in mind the relationship between biomass specific growth rate (μ) and the substrate degradation rate (rs, mg COD $L^{-1}day^{-1}$), ($\mu = -a\frac{r_s}{X_{v,r}}$), results are as follows:

$$\frac{1}{\theta_c} = -a\frac{r_S}{X_{v,r}} - b \tag{9}$$

where a represents the organic matter fraction used in the synthesis of new cellular material (mg VSS mg^{-1} COD). The substrate mass balance at steady state can be given as follows:

$$Qs_o = Qs_e - r_s V$$

i.e.

$$\frac{s_o - s_e}{\theta} = -r_s \tag{10}$$

Substituting Eq. (10) in (9), we obtain:

$$X_{v,r} = \frac{a(s_o - s_e)\theta_c}{(1 + b\theta_c)\theta} = \frac{a(s_a - s_e)\theta_c}{(1 + b\theta_c)\theta_a} \tag{11}$$

where s_a is the substrate concentration in the wastewater entering the biological reactor (mg COD L^{-1}), s_e is the substrate concentration in the wastewater leaving the biological reactor (and in the clarifier) (mg COD L^{-1}), and s_o is the soluble substrate concentration in the influent of the biological reactor (mg COD L^{-1}).

3.1. Biomass recirculation ratio

The biomass recirculation rate, r, is determined from the mass balance of VSS in the clarifier, assuming $X_{v,e} = 0$ mg VSS L^{-1},

$$QX_{v,r} = \Delta X_v + Q_a X_{v,a} + rQ_a X_{v,u}$$

As explained above, $Q_a X_{v,a}$ represents the mass flow rate of the volatile suspended solids in the wastewater, hardly biodegradable, which remain in the system.

Thus, if $Q = (1 + r)Q_a$, then,

$$r = \frac{Q_a X_{v,r} - \Delta X_v - Q_a X_{v,a}}{Q_a (X_{v,u} - X_{v,r})} \tag{12}$$

3.2. Oxygen demand

Oxygen is required in the oxidation of substrate essential for energy production, which is essential for the survival of the cells, and in the process of biomass endogenous respiration (auto-oxidation).

3.2.1. Oxidation of substrate for energy production

The mass of oxygen m_1 (mg O_2 day^{-1}), required per unit time, is given by:

$$m_1 = a'(s_o - s_e)Q$$

or

$$m_1 = a'\frac{s_a - s_e}{1 + r}Q = a(s_a - s_e)Q_a$$

where a' represents the ratio between the amount of oxygen consumed and the amount of substrate removed (mg O_2 mg^{-1} COD), and is a parameter related to the organic matter fraction used for energy production.

3.2.2. Endogenous respiration

The mass of oxygen required per day, in the process of endogenous respiration m_2 (mg O_2 day^{-1}), is given by:

$$m_2 = b' X_{v,r} V$$

where b' is the mass of oxygen consumed per day and per unit of biomass in the biological reactor, in the process of auto-oxidation of the cells (mg O_2 mg^{-1} VSS day^{-1}).

Thus, the mass of the oxygen supplied to the reactor per day ($m = m_1 + m_2$), can be expressed as:

$$m_{(O_2)} = a'(s_a - s_e)Q_a + b' X_{v,r} V \tag{13}$$

i.e.,

$$\frac{m_{(O_2)}}{X_{v,r}V} = a'\frac{(s_a - s_e)Q_a}{X_{v,r}V} + b' \tag{14}$$

The values of a´ and b´ can be calculated, respectively, from the slope and intercept of the straight line representing $\frac{m_{(O_2)}}{X_{v,r}V}$ as a function of $\frac{(s_a - s_e)Q_a}{X_{v,r}V}$. The required values of $\frac{m_{(O_2)}}{X_{v,r}V}$ for plotting against $\frac{(s_a - s_e)Q_a}{X_{v,r}V}$ were experimentally determined by measuring the oxygen uptake rate (OUR, mg O_2 day^{-1}) for different values of VSS in the reactor ($X_{v,r}$). OUR is the slope of the line representing the oxygen concentration decay along time in a batch mode respirometer experiment using a mixed liquor sample collected from the reactor.

3.2.3. Sludge in excess flow rate, Q´´ and final effluent flow rate, Q´

The total mass balance of the volatile matter in suspension, assuming $X_{v,e} = 0$ mg VSS L^{-1}, is given by:

$$Q''X_{v,u} = \Delta X_v + Q_a X_{v,a}$$

i.e.

$$Q'' = \frac{\Delta X_v + Q_a X_{v,a}}{X_{v,u}} \tag{15}$$

Moreover,

$$Q' = Q_a - Q'' \tag{16}$$

3.3. Excess of biomass to be removed

The excess of biomass to be removed from the system results from two antagonistic processes: biomass production corresponding to the synthesis of new cells and destruction of biomass by endogenous respiration.

Therefore, the excess of biomass to be removed from the system per unit time (ΔX_v) (mg VSS day^{-1}), can be given as:

$$\Delta X_v = a(s_a - s_e)Q_a - bX_{v,r}V \tag{17}$$

Dividing both sides by ($X_{v,r}V$), we get:

$$\frac{\Delta X_v}{X_{v,r}V} = a\frac{(s_a - s_e)Q_a}{X_{v,r}V} - b \tag{18}$$

where a is the fraction of organic material for the synthesis of new cells (mg VSS mg^{-1} COD); b is the rate of cellular material degradation by endogenous respiration (auto-oxidation) or fraction of the cellular material oxidized per unit time (mg VSS mg^{-1} VSS day^{-1}).

The representation of $\frac{\Delta X_v}{\Delta X_{v,r}V}$ as a function of $\frac{(s_a - s_e)Q_a}{X_{v,r}V}$ can be used to calculate the parameters a and b.

In addition to ΔX_v two more contributions must be considered in the calculation of the excess of sludge to be removed per unit time:

- Excess of nonvolatile matter in suspension:

$$\begin{aligned}\Delta X_{nv} &= Q''X_{nvu} = Q_a X_{nv,a} - QX_{nv,e} \\ &= Q_a X_{nv,a} - (Q_a - Q'')X_{nv,e} \\ &= Q_a(X_{nv,a} - X_{nv,e}) + Q''X_{nv,e}\end{aligned} \tag{19}$$

- Volatile matter in suspension present in the feeding wastewater ($Q_a X_{v,a}$), admitting that it passes through the system without degradation.

Assuming $X_{v,e} = 0$, the excess of sludge to be removed, ΔX_t, can then be calculated as:

$$\Delta X_t = \Delta X_v + Q_a(X_{nv,a} - X_{nv,e}) + Q''X_{nv,e} + Q_a X_{v,a} \tag{20}$$

3.4. Hydraulic residence time in the reactor

The hydraulic residence time in the reactor can be calculated by using two different criteria:

(i) The final effluent quality is critical, i.e. the substrate removal rate is the limiting step.

Assuming a pseudo-first-order kinetics ($r_s = -ks_e X_{v,r}$), a mass balance at the reactor gives:

$$\theta = \frac{s_o - s_e}{ks_e X_{v,r}} = \frac{s_a - s_e}{ks_e X_{v,r} \times (1 + r)} \tag{21}$$

(ii) The substrate/micro-organism ratio (F/M) is determinant, i.e. the characteristics of good biological sludge settleability control the process.

In this case, results are as follows:

$$\theta = \frac{s_o}{X_{v,r}(F/M)} = \frac{s_a + rs_e}{(1 + r)X_{v,r}(F/M)} \tag{22}$$

To calculate the two values of θ, it is necessary to calculate the recirculation rates.

If the effluent quality is decisive,

$$r_1 = \frac{X_{v,r} - a(s_a - s_e) + b\frac{s_a - s_e}{ks_e} - X_{v,a}}{X_{v,u} - X_{v,r}} \tag{23}$$

However, if the ratio F/M is crucial,

$$r_2 = \frac{[X_{v,r} - a(s_a - s_e)] \times \left(\frac{F}{M}\right) + bs_a - X_{v,a}\left(\frac{F}{M}\right)}{(X_{v,u} - X_{v,r}) \times \left(\frac{F}{M}\right) - bs_e} \tag{24}$$

Substituting r given by Eq. (23) in (22) and r given by Eq. (24) in (22), we get two values for θ. For design purposes, one must choose the larger value. In the present study, the larger one was that corresponding to the recirculation rate calculated by Eq. (23).

4. Results and discussion

All conditions assumed for modeling purposes, as described in section 3, were checked. The condition of

Table 3
Characteristics of the wastewater before and after biological treatment by activated sludge (with biomass recycle)

Run	Raw wastewater					Treated wastewater				
	Q_a (L h^{-1})	pH	COD (mg L^{-1})	TOC (mg L^{-1})	TSS (mg L^{-1})	Q_e (L h^{-1})	pH	COD (mg L^{-1})	TOC (mg L^{-1})	TSS (mg L^{-1})
1	0.3	6.95	400	84.2	812	0.8	6.53	20	10.9	10
2	0.5	6.66	415	85.9	832	1.0	7.30	25	12.7	15
3	0.7	6.63	410	88.1	842	1.2	7.20	31	14.2	20
4	1.0	6.54	435	84.6	867	1.5	7.56	45	14.9	25
5	1.2	7.06	440	85.6	890	1.7	7.03	50	16.0	34

perfect mixing was proven from dissolved oxygen measurements in different points inside the reactor. COD and TOC were sporadically measured at the outlet of the reactor and the obtained values were similar to those found at the clarifier outlet. The amount of biomass in the clarification tank was not negligible (about 25% of the amount in the reactor), but that does not matter because the mean cell retention time was not calculated.

4.1. Removal efficiency

Tables 3 and 4 present the characteristics of the wastewater before and after biological activated sludge process with and without biomass recirculation. The COD and TOC removal efficiencies for different influent flow rates in the systems with and without biomass recycle are shown in Fig. 2(a) and (b). Fig. 2(a) shows that highest removal efficiency (COD = 95%, TOC = 87%, and TSS = 99%) was obtained for the lower flow rate 0.3 L h^{-1} (corresponding to a hydraulic residence time of 20 h), when the reactor was operated with sludge recycling. The global removal of organic matter ($COD_{in}-COD_{out}$ or $TOC_{in}-TOC_{out}$) in activated sludge systems operating with or without biomass recycle depends on the kinetic constant, the concentration of biomass (TSS) in the biological reactor and the hydraulic residence time. The kinetic constant was 7% higher in the system without biomass recycle, probably due to a lower concentration of metabolites, but the average concentration of biomass in the reactor was approximately 9% lower. Consequently, as the hydraulic residence times were identical for both systems, except that corresponding to the flow rate of 2.0 L h^{-1} that only existed for the system without biomass recirculation, the overall removal of organic matter was higher in the system with biomass recycle (25 and 15% for COD and TOC, respectively). Additionally, when dividing the amount of organic matter removed (S_a-S_e) by the inlet concentration (S_a) to obtain the overall removal efficiency, the average COD and TOC removal efficiencies were about 2 and 4% higher in the system with recirculation of biomass.

The removal efficiency of COD, achieved in the aeration tank unit of the WWTP was only 29% (Table 1), when the hydraulic residence time and biomass concentration in the reactor were 4.6 h and 106 mg VSS L^{-1}, respectively. Moreover, COD removal efficiencies were comparatively higher than those obtained by Shokrollahzadeh et al. [17] during the treatment of wastewater from a petrochemical WWTP

Table 4
Characteristics of the wastewater before and after biological process by activated sludge (without biomass recycle)

Test	Raw wastewater					Treated wastewater				
	Q_a (L h^{-1})	pH	COD (mg L^{-1})	TOC (mg L^{-1})	TSS (mg L^{-1})	Q_e (L h^{-1})	pH	COD (mg L^{-1})	TOC (mg L^{-1})	TSS (mg L^{-1})
1	0.3	7.01	320	75.3	730	0.3	7.02	20	10.2	15
2	0.5	7.08	324	76.9	740	0.5	7.13	28	12.7	20
3	0.7	6.96	322	76.2	760	0.7	6.98	30	14.1	23
4	1.0	7.05	320	74.9	800	1.0	7.06	36	16.5	30
5	1.2	7.30	316	75.1	820	1.2	7.34	47	20.8	36
6	2.0	7.02	380	94.4	940	2.0	7.04	60	37.9	40

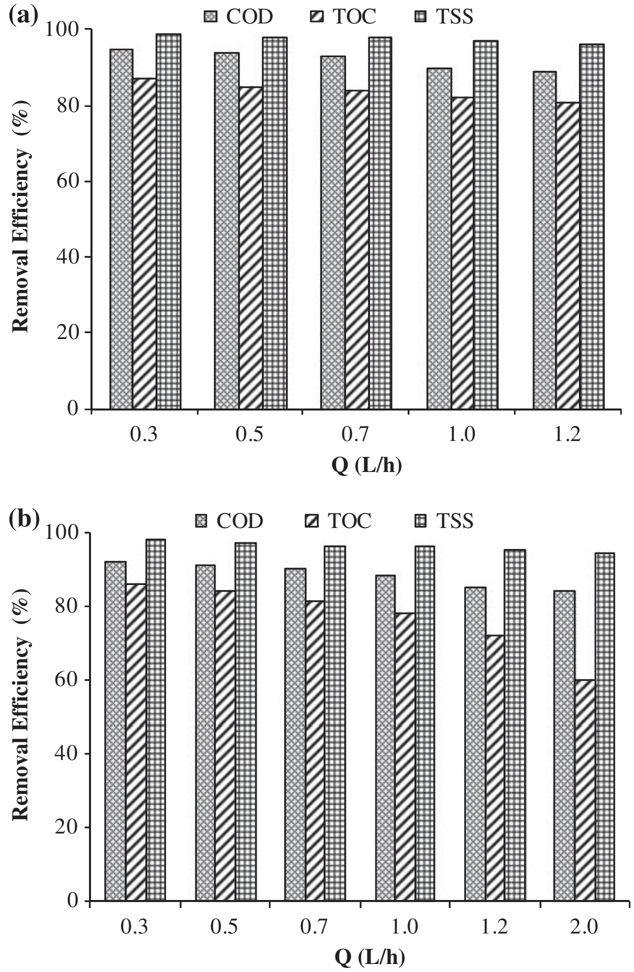

Fig. 2. Removal efficiency of COD, TOC and TSS in the biological process with (a) and without (b) sludge recycle.

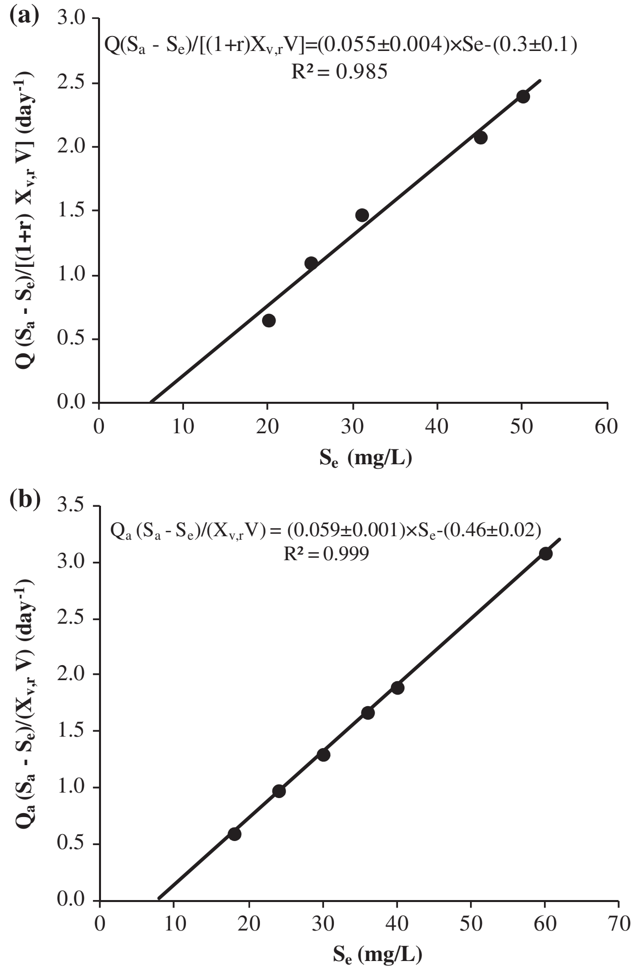

Fig. 3. Linearization of the pseudo-first-order kinetic model for the biological process with (a) and without (b) sludge recycle.

in Iran (88 and 89% COD reduction, the remaining COD concentration not less than 80 mg L^{-1} even at low input COD). In the present study, the COD concentration in the effluent, both with and without biomass recirculation, was between 20 and 60 mg L^{-1} at varying flow rates.

4.2. Kinetic modelling

Assuming that a residual substrate concentration (S_n) exists, Eq. (21) can be rewritten as follows:

$$\frac{Q(s_a - s_e)}{X_{v,r}(1 + r)V} = k(s_e - s_n) \tag{25}$$

where s_n is the nonbiodegradable residual soluble substrate concentration (mg COD L^{-1}).

Fig. 3 depicts the amount of substrate removed per unit volume of the reactor, normalized by the concentration of biomass in the reactor as a function of substrate concentration at the outlet of reactor (Eq. (25)). The values of k and S_n were reported to be 0.055 ± 0.004 mg^{-1} VSS L day^{-1} and 0.0591 ± 0.0004 mg^{-1} VSS L day^{-1}; and 6 ± 2 mg L^{-1} and 7.8 ± 0.3 mg L^{-1}, respectively, for the biological process with and without sludge recycle. A slightly higher value for k (0.074 day^{-1}) has been previously reported for aerobic biological treatment of refinery wastewater [18], which can be due to the difference in the properties of the refinery wastewaters.

4.3. Oxygen consumption

The fitting of Eq. (14) to the experimental results allows to estimate the parameters a' and b'. Fig. 4(a) and (b) shows good agreement between the predicted and experimental values, resulting in the following

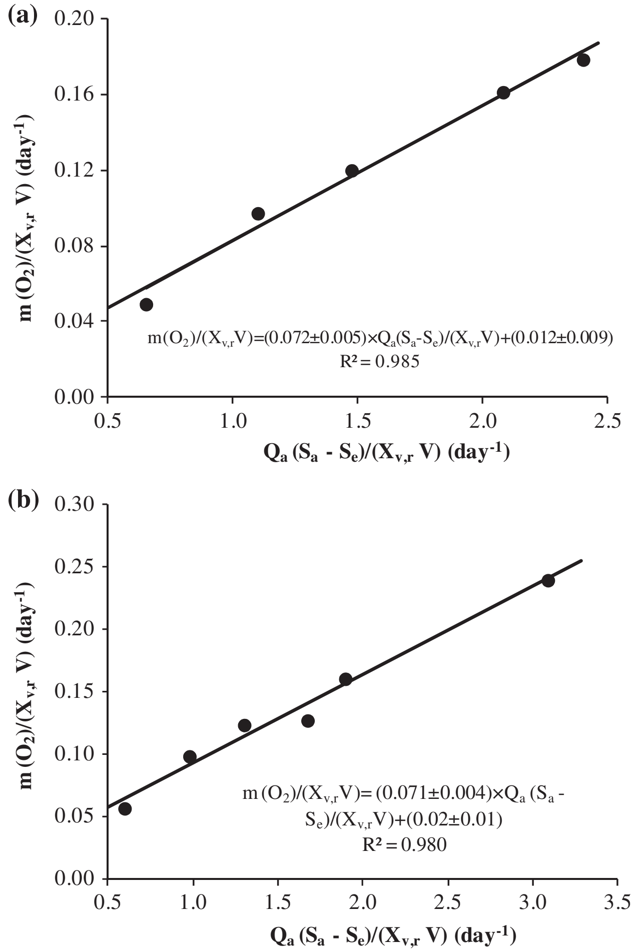

Fig. 4. Specific oxygen consumption as a function of the organic matter for the biological process with (a) and without (b) sludge recycle.

parameter values: $a' = 0.071 \pm 0.005$ mg O_2 mg^{-1} COD removed and 0.069 ± 0.005 mg O_2 mg^{-1} COD removed, and $b' = 0.012 \pm 0.009$ mg O_2 mg^{-1} VSS and 0.024 ± 0.007 mg O_2 mg^{-1} VSS, respectively, for the biological process operating with and without recirculation of sludge. The parameter a' only depends on the substrate and biomass characteristics, and no significant difference between the two operating systems should be expectable. The parameter b' increases with the mean cell residence time, which is slightly higher in the system with biomass recycle.

4.4. Biomass production

The study on the biomass production was carried out to determine the accumulation of biological sludge in the clarifier over time and the amount of sludge produced as a function of the COD load to the reactor. The amount of sludge produced was calculated from the volume obtained after a settling period of 30 min and the concentration of TSS and VSS in the clarified sludge. Tables 5 and 6 shows the values obtained for the rate of production of sludge depending on the COD load. The results indicate that higher COD loads fed to the reactor, correspond to higher biomass production. Fig. 5(a) and (b) shows the production of sludge in mg TSS day^{-1} and mg VSS day^{-1}, as a function of the COD load ($Q_a \times S_a$).

The parameters associated with the production (a) and decay (b) of biomass were calculated through Eq. (18), and are presented in Table 7 with other kinetic and stoichiometric parameters. The biomass production per unit of reactor volume, normalized by $X_{v,r}$, as a function of the organic matter (COD) removed per unit of reactor volume, also normalized by $X_{v,r}$, is shown in Fig. 6(a) and (b). The value of b (0.07 ± 0.06 and 0.03 ± 0.07 mg VSS mg^{-1} VSS day^{-1} for the systems with and without sludge recycle, respectively) is in agreement with the typical values of b (given for chemical and petrochemical refinery wastewaters) [18]. The experimental and calculated values of the excess of sludge to be removed are compared in Table 8, showing maximum deviations in the order of 12–22%.

Table 5
Sludge production rate as a function of the feed flow rate (with biomass recycle)

Flow rate (Q_a) (L day^{-1})	Time (t) (h)	COD (S_a) (mg L^{-1})	V^* (L)	TSS* (mg L^{-1})	VSS* (mg L^{-1})	Sludge production rate	
						mg TSS day^{-1}	mg VSS day^{-1}
7.2	20	400	0.45	1,364	1,165	737	629
12.0	18	415	0.54	1,889	1,606	1,360	1,156
16.8	22	410	0.60	3,330	2,851	2,180	1,866
24.0	23	435	0.62	4,353	3,731	2,816	2,414
28.8	23	440	0.76	5,124	4,490	4,063	3,561

*sludge characteristics (TSS, VSS, and volume produced during the operation time t, after a sedimentation period of 30 min).

Table 6
Sludge production rate as a function of feed flow rate (without biomass recycle)

Flow rate (Q_a) (L day^{-1})	Time (t) (h)	COD (S_a) (mg L^{-1})	Volume* (L)	TSS* (mg L^{-1})	VSS* (mg L^{-1})	Sludge production rate	
						mg TSS day^{-1}	mg VSS day^{-1}
0.3	23	320	0.40	1,525	1,274	637	532
0.5	21	324	0.43	1,990	1,654	978	813
0.7	19	322	0.55	2,830	2,346	1,966	1,630
1.0	23	320	0.58	3,620	3,077	2,191	1,862
1.2	22	316	0.62	5,074	4,331	3,432	2,930
2.0	22	380	0.65	7,499	6,417	5,318	4,550

*Sludge characteristics (TSS, VSS, and volume produced during the operation time t, after a sedimentation period of 30 min).

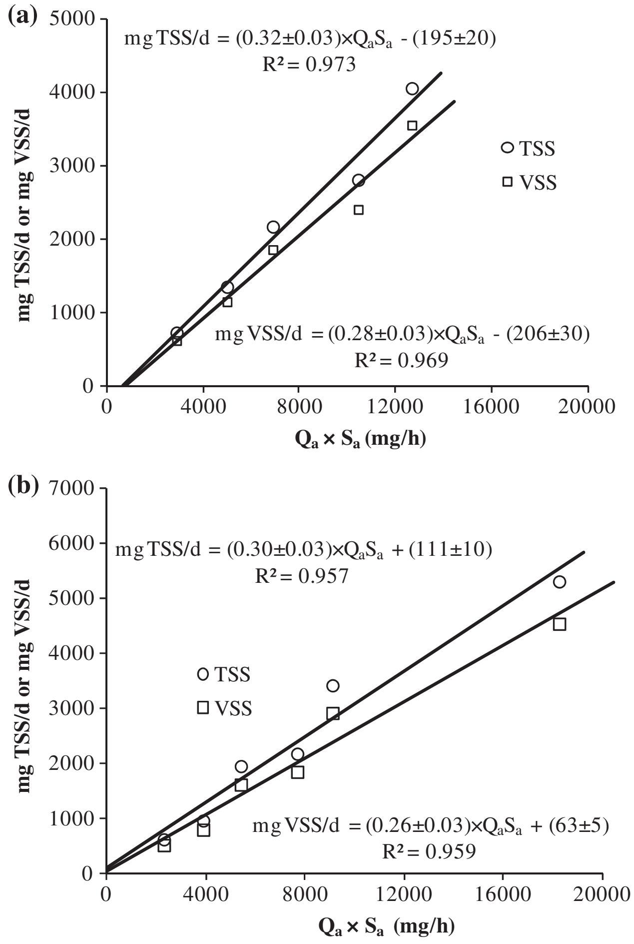

Fig. 5. Sludge production, in terms of mg TSS day^{-1} and mg VSS day^{-1}, as a function of the organic matter fed to the biological reactor with (a) and without (b) sludge recycle.

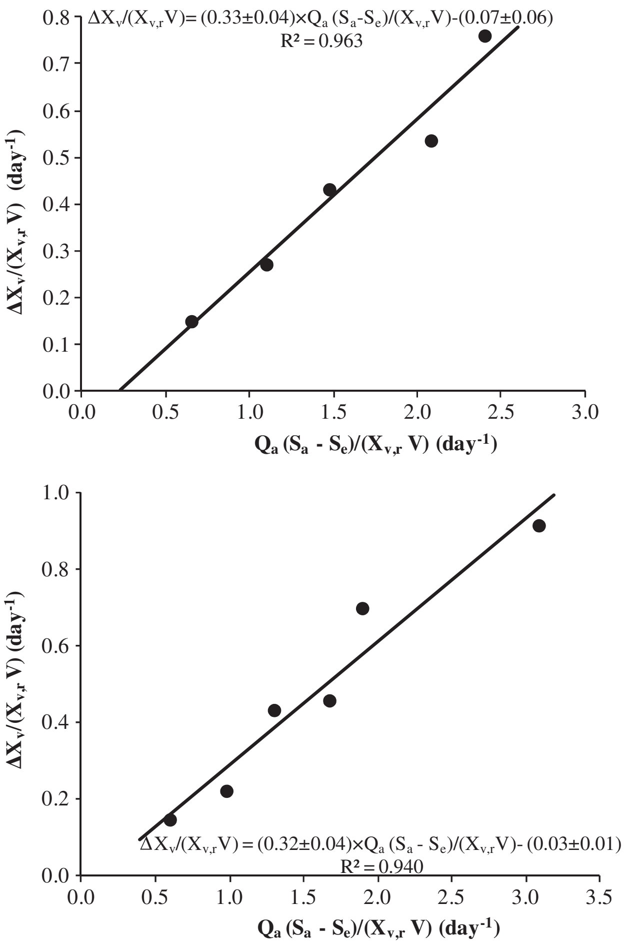

Fig. 6. Sludge production in the biological reactor with (a) and without (b) sludge recycle as a function of organic matter removed after dehydration.

Table 7
Kinetic and stoichiometric parameters obtained from biological degradation experiments

Parameter	Units	System with sludge recycle	System without sludge recycle
k	mg VSS L^{-1} day^{-1}	0.055 ± 0.004	0.0591 ± 0.0004
a'	mg O_2 mg^{-1} COD	0.071 ± 0.005	0.069 ± 0.005
b'	mg O_2 mg^{-1} VSS day^{-1}	0.012 ± 0.009	0.024 ± 0.007
a	mg VSS mg^{-1} COD	0.33 ± 0.04	0.32 ± 0.04
b	mg VSS mg^{-1} VSS day^{-1}	0.07 ± 0.06	0.03 ± 0.07

Table 8
Excess of sludge to be removed from the system

S_a (mg L^{-1})	S_e (mg L^{-1})	ΔX_u (exp.)* (mg VSS day^{-1})	$X_{v,r}$ (mg VSS L^{-1})	V (L)	ΔX_u (calc.)* (mg VSS day^{-1})
320	18	532	610	6	578
324	24	813	615	6	1,036
322	30	1,630	630	6	1,454
320	36	1,862	680	6	2,059
316	40	2,930	700	6	2,420
380	60	4,550	830	6	4,780

*exp.—experimental; calc.—calculated.

The WWTP of the Oporto refinery includes an activated sludge aeration tank having a volume of 1,606 m^3, a feed flow rate of 350 $m^3 h^{-1}$, a sludge recycle of 0.5, and a hydraulic residence time of 4.6 h. Considering five monitoring surveys (Table 2), the aeration tank inlet stream showed an average BOD_5 of 165.4 mg O_2 L^{-1} and a removal percentage of only 25%. The average biomass concentration, expressed in terms of VSS, in the aeration tank is 106 mg L^{-1}, much lower than the usual value in activated sludge systems.

Considering the average biomass concentration, hydraulic retention time, BOD_5 concentration in the inlet stream of the aeration tank, and $k = 0.055$ mg^{-1} VSS L day^{-1} (Table 7), a BOD_5 of 78 mg O_2 L^{-1} in the outlet stream of the aerated tank was calculated using Eq. (28), which is lower than the average BOD_5 observed in the monitoring program (124.2 mg O_2 L^{-1}). Taking the a´ and b´ values presented in Table 7, and using Eq. (13), a consumption of 53.2 kg day^{-1} oxygen was calculated. Eq. (18) was used to calculate the biomass production, considering the parameters a and b from Table 7, resulting in 11.9 kg VSS day^{-1}.

5. Conclusions

The treatment of a real refinery wastewater using an activated sludge biological reactor was successfully achieved, obtaining removal efficiencies for COD, TOC and TSS, of 94–95, 85–87, and 98–99%, respectively. A pseudo-first-order kinetic model was able to describe the rate of degradation of organic matter with and without sludge recycle, achieving rate constant (k) values of 0.055 and 0.059 mg^{-1} VSS L day^{-1}, with and without biomass recirculation, respectively. The organic matter removal efficiency in the system with biomass recycle is slightly higher than the one achieved in the system without biomass recycle. The parameters related with consumption of oxygen in the biological reactor obtained were a' (0.071/0.069 mg O_2 mg^{-1} COD) and b' (0.012/0.024 mg O_2 mg^{-1} VSS day^{-1}), and the parameters related to the production and destruction of biomass were $a = 0.33/0.32$ mg VSS mg^{-1} COD; $b = 0.07/0.03$ mg VSS mg^{-1} VSS day^{-1}, considering the operation of the reactor with and without recirculation.

Acknowledgments

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Nomenclature

a — organic matter fraction used in the synthesis of new cellular material (mg VSS mg^{-1} COD)
b — rate of cellular material degradation by endogenous respiration (auto-oxidation) or fraction of the cellular material oxidized per unit time (specific decay rate of biomass) (mg VSS mg^{-1} VSS day^{-1})
a' — ratio between the amount of oxygen consumed and the amount of substrate removed (mg O_2 mg^{-1} COD)
b' — mass of oxygen consumed per day and per unit of biomass in the biological reactor, in the process of auto-oxidation of the cells (mg O_2 mg^{-1} VSS day^{-1})
BOD_5 — biochemical oxygen demand (mg O_2 L^{-1})
COD — chemical oxygen demand (mg O_2 L^{-1})
DO — dissolved oxygen (mg O_2 L^{-1})
k — kinetic constant (mg VSS^{-1} L day^{-1})
m — mass of the oxygen supplied to the reactor per day (mg O_2 day^{-1});
m_1 — mass of oxygen required per day for energy production (mg O_2 day^{-1})
m_2 — mass of oxygen required per day, in the process of endogenous (mg O_2 day^{-1})
NVSS — non-volatile suspended solids (mg L^{-1})
OUR — oxygen uptake rate (mg O_2 L^{-1} day^{-1})
Q_a — influent flow rate (L day^{-1})
Q_r — sludge recycle flow rate (L day^{-1})
Q — combined feed flow rate (L day^{-1})
Q' — effluent flow rate (L day^{-1})
Q'' — excess sludge flow rate (L day^{-1})
Q_u — clarifier discharge flow rate (L day^{-1})
r — recycle ratio
r_s — substrate degradation rate (mg COD L^{-1} day^{-1})
r_g — net biomass production rate (mg VSS L^{-1} day^{-1})
S_i — soluble substrate concentration in stream i (mg COD L^{-1})
S_a — soluble substrate concentration in the feed (mg COD L^{-1})
S_e — soluble substrate concentration in the effluent of the biological reactor (and in the clarifier) (mg COD L^{-1})
S_n — non-biodegradable residual soluble substrate concentration (mg COD L^{-1})
S_o — soluble substrate concentration in the influent of the biological reactor (mg COD L^{-1})
TOC — total organic carbon (mg C L^{-1});
TSS — total suspended solids (mg L^{-1})
TPH — total petroleum hydrocarbon (mg L^{-1});
VSS — volatile suspended solids (mg L^{-1})
V — reactor volume (L)
$X_{v,i}$ — volatile suspended solids concentration in stream i (mg VSS L^{-1})
$X_{v,a}$ — volatile suspended solids concentration in the feed (mg VSS L^{-1})
$X_{v,o}$ — volatile suspended solids concentration in the influent of the biological reactor (mg VSS L^{-1})
$X_{v,r}$ — volatile suspended solids concentration in the effluent of the biological reactor (mg VSS L^{-1})
$X_{v,e}$ — volatile suspended solids concentration in the final effluent (mg VSS L^{-1})
$X_{v,u}$ — volatile suspended solids concentration in the sludge line of the clarifier (mg VSS L^{-1})
$X_{nv,i}$ — nonvolatile suspended solids concentration in stream i (mg NVSS L^{-1})
$X_{nv,a}$ — nonvolatile suspended solids concentration in the feed (mg NVSS L^{-1})
$X_{nv,o}$ — nonvolatile suspended solids concentration in the influent of the biological reactor (mg NVSS L^{-1})
$X_{nv,r}$ — nonvolatile suspended solids concentration in the effluent of the biological reactor (mg NVSS L^{-1})
$X_{nv,e}$ — nonvolatile suspended solids concentration in the final effluent (mg NVSS L^{-1})
$X_{nv,u}$ — nonvolatile suspended solids concentration in the sludge line of the clarifier (mg NVSS L^{-1})
ΔX_v — excess of volatile suspended solids to be removed from the system (mg VSS day^{-1})
ΔX_{nv} — excess of nonvolatile suspended solids to be removed from the system (mg NVSS day^{-1})
ΔX_t — excess of total sludge to be removed from the system (mg VSS day^{-1})
θ_a or θ — mean hydraulic retention time of mixed liquor in the system (day)
θ_c — mean cell retention time, or age of the biological sludge (day)
μ — biomass specific growth rate (mg VSS mg^{-1} VSS day^{-1})

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