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Heavy Metal Removal Investigation in Conventional Activated Sludge Systems

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Abstract

The combination of industrial and domestic wastewater in municipal WWTPs (waste water treatment plants) may be economically profitable, but it increases the difficulty of treatment, and also has some detrimental effects on the biomass and causes a low-quality final effluent. The present study evaluates the treatment process both in the presence and absence of heavy metals using ASM3 (activated sludge model no.3) so as to improve the model by means of incorporating other novel inhibitory kinetic and settler models. The results reveal that the presence of heavy metal, a case study for copper and cadmium at a concentration of 0.7 mgL^{-1} in a biological treatment system has a negative effect on heterotrophic bacteria concentration by 25.00 %, and 8.76 % respectively. Meanwhile, there are no important changes in COD (chemical oxygen demand), SS (total suspended solids) and TN (total nitrogen) in the final effluent in the conventional system. However, all these parameters are acceptable and consistent with EU Commission Directives. The results indicate that ASM3 can predict and provide an opportunity of the operation for an activated sludge wastewater treatment plant that receives the effluent from an industrial plant.

Keywords: Activated Sludge; ASM3; Heavy Metal; Heterotrophs; Kinetic Models.

1. Introduction

Industrial wastewater discharged from the industries such as textile dyeing, petroleum, metal finishing, automobile, electro-plating, and leather tanning cause heavy metals entering into the life cycle. So, this becomes one the most important environmental problem in the world. The detrimental effects generally depend on the type and the concentration of the heavy metals. The most frequently encountered heavy metals present in the industrial effluents are copper, mercury, zinc, lead, cadmium, iron, chromium, cobalt and nickel. There are many treatment technologies applied for the removal of heavy metals from wastewaters. Among them the most frequently studied technologies are ion-exchange, adsorption and membrane filtration [1]. Ong et al. [2] give the following ranking of the toxicity of the heavy metals for biological treatment: Cd > Cu > Zn > Cr > Pb, which differs from previously mentioned rankings as these have focused on the human organism. The effect on the wastewater treatment process is mainly the direct impact on the metabolism of microorganisms, but in the case of human beings the focus is mostly on the nervous system and cells [2, 3]. The concerns on metals in urban wastewater treatment plants (WWTPs) are mainly related to its contents in discharges to environment, namely in the final effluent and in the sludge produced. In the near future, more restrictive limits will be imposed to final effluents, due to the recent guidelines of the European Water Framework Directive (EUWFD). Concerning the sludge, at least seven metals (Cd, Cr, Cu, Hg, Ni, Pb and Zn) have been

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regulated in different countries, four of which were classified by EUWFD as priority substances and two of which were also classified as hazardous substances.

There are also some other methods such as chemical precipitation, coagulation-flocculation, and flotation. A study [4] on the adsorption technique using chitosan and modified chitosan in the heavy metal ion removal concluded that chitosan has considerable advantageous in low cost, biocompatibility, biodegradability, excellent adsorption performance, environmentally friendliness, and bioactivity and also modified chitosan has a great advantageous in many points over the conventional adsorbents. Çeçen et al. [5] investigated the effect of Cr, Pb, Hg, Cd, and Ag on nitrifying sludge respiration by depicting the highest inhibitory effect of Ag and the lowest inhibitory effect of Cr (either trivalent or hexavalent, their effects are similar).

The biological wastewater treatment is not an efficient process due to the toxic cation effect on the biomass for the wastewater with high metal concentrations. The toxicity of metals influences the microbial biomass growth and treatment efficiency inversely. If present in low concentrations, some metals may act a micronutrient, however, in high concentrations they may cause the cell break off. Since the irreversible inhibition of some enzymes, the heavy metal concentration at ppm level (mg/L) is known to be toxic. The toxicity of heavy metals in an activated sludge system was investigated [6] for copper, zinc and nickel and it was determined that the nitrifiers had higher sensitivity than heterotrophic bacteria to these metals. The metal accumulation capability of biomass was the highest in copper case and it was indicated that the presence of heavy metals reduces microbial diversity abundance in activated sludge systems. The effect of copper and zinc, which were studied on biomass, separately and combined [7], showed that copper was more toxic than zinc. According to the results one can say that the presence of copper up to 5 mg/L, the bio-kinetic parameters was not affected adversely, but serious upsets were caused in the system when concentration increased to 10 mg/L and higher.

Toxicity effect changes with heavy metal ions and organisms' type and concentrations and also the environmental conditions [8] such as temperature, pH, dissolved oxygen (DO), ionic strength, the other metal ions presence, together with the operating parameters such as, hydraulic residence time (HTR) and solids retention time (SRT). The experiments were performed for the synthetic wastewater containing 14 mg/L copper (II) [9] indicated that chemical oxygen demand (COD) removal percentage increased with increasing SRT both in the presence and the absence of copper. It was also shown that the growth yield coefficient decreased and the death rate constant increased in the presence of 15 mg/L copper(II) [10]. All heavy metals are toxic to the bacterial life and inhibit the microbiological processes at moderate and high concentrations, although they stimulate microorganisms at low concentrations. Copper inhibits the heterotrophic biomass at low concentrations and is more toxic than lead, zinc and nickel. In fact, copper had a very important negative effect on the bacterial communities in the activated sludge systems and their performance in anaerobic-anoxic-aerobic processes. In order to overcome copper toxicity, the bacterial species showed different adaptation and tolerances. Some species were stimulated also in high concentrations of copper [11]. The Illumina MiSeq Sequencing analysis in order to classify the microbial community showed that the system lost the chemical oxygen demand and ammonia nitrogen removal efficiency at 40 mg L^{-1} copper concentration.

Bringing together industrial and domestic wastewater in municipal WWTPs may be economically profitable for treatment purposes; yet the consequences direct as regards the difficulty of treatment and unexpected impact on biomass and end-product.

Hence there is a need to evaluate behavior of WWTPs with and without heavy metals in activated sludge systems. Activated sludge models were derived for domestic wastewater treatment systems; however, they found a place in the application of the industrial biological wastewater treatment systems. For instance, a cooking wastewater biological treatment process was simulated [12] and optimized by ASM3 and then the model parameters compared with that of wastewaters having different industrial sources such as pulp mill, tannery and palm oil mill. It was shown that the ASM3 model could predict the performances of coking wastewater treatment plant successfully in removing chemical oxygen demand and ammonium nitrogen. ASM1 (activated sludge model 1) was also used for waste water treatment of pulp and paper mills, where estimated and correlated heterotrophic growth rate and lysis rate constants with temperature were reported as maximum 9.69 d^{-1} and 1.96 d^{-1} respectively [13].

In the modeling of activated sludge systems, several mathematical models have been suggested and the effects of heavy metals on the performance of the activated sludge systems on the growth rate have been studied. However only limited number of studies concerning the lysis rate constants in the presence of heavy metals is reported though its importance. In order to evaluate the effects on heterotrophic growth and lysis rate, a novel modeling concept was established and concluded that the growth rate decreased while decay rate was increasing with heavy metal concentration and the inhibition coefficients of 1.21 and 1.82 mgL^{-1} for Cu and Cd, respectively [14]. In order to determine the net maximum specific growth rate as a function of concentrations of heavy metals, the inhibitory effects of copper and zinc on autotrophic bacteria was studied [15]. The results reveal the stronger inhibitory effect of Cu compared to Zn and nitrification process was completely inhibited at 1.2 mg/l for Cu and Zn. IC_{50} (median inhibition concentration) values were also found as 0.08 mg/l and 0.35 mg/l for Cu and Zn respectively.

Although WWTPs are not are not designed to remove metals, the study of metals behavior in these systems is a crucial issue to develop predictive models that can help more effectively the regulation of pre-treatment requirements and contribute to optimize the systems to get more acceptable metal concentrations in its discharges so, In the present study, a dynamic model based on ASM3 [16] is used to assess the behavior of the activated sludge process at a full scale domestic wastewater treatment plant. Actually, activated sludge models only consider domestic wastewater treatment. However, if they are extended in order to cover the growth and lysis rates of heterotrophic and autotrophic bacteria with metal presence, they could be applied to the industrial wastewater treatment containing heavy metals, as well.

The ultimate goal is to improve ASM3 by a combination of laboratory tests and process modeling to assess the effects of heavy metals on the process of an activated sludge wastewater treatment that receives the effluent from an industrial plant. This evaluation will take copper and cadmium into account in the process; some of the ASM3 original default parameter values were changed according to the results of the batch experiments to predict the effects of heavy metals on activated sludge treatment plants. At the end, a new model is proposed and coupled with ASM3 considering the growth and the lysis processes in activated sludge under aerobic conditions. The outcomes of the present study are expected to enlighten the perspectives of the growth and lysis processes in activated sludge containing heavy metals such as copper and cadmium as a case study. Therefore, the activated sludge systems should be modeled, simulated and optimized for the industrial waste water treatment to explore the effect of different heavy metals on the model parameters.

2. Materials and Methods

In the present study, the wastewater treatment model improved for conventional systems is simulated in order to include the heavy metals (Cu) and (Cd), then the results are evaluated. The conventional system is continuously aerated.

2.1. Data Collection

For the purpose of the present study, it is referred to the data formally obtained in one other works. Novel inhibitory kinetic models which include non-competitive kinetic, linear regression models for X_H are derived using the values of growth and lysis rate constants obtained from the batch results [14] which show that the inhibitory effect of these two heavy metals was in a good agreement with non-competitive inhibition kinetic at different concentration. The R-squared values of regression lines at different cadmium concentration for growth and lysis constants are 0.97 and 0.92, respectively (Equations 1 and 2). The R-square values of regression lines at different copper concentration for growth and lysis constants are 0.98 and 0.74, respectively (Equations 3 and 4).

Linear regression model in case of cadmium is as follows:

$$\mu_H = -1.8683 \times \text{concentration of cadmium} + 4.5197 \tag{1}$$

Where μ_H represents heterotrophic growth rate constant

$$b_H = 0.0448 \times \text{concentration of cadmium} + 0.3122 \tag{2}$$

Where b_H denotes the heterotrophic lysis rate constant

Linear regression model in case of copper is as follows:

$$\mu_H = -2.3692 \times \text{concentration of copper} + 4.51 \tag{3}$$

$$b_H = 0.1689 \times \text{concentration of copper} + 0.3122 \tag{4}$$

In the present study these novel kinetic models for heavy metal model obtained from the batch experiments [14] are combined with ASM3 model.

2.2. Aeration Tank Model

In the modeling of an activated sludge tