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Modeling of phenol and cyanide removal in a full-scale coke-oven wastewater treatment plant

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ABSTRACT

The BioWin general activated sludge (AS) model (EnviroSim Associates, Ltd, Canada) was extended to predict the kinetics of phenol and cyanide removal from coke-oven wastewater mixed with sewage. To apply the modeling for this type of wastewater, a different model structure and an accurate estimation of the stoichiometric and kinetic parameters are required. In this study, additional processes for the phenol and cyanide were added to the BioWin AS model. Due to the inhibitory effect phenol and cyanide have on biological processes, the Haldane equation was used rather than the Monod equation that is typically used in wastewater modeling. A sensitivity analysis was performed to select the most sensitive parameter in the extended model. The model was calibrated under steady-state conditions and validated under dynamic-flow conditions. Adjustments were made only to the most sensitive parameters of the extended model processes related to phenol and cyanide. The new calibrated parameters were compared to the existing parameters from the literature, which were based on batch lab-scale experiments with synthetic wastewater. The extended model was capable of describing COD, ammonium, phenol, and cyanide removal in a full-scale coke-oven wastewater treatment plant under dynamic conditions.

Keywords: Coke-oven wastewater; Phenol; Cyanide; Nitrification; BioWin AS model

1. Introduction

Coke-oven wastewater is produced in coal coking, washing of coke gas, and byproduct recovery process of coke factories in the steel manufacturing. The characterization of coke-oven wastewater is very complicated [1]. Phenols are the main organic components, representing approximately 40–80% of the total COD [1,2]. Other organics include oil, grease, tar, and heterocyclic compounds containing oxygen, nitrogen, and sulfur. The inorganic constituents of coke-oven wastewater mainly include cyanides, thiocyanates, and ammonium. Coke-oven wastewater is considered to be the most toxic type of wastewater that is discharged into the environment.

Phenols and cyanide are toxic to human and aquatic life, and they have a strong inhibitory effect on biodegradation. Reports of the effective removal of phenol, and cyanide by heterotrophs in aerobic and anaerobic treatments can be found in the literature [3–5]. A common type of cyanide-degrading organism

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consists of a heterogeneous mixture of commonly found indigenous soil bacteria, which have adapted to cyanide exposure over time [6]. There are four main pathways for the biodegradation of cyanide: hydrolytic, oxidative, reductive, and substitution/transfer [6,7].

The high concentration of nitrogen compounds in coke-oven wastewater is inhibitory to biodegradation. Pre-treatment steps, such as ammonia stripping, are used to reduce the free ammonia that also inhibits biodegradation [1]. The physical, chemical, and biological properties of industrial wastewater, the variation in flow and composition of the wastewater make the operation of an industrial wastewater treatment plant (WWTP) complicated. The activated sludge (AS) system and its modifications are now the most commonly used biological wastewater treatment system; this system is used to treat both domestic and industrial wastewater [8]. This system requires a high degree of operational control and management. The operator of an AS plant must have a full understanding of the complex process involved in the plant's mechanics in order to achieve maximum removal efficiency. Mathematical modeling can be used to help the operator understand the different treatment processes, as well as to help the operator predict the effect(s) different production scenarios may have on the WWTP [9].

Much research has been conducted over the last three decades regarding the use of computer modeling to help understand the behavior of AS systems. The main takeaway of this research has been the development of the Activated Sludge Model No. 1 (ASM1), which was developed by a task group of the International Water Association (IWA) [10]. The ASM1 provided the matrix notation system and the nomenclature used in future models (the ASM2, ASM2d, and ASM3). Barker and Dold [11] also formulated a general model for BNR in AS systems. This model was based on the ASM1 with respect to the use of carbonaceous compound removal, nitrification, and denitrification for biological phosphorus removal. Barker and Dold's model was improved by EnviroSim for use in the BioWin general AS model, which was incorporated into BioWin software (EnviroSim Associates, Ltd, Canada). BioWin software and its model are now used worldwide, and both are recognized by the IWA.

Many studies have examined AS modeling of full-scale municipal treatment plants. However, few studies have examined AS modeling applications for full-scale coke-oven WWTPs. Lee et al. [12] attempted to model a coke-oven WWTP using parallel hybrid artificial intelligence (black-box modeling) with a model matrix based on the performance of the ASM1. For this attempt, modifications were made to the ASM1. For example, cyanide organisms were introduced, and it was assumed that phenolic compounds would be readily biodegradable organic constituents. However, the study found that while the new model could predict the general characteristics of the processes, it could not simulate real plant data. This was especially true when the model was under acute shock caused by phenol and cyanide loads. The ASM1 alone could not accurately predict the dynamics of the plant. It also could not predict the phenol concentration, nor could it anticipate the inhibitory effect of this concentration on the micro-organism. Moreover, other studies have examined modeling for refinery effluent [8] which have similarities to the coke industry effluents. However, these studies all focused on COD and nitrification in general; none of them focused extensively on phenol or cyanide removal.

A variety of kinetic substrate inhibition models have been used to describe the dynamics of microbial cultures for treating phenol and cyanide [4,13]. However, these studies have all been based on batch lab-scale experiments with synthetic wastewater. Furthermore, to our knowledge, establishing, and calibrating the kinetics and stoichiometry of phenol and cyanide removal for a full-scale coke-oven WWTP has not been done before. Therefore, in this study, the BioWin general AS model was extended to accurately describe and predict the kinetics of phenol and cyanide removal. The application of this extended model was carried out for a full-scale coke-oven WWTP in Egypt. This model could be useful for operational decision-making, as well as for optimization of industrial wastewater containing phenol and cyanide pollutants.

2. Materials and methods

2.1. Data collection

Many protocols for AS modeling, such as the STOWA, WERF, BIOMATH, HSG, and GMP unified protocols, have been developed and widely used by researchers for efficient process simulation. The most recent protocol is the GMP unified protocol, which was proposed by the GMP task group [14]. This protocol was applied in the present study. This study covers the WWTP of a coke factory located in Helwan, Egypt. This coke-oven WWTP is based on oxidation ditches process. It has been in operation since 1989, and it is designed for phenol, COD, cyanide, and ammonium removal.

Technical and operational data for the plant and its performance, both past and current, were provided by the staff of the WWTP. A summary of the operational flow of the coke-oven WWTP is included in

Table 1
Operational flow data for the coke-oven WWTP

Flow	Average flow rates
Influent coke wastewater (Q_{IND})	170 m^3 h^{-1}
Influent domestic wastewater (Q_{INF})	20 m^3 h^{-1}
Effluent flow (Q_{EFF})	188.5 m^3 h^{-1}
Return sludge (Q_{RAS})	180 m^3 h^{-1}
Excess sludge (Q_{EX})	3.2 m^3 h^{-1}

Table 1. The configuration of the plant consists of an equalization pond, a stripping tank, two modules of oxidation ditches, and two secondary clarifiers. A summary of the reactor dimensions is included in Table 2. The WWTP is operated with a semi-constant flow, as the wastewater is generated from different steps of the coking process. It is first discharged to the equalization pond and is then released at a semi-constant rate to the WWTP. The equalization pond helps remove some of the free ammonia, reduce the impact of the shock loads, and remove oil and grease from the wastewater. Upon entering the oxidation ditches, the domestic wastewater from the labor buildings is mixed with industrial wastewater.

Due to strong pH variations in the wastewater, the pH is monitored and controlled before the biological step involving the addition of phosphoric acid and lime. Each module of the oxidation ditches is aerated by three surface aerators, each with a constant power supply of 45 KW. The return sludge (Q_{return}) is pumped to the inlet of the oxidation ditches, and the excess sludge (Q_{ex}) is pumped to the drying step. Finally, the treated effluent is pumped and reused by coke-oven factory and the excess water is pumped to the nearby municipal WWTP.

Data from the last 10 years of the plant's operations were collected from the coke-oven WWTP. The 2014 yearly routinely collected average measurements on the influent of the oxidation ditches and the effluent of the treatment plant are presented in Table 3. The raw sewage temperature was 13–34°C, with an annual average of approximately 23°C.

For wastewater characterization and calibration, a detailed sampling campaign was conducted daily between 27 September 2014 and 3 October 2014 (seven samples). Samples were collected from the locations shown in Fig. 1. Each sample was analyzed for the parameters presented in Table 4, including: total COD; filtered COD with a 0.45 mm filter ($COD_{filt.}$); total Kjeldahl nitrogen (TKN); volatile suspended solids (VSS); total suspended solids (TSS); ammonia nitrogen (NH_4-N); free ammonia (NH_3-N); nitrite nitrogen (NO_2-N); nitrate nitrogen (NO_3-N); phosphate phosphorus (PO_4-P); phenol; cyanide; calcium; magnesium; and temperature (T). Moreover, dissolved oxygen (DO) and pH were measured at different sampling points over the length of the oxidation ditches to describe the biological conversion as a function of the reactor length. The average measurements of the sampling program performed by the researcher are presented in Table 4. The temperature was at the optimum level for growth of bacteria during the sampling program, at which time the sewage temperature was approximately 27°C.

Table 3
Yearly average for 2014 of routine measurements of the influent and effluent of the coke-oven WWTP in g m^{-3}

Description	Influent of oxidation ditches	Effluent
COD_{tot}	1,459	156
BOD_5	624	54
Phenol	178	1.3
Cyanide	10.7	1.0
NH_4-N	535	511
NH_3-N	180	106
NO_3-N	2	13.9
PO_4-P	6	0.3

2.2. Plant model setup

The simulation of the coke-oven WWTP was performed with BioWin software V4.1 (EnviroSim Associates, Ltd, Canada). The process was modeled on the flow scheme in Fig. 2, and the hydraulic and operational parameters used are presented in Table 1. Coke-oven wastewater and domestic wastewater were represented separately in the model. In the oxidation ditches, the mixed liquor flowed continuously around

Table 2
Reactor volumes for the coke-oven WWTP

Element name	Volume (m^3)	Area (m^2)	Depth (m)	HRT (h)
Anaerobic Equalization pond	81,600	27,200	3	480
Oxidation ditches (2 × 3,500 m^3)	7,000	1,400	5	19
Clarifiers (2 × 1,600 m^3)	3,200	800	4	2.4

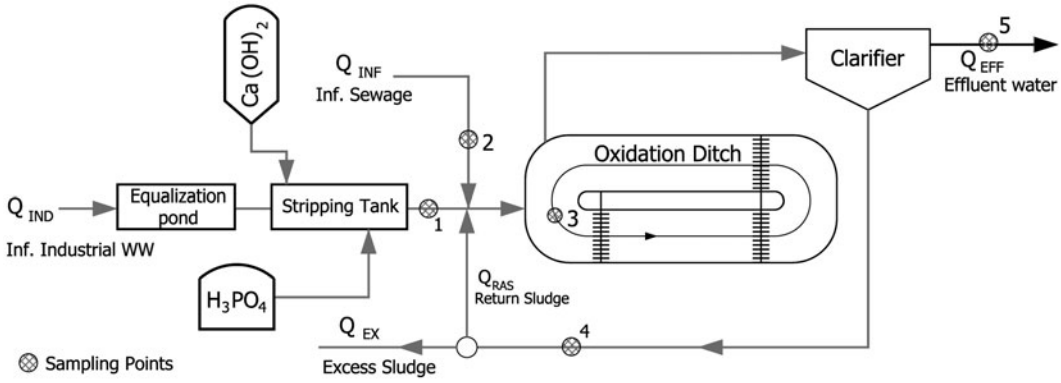

Fig. 1. Simplified schematic diagram of the coke-oven WWTP, including sampling points.

a looped channel with a channel flow rate of 10–40 times the rate of the influent flow. This resulted in strong dilution of the influent, which helped reduce the inhibitory effect that may have been caused by high concentrations of free ammonia, phenol, and cyanide. The plug-flow characteristics of the oxidation ditches were modeled as 10 completely mixed bioreactors in a series, which had an internal recycle flow of 1,250 m^3/h. This was done in order to sustain a dilution level of 15 times (recycle flow/influent flow), which has been verified through the velocity measurements in the reactor. The amount of suspended solids discharged in the effluent was considered during the sludge retention time (SRT) calculation. The DO concentrations found in the model of each unit were controlled using a power supply for each surface aerator and were then compared with the measured values of DO.

Influent characterization is one of the main elements affecting the quality of predictions made by a model. Characterization can be defined as the process of converting the available measurement data from the WWTP into data that can be used in the model [15]. In the present study, several biological tests and complementary physical–chemical analyses were performed to characterize the wastewater and sludge composition. Industrial wastewater characterization was performed according to the guidelines presented by [16]. For our extended model, an additional COD fraction for the phenol (F_{ph}) was developed, based on the fact that the phenol is a part of the soluble and readily biodegradable COD. The phenol concentration (S_{ph}) was measured according to the standard methods [17]; this measurement was then multiplied by a theoretical factor of 2.4 to convert the number to the COD [18]. The COD fractions for the coke-oven wastewater, as determined by the wastewater characterization, are summarized in Table 5. The influent characteristics of the coke-oven wastewater were entered into the BioWin software, as presented in Table 6. For characterization of the domestic wastewater (20 m^3/h), the default values of the BioWin characterization were used. The data were evaluated by applying mass balances of COD throughout the WWTP.

The BioWin AS model was used as a closed box to calculate the biological conversions in the reactors. The BioWin AS model has more than 50 state variables and over 70 process expressions describing the biological processes typically occurring in municipal WWTPs [19]. These biological processes are: (1) the growth and decay of ordinary heterotrophic organisms (OHOs); (2) the growth and decay of methylotrophs; (3) hydrolysis, adsorption, ammonification, and assimilative denitrification; (4) the growth and decay of the ammonia-oxidizing biomass (AOB); (5) the growth and decay of the nitrite-oxidizing biomass (NOB); (6) the growth and decay of the anaerobic ammonia oxidizers (ANAMMOX); and (7) the growth and decay of the polyphosphate-accumulating organisms (PAOs).

To predict the kinetics and behavior of coke-oven WWTPs, it may be necessary to extend the model using additional processes and kinetic reactions for the removal of phenol and cyanide. Four additional model processes (BioWin AS model extension) were added for the degradation of the phenol and cyanide (Table 7). Inhibition of bacteria by high concentrations of phenol and cyanide has been reported in the literature [13,20]. Many previous laboratory studies examining the biological treatment of phenol and cyanide in synthetic wastewater [4,21,22] have indicated that the Haldane relationship (Eq. (1)) best represents the growth rate (μ) of micro-organisms in inhibitory substrate degradation, as opposed to the Monod equation (Eq. (2)), which is typically used in wastewater modeling:

Table 4
Average values of concentrations in g m^{-3} (pH is unitless) measured during the sampling program and applied during the sampling campaign

Parameters/Location	COD_{tot}	$COD_{filt.}$	BOD_5	Phenol	Cyanide	NH_4-N	NH_3-N	NO_2-N	NO_3-N	TKN	DO	TSS	VSS	Mg	Ca	pH
1	1,335	957	618	180	10.7	465	193	1.8	0	850	0	194	189	10	25	8.7
2	500	170	245	–	–	18	–	0	0	30	0	243	192	15	80	7.5
3	–	–	–	–	–	–	–	–	–	–	3.5	4,071	3,347	–	–	8
4	–	–	–	–	–	–	–	–	–	–	–	8,114	6,668	–	–	7.6
5	193	175	31	1.1	1.05	390	148	10	0	–	1.5	51	40	9	22	7.5

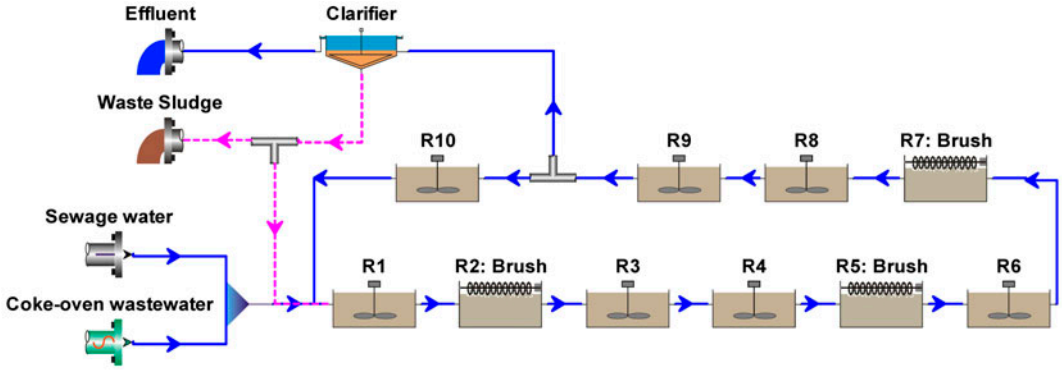

Fig. 2. Process representation of the coke-oven WWTP in BioWin software.

Table 5
Classification of the influent COD fractions for the coke-oven wastewater

Fraction	Description	Mean value measured	Default
F_{bs}, g COD per g COD_{tot}	Readily biodegradable	0.57–F_{ph}	0.16
F_{ph}, g COD per g COD_{tot}	Phenol	2.4 × measured phenol/COD_{tot}	
F_{xp}, g COD per g slowly biodegradable COD	Non-colloidal slowly biodegradable	0.7	0.75
F_{us}, g COD per g COD_{tot}	Non-biodegradable soluble	0.14	0.05
F_{up}, g COD per g COD_{tot}	Non-biodegradable particulate	0.04	0.13

Table 6
Influent characteristics of the coke-oven wastewater for the BioWin AS model

Parameter	Description	Value	Unit
X_{sp}	Slowly bio. COD (part.)	258	g COD m^{-3}
X_{sc}	Slowly bio. COD (colloid.)	59	g COD m^{-3}
X_i	Particulate inert COD	54	g COD m^{-3}
X_{on}	Particulate bio. organic nitrogen	90	g N m^{-3}
X_{op}	Particulate bio. organic phosphorus	1.78	g P m^{-3}
X_{in}	Particulate inert nitrogen	1.47	g N m^{-3}
X_{ip}	Particulate inert phosphorus	0.46	g P m^{-3}
P_{Plo}	Releasable stored poly phosphorus	0.01	g P m^{-3}
S_{bsc}	Readily bio. COD (without phenol)	329	g COD m^{-3}
$N_{H_3\text{-}N}$	Ammonia nitrogen	650	g N m^{-3}
N_{os}	Soluble bio. organic nitrogen	90	g N m^{-3}
N_2	Dissolved nitrogen gas	16	g N m^{-3}
$P_{O_4\text{-}P}$	PO_4-P (Sol. & Me Complexed)	5	g P m^{-3}
S_{us}	Sol. inert COD	160.4	g COD m^{-3}
N_{us}	Sol. inert TKN	17	g N m^{-3}
I_{SS}	Inert suspend solids	25	g m^{-3}
Mg	Magnesium	10	g m^{-3}
S_{Ca}	Calcium	25	g m^{-3}
S_{CO_2}	Total CO_2	5.0	mmol L^{-1}
S_{ph}	Phenol	180	g m^{-3}
S_{cn}	Cyanide	11.2	g m^{-3}
DO	Dissolved oxygen	0	g m^{-3}

Table 7
Additional matrix equations for the phenol and cyanide removal in the BioWin AS model

Component, i → Processes, j ↓	State variables already in BioWin AS model									New defined			
	1 $N_{H_3\text{-}N}$	2 $N_{O_3\text{-}N}$	3 $P_{O_4\text{-}P}$	4 DO	5 X_{sp}	6 X_{on}	7 X_{op}	8 Z_{bh}	9 Z_e	10 S_{ph}	11 S_{cn}	12 Z_{cn}	
	Observed Transformation Rates [M L^{-3} T^{-1}], $r_i = \sum_j \upsilon_{ij}\rho_j$ over all processes$j$												Rate equations, ρ_j [M L^{-3}]
1 Aerobic growth of heterotrophs on Phenol	$-i_{XBN}$	0	$-i_{XBP}$	$\frac{-(1-Y_{Hph})}{Y_{Hph}}$	0	0	0	1	0	$\frac{-1}{Y_{Hph}}$	0	0	$\mu_{hph}\frac{S_{ph}}{\left(K_{sph}+S_{ph}+\frac{S_{ph}^2}{K_{iph}}\right)}\times\frac{S_{po4p}}{(K_{lp}+S_{po4p})}\times\frac{DO}{(K_{OH}+DO)}\times Z_{bh}$
2 Anoxic growth of heterotrophs on Phenol	$-i_{XBN}$	$\frac{-(1-Y_{Hph})}{(2.86\,Y_{Hph})}$	$-i_{XBP}$	0	0	0	0	1	0	$\frac{-1}{Y_{Hph}}$	0	0	$\eta_g\times\mu_{hph}\frac{S_{ph}}{\left(K_{sph}+S_{ph}+\frac{S_{ph}^2}{K_{iph}}\right)}\times\frac{S_{po4p}}{(K_{lp}+S_{po4p})}\times\frac{K_{OH}}{(K_{OH}+DO)}\times\frac{S_{NO}}{(K_{NO}+S_{NO})}\times Z_{bh}$
3 Aerobic growth of cyanide-degrading organisms	$-i_{XBN}$	0	$-i_{XBP}$	$\frac{-(1-Y_{cn})}{Y_{cn}}$	0	0	0	0	0	0	$\frac{-1}{Y_{cn}}$	1	$\mu_{cn}\times\frac{S_{cn}}{(k_{cn}+S_{cn}+\frac{S_{cn}^2}{K_{icn}})}\times\frac{DO}{(K_{Osc}+DO)}\times Z_{bcn}$
4 Decay of cyanide -degrading organisms	0	0	0	0	$1-f_b$	$i_{XBN}-i_{XPN}\times f_b$	$i_{XBP}-i_{XPP}\times f_b$	0	f_b	0	0	−1	$b_{cn}\times Z_{cn}$
Stoichiometric Parameters: Heterotrophic yield on phenol: Y_{Hph} Cyanide-degrading organisms yield: Y_{cn} Endogenous Fraction of organisms: f_b Mass N/Mass COD in biomass: ix_{BN} Mass P/ Mass COD in biomass: i_{XBP} Mass N/ Mass COD in products from biomass: i_{XPN}Mass P/Mass COD in products from biomass: i_{XPP}	Ammonia N, [M (N) L^{-3}]	Nitrate N, [M (N) L^{-3}]	Phosphate P, [M (P) L^{-3}]	Dissolved oxygen [M (−COD) L^{-3}]	Slowly bio. COD [M (COD) L^{-3}]	Particulate bio. org. N [M (N) L^{-3}]	Particulate bio. org. P [M (P) L^{-3}]	Heterotrophs [M (COD) L^{-3}]	Endogenous products [M (COD) L^{-3}]	Soluble phenol [M (COD) L^{-3}]	Soluble cyanide [M (CN) L^{-3}]	Cyanide biomass [M (COD) L^{-3}]	*Kinetic Parameters:* Heterotrophic growth on phenol: μ_{hph}, K_{sph}, K_{iph}, K_{lp}, K_{OH} Cyanide-degrading organisms growth and decay: μ_{cn},k_{cn}, K_{icn}, K_{Osc} Correction factor for anoxic growth of heterotrophs: η_g												

$$\text{Haldane equation: } \mu = \mu_{max}\frac{S}{(K_s + S + \frac{S^2}{K_i})} \quad (1)$$

$$\text{Monod equation: } \mu = \mu_{max}\frac{S}{(K_s + S)} \quad (2)$$

where μ_{max} = the maximum growth rate, S = the concentration of the substrate, K_s = the half-saturation constant, and K_i = the inhibition constant.

2.2.1. Kinetics of phenol degradation

In Table 7, two processes were used for the degradation of the phenol, as proposed by Baker et al. [23]. Heterotrophs (Z_{bh}) were assumed to grow on the phenolic compounds (S_{ph}) under aerobic conditions at the rate of (ρ_1) and under anoxic conditions at the rate of (ρ_2) (Table 7). Phenol is considered to be readily biodegradable [12], and as such, no hydrolysis process was added. The decay process for the heterotrophs already existed in the BioWin AS model. Growth of the heterotrophs on S_{ph} was assumed to be limited by the phenol concentration, as follows the Haldane equation (Eq. (1)). Moreover, the switching functions were assumed for DO [10], and the phosphate concentration [23] followed the Monod equation (Eq. (2)). The process rate of (ρ_2) was similar to the process rate of (ρ_1); only the switching functions were modified, and the correction factor for anoxic growth of heterotrophs (η_{grow}) was introduced, as proposed by Henze et al. [10].

2.2.2. Kinetics of cyanide degradation

Two processes were used for the degradation of cyanide, as proposed by Lee et al. [12]. A cyanide-degrading organism (Z_{cn}) was defined in the extended model as an active biomass. Z_{cn} is assumed to grow on cyanide (S_{cn}) under aerobic conditions at the rate of (ρ_3) (Table 7). The overall decay rate of the cyanide-degrading organism is suggested as a first-order process at the rate of (ρ_4) (Table 7). Growth of the cyanide-degrading organisms was assumed to be limited by the cyanide concentration, as follows the Haldane equation (Eq. (1)). Moreover, the switching function for the DO was proposed [10], as follows the Monod equation (Eq. (2)).

The model assumes that during the decay process, there is a release of inert endogenous products (Ze), slowly biodegradable COD (X_{sp}), particulate biodegradable organic nitrogen (X_{on}), and particulate biodegradable organic phosphorus (X_{op}). The hydrolysis processes for these compounds already exist in the BioWin built-in model.

2.2.3. Model formulation

As per the ASM description [10], the concentration of any component may be affected by a number of different processes. The matrix representation of the model (Table 7) allows for easy recognition of the fate of each component, which helps with the preparation of mass balance equations. The observed transformation rate (r_i) is obtained by adding together the products of the stoichiometric coefficients (v_{ij}) and the process rate (ρ_j) for the component (i) (Table 7). The notations and initial values of the stoichiometric and kinetic parameters of the extended model are shown in Table 8. It should be noted that the model presented in Table 7 is an extension for the original model (the BioWin AS model). When calculating the observed transformation rate of any component, the software combines the existing processes in the built-in model with the processes proposed in the extended model.

2.3. Sensitivity analysis

Sensitivity analysis is a process that usually occurs before the calibration process occurs. The sensitivity analysis process lets the user know which of the model parameters have a significant influence on the output of the model. In the present study, a procedure based on EPA guidelines [24] was used. Two different sensitivity coefficients are calculated: the normalized sensitivity coefficient (S_{ij}) and the mean root-square sensitivity measure (δ_j^{msqr}). S_{ij} is defined as the ratio of the change in the output variable (y_i) to the change in the input variable (x_i) (Eq. (3)). Each parameter, in both the extended model and the built-in BioWin AS model, was increased above and decreased below the reference point values in increments of 10, 30, and 50% ($\Delta x_i/x_i$) for the S_{ij} calculations. Then, the δ_j^{msqr} was calculated as the mean root-square of the calculated S_{ij} for each parameter (Eq. (4)). Five output variables (COD, BOD_5, phenol, TKN, and cyanide) describing the quality of the effluent were taken into account during the calculations of S_{ij} and δ_j^{msqr}.

$$S_{ij} = \left|\frac{\Delta y_i/y_i}{\Delta x_i/x_i}\right| \quad (3)$$

$$\delta_j^{msqr} = \sqrt{\frac{1}{n}\sum_{i=1}^{n} S_{ij}^2} \quad (4)$$

Table 8
Stoichiometric and kinetic parameters for the phenol and cyanide extended model

Symbol	Characterization	Initial values used	Literature range	Refs.	Units
Y_{ph}	Heterotrophic Yield on phenol COD	0.6	0.6	[29]	g COD per g COD
μ_{hph}	max specific growth rate of heterotrophs on phenol (S_{ph})	4.3	3.6–10.5	[29]	d^{-1}
K_{sph}	Phenol substrate half sat.	257	3.9–257	[29]	g COD m^{-3}
K_{iph}	Phenol inhibition coefficient	163	72–2,434	[29]	g COD m^{-3}
k_{lp}	Heterotrophs phosphorus Half sat.	1	1	[23]	g P m^{-3}
η_g	Correction factor for anoxic growth of heterotrophs	0.6	0.6	[10][a]	d^{-1}
K_{OH}	DO half sat. for aerobic growth of heterotrophic bacteria	0.05	0.05	BioWin[a]	g O_2 m^{-3}
K_{NO}	Nitrate half sat. for anoxic growth of heterotrophic bacteria	0.5	0.5	[10]	g N m^{-3}
Y_{cn}	cyanide-degrading organisms yield	0.35	–	This study[c]	g COD per g CN
μ_{cn}	max specific growth rate of cyanide-degrading organisms	0.252	0.252	[30]	d^{-1}
K_{cn}	Cyanide substrate half sat.	1.9	1.9	[30]	g CN m^{-3}
K_{ic}	Cyanide inhibition coefficient	12.5	12.5	[30]	g CN m^{-3}
K_{Osc}	DO half sat. for aerobic growth of cyanide-degrading organisms	0.05	0.05	BioWin[a]	g O_2 m^{-3}
b_{cn}	Decay coefficient of cyanide-degrading organisms	0.06	–	This study[b]	d^{-1}
f_b	Endogenous Fraction of organisms	0.08	0.08	[10]	–
i_{XBN}	Nitrogen content of active mass	0.068	0.07	[10]	g N per g COD
i_{XBP}	Phosphorus content of active mass	0.021	0.02	[10]	g P per g COD
i_{XPN}	Nitrogen content in products from biomass.	0.06	0.06	[10]	g N per g COD
i_{XPP}	Phosphorus content in products from biomass.	0.02	0.02	[10]	g P per g COD

[a]This coefficient was assumed as for municipal AS system.
[b]Based on OUR tests.
[c]Based on batch tests.

3. Results and discussion

3.1. Plant performance

Based on data provided by the staff of the WWTP and the sampling campaign, it is clear that the WWTP examined in this study is performing well in terms of its treatment of COD, phenol, and cyanide. Despite the relatively high SRT of 31 d, the elimination of total ammonia ($NH_3 + NH_4$) was limited in WWTP to about 15–20%. This was concluded from the measurements taken during the sampling program as well as from the measurements taken in the past (Tables 3 and 4). The DO measurements showed that the DO was always above 1.5 mg/l in aerated zones; therefore, DO was not a limiting parameter for the nitrification process. Nitrifying bacteria are highly sensitive to a number of environmental factors, including DO concentration, temperature, pH, free ammonia in cases of high pH, free nitrous acid (FNA) in cases of low pH, and elevated BOD. Moreover, there have been several reports stating that nitrification is inhibited by the presence of toxic or inhibiting substances, such as phenol, cyanide, and the other toxic compounds found in coke-oven wastewater [2,25].

It is common for problems to occur during the nitrification process in WWTPs treating high-strength ammonium wastewater. In the high-strength ammonium wastewater, when the nitrogen-loading rate (NLR) was much greater than the maximum nitrification rate of the system, ammonium accumulated in the reactor. Although the stripping step occurred and a buffer was added, high concentrations of free ammonia were presented (Tables 3 and 4). Free ammonia is a function in total ammonia concentration and pH values, according to Eq. (5) [26], where (T) is the temperature and TAN is the total ammonia ($NH_3 + NH_4$) as

(mg N l^{-1}). The pH level of the influent was about 8.5 after the buffer was added and was about 7.5 in the effluent of the plant:

$$NH_3\text{-}N = \frac{17}{14} \times \frac{TAN \times 10^{pH}}{e^{6344/(273+T)} + 10^{pH}} \quad (5)$$

It has been reported that the AOB is completely inhibited at free ammonia concentrations of 150 g N/m^3, while the NOB can be inhibited at free ammonia concentrations as low as 2.8 g N/m^3. However, to our experience, nitrifying bacteria can adapt to high free ammonia or FNA concentrations or other environmental conditions following long exposure to such conditions. However, because of the sensitivity of the nitrifying bacteria, it is recommended when treating high-strength ammonium wastewater that start-up is carried out with a gradual and controlled increase of the NLR. This allows the nitrification rate to remain as close as possible to the maximum nitrification rate, therefore resulting in low ammonium concentrations in the reactor [27]. This strategy must also be applied during operation to avoid high free ammonia if the plant experiences any accumulation in ammonium.

3.2. Sensitivity analysis

In this study, a sensitivity analysis was performed for all stoichiometric and kinetic parameters related to phenol and cyanide treatment processes. Only kinetic or schematic parameters with $S_{i,j}$ values of more than 0.25 were considered as sensitive parameters. Six parameters related to the extended model were found to be sensitive (see Table 9). These parameters were: the maximum specific growth rate of the heterotrophs on the phenol (μ_{hph}), the half-saturation coefficient of the phenolic (K_{sph}), the yield of the phenol COD (Y_{ph}), the maximum specific growth rate of the cyanide (μ_{hcn}), the decay coefficient of the cyanide-degrading micro-organism (b_{CN}), and the half-saturation coefficient of the cyanide (k_{CN}).

For the BioWin AS model, the sensitivity analysis was performed on the parameters related to the OHO, AOB, and NOB. In this study, the sensitivity analysis showed that the maximum specific growth rate of the OHO (μ_{maxH}) under aerobic conditions and the aerobic decay rate of the OHO (b_H) were the most effective parameters for the COD and phenol calibration. Meanwhile, the decay rate of the AOB ($b_{aerob,A}$) and the maximum specific growth rate of the AOB (μ_{maxA}) were the most effective for ammonia calibration (Table 9).

Table 9
Values of the root mean root-square sensitivity measure (δ_j^{msqr}) of the model stoichiometric and kinetic parameters

Parameters	COD	BOD_5	TKN	Phenol	Cyanide
Phenol and cyanide extended model					
μ_{hph}	–	–	–	3.40	–
K_{sph}	–	–	–	3.16	–
Y_{ph}	–	–	–	3.12	
μ_{hcn}	–	–	–	–	2.90
k_{CN}	–	–	–	–	1.63
b_{CN}	–	–	–	–	1.40
BioWin AS model					
b_H	0.36	2.85	–	2.71	–
μ_{maxH}	–	2.04	–	–	–
$b_{aerob,A}$	–	0.86	4.05	–	–
μ_{maxA}	–	0.87	4.00	–	–

Notes: During δ_j^{msqr} calculation, only parameters with $S_{i,j}$ values of more than 0.25 were considered.

3.3. Model calibration

After characterization of the main operational parameters was complete, the model of the coke-oven WWTP was calibrated. A stepwise approach was applied, as proposed by Hulsbeek et al. [16]. First, the sludge production was fixed (sludge concentration, SRT, sludge production, and N-content sludge) on the basis of yearly average measurements. Next, the phenol and cyanide were calibrated on the basis of yearly average measurements. Finally, the nitrification was calibrated.

The characterization of the influent was the most important step in the calibration process. Once the MLSS concentration was calibrated, there was no need to calibrate the model for the effluent COD [8,28]. However, sludge production was generally compensated for by the simulated oxygen consumption of the process [9]. Because the SRT was fixed according to the TSS balance, the sludge COD concentration in the process was determined mainly by the influent non-biodegradable particulate ratio to the total COD (F_{up}). Increasing the F_{up} therefore led to an increase in the COD during the process, and vice versa. By adjusting the influent ratio of F_{up}, and adjusting the maximum specific growth rate of the OHO under aerobic conditions (μ_{maxH}), the model described the measured the MLVSS in the reactor using a conversion factor F_{cv} (COD/VSS) of 1.42 gCOD/gMLVSS.

Calibration of the phenol and cyanide removal model was performed using steady-state analyses based on the mean operation data from the treatment plant. The model was first run using the initial values

Table 10
The calibrated parameters for the phenol and cyanide extended model

Parameter	Characterization	Calibrated value	Units
μ_{bh}	max specific growth rate of heterotrophs on S_{ph}	4	d^{-1}
K_i	Phenol inhibition coefficient	450	g COD m^{-3}
K_{sph}	Half-saturation coefficient for phenolics	75	g COD m^{-3}
b_{cn}	Decay coefficient of cyanide-degrading organisms	0.07	d^{-1}

of the stoichiometric and kinetic parameters of the phenol and cyanide taken from the literature (see Table 8). The calibration was done using a stepwise adjustment of the selected parameters shown in Table 10 until the outputs were found to be similar to the actual measured outputs. The calibrated values found for the model parameters were within the range reported in the literature. The available parameters in the literature were based on batch-scale laboratory or pilot studies. Moreover, use of the extended model for the phenol was effective in the COD calibration.

Regarding the nitrification process, the model initially did not predict this process sufficiently. Calibration of the nitrification was performed by reducing the maximum specific growth rate (μ_{maxA}) to 0.6 d^{-1} from its default value of 0.9. The decay rate of the AOB was adjusted to 0.20 from 0.17 d^{-1}. This was in agreement with the range reported by previous studies regarding the treatment of oil refinery wastewater [8]. Other stoichiometric and kinetic parameters related to the nitrification process were set to the default values. After calibration, the BioWin AS model was able to predict the low performance of the nitrification process. Unlike the famous ASM family, parameters like temperature, and pH prediction were included in the BioWin AS model, which made it more preferable for use in the present study. Our trial used the ASM3 (data were not shown) instead of the BioWin AS model. In the ASM3, nitrification occurred very well, unlike it did in reality. Optimization of different scenarios can be proposed for better nitrification. However, this was outside of the scope of this paper.

3.4. Model validation

Re-calibration under dynamic conditions can be done to improve the accuracy of model prediction. However, in our case, re-calibration did not result in different values for the calibrated parameters, because the plant operation was in an almost steady state due to the existing equalization bond. Model validation was performed by predicting the concentrations of the phenol, cyanide, COD, and TKN in the effluent. This was done using the dynamic simulation based on the influent data from the year 2014 recorded by the WWTP. The simulated values for phenol and cyanide were compared with the values obtained from the recorded effluent measured data in the same period and are presented in Fig. 3. The simulated values for COD and TKN were compared with the values obtained from the recorded effluent measured data in the same period and are presented in Fig. 4. TKN is the sum of organic nitrogen, free ammonia, and ammonium and it was chosen to compare effluent and influent concentrations in Fig. 4. Measured TKN in effluent (Fig. 4) was taken as the sum of only free ammonia and ammonium, as most of organic nitrogen

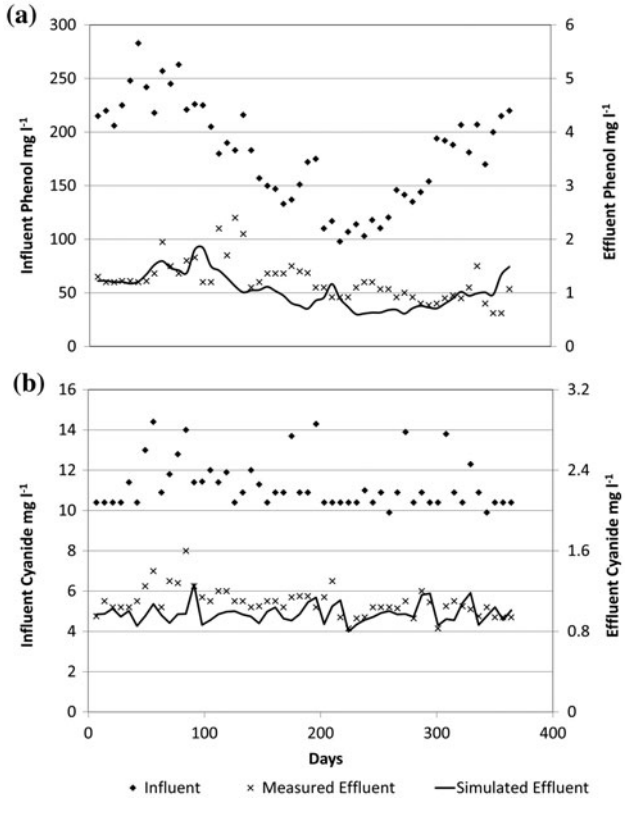

Fig. 3. Simulation results for the coke-oven WWTP compared to the measured data for the phenol (a) and cyanide (b).

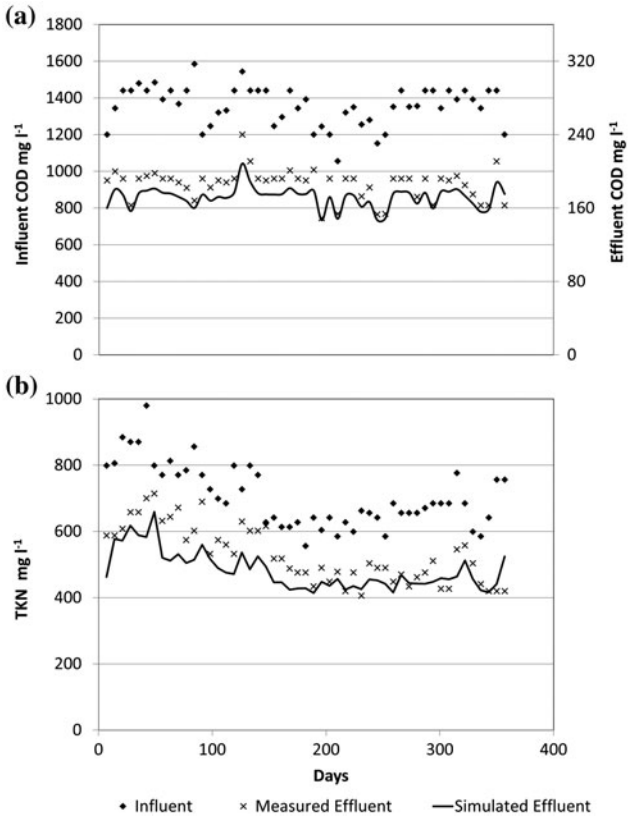

Fig. 4. Simulation results for the coke-oven WWTP compared to the measured data for the COD (a) and TKN (b).

in the influent is converted to ammonium during biodegradation. The modified model showed a good representation of the WWTP.

In order to check the accuracy of the model prediction, the average relative deviation (ARD) [24] was calculated according to Eq. (6), where m_i is the measured value, p_i is the model predicted value of the output variables, and N is the number of dynamic simulation observations:

$$\mathrm{ARD} = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{(m_i - p_i)}{m_i}\right| \quad (6)$$

The goodness of fit for the dynamic simulations was tested using the ARD values. For the COD, TKN, and cyanide, the variance between the measured and predicted values of the output variables did not exceed 15%. The ARD values were 7.7, 10.3, and 11.8% for the COD, TKN, and cyanide, respectively. For the phenol, the ARD was found to be 24.8%. However, this does not mean that the model did not predict the phenol well, as there were very low values of phenol in the effluent (1.0–1.5 mg/l) compared to the influent (180 mg/l), which made any small variation in the effluent phenol level reflect a high ratio of ARD. These results confirmed that the model calibration and validation had been performed correctly.

4. Conclusions

In this study, the BioWin AS model was extended by adding four additional processes for phenol and cyanide removal. The modified model was calibrated and validated, and it showed a good representation of a full-scale coke-oven WWTP. The proposed model was calibrated under steady-state conditions and validated under dynamic-flow conditions. Nineteen new stoichiometric and kinetic parameters related to the phenol and cyanide removal in the extended model were defined and adjusted. The new calibrated parameters were compared to the available parameters from the literature, which had been based on batch lab-scale experiments or pilot studies. The model was able to describe the performance of the coke-oven wastewater treatment regarding COD, phenol, and cyanide removal. Although the ASM-family models, including the BioWin AS model, were originally developed and applied for use with municipal wastewater, this study shows the suitability of ASM-based models for industrial wastewater treatment or mixed municipal–industrial wastewater if the model is extended with the suitable process expressions dealing with specific industrial wastewater pollutants. For future proposal, extended model in this study can be used to optimize plant performance regarding COD, phenol, cyanide, and nitrogen removal.

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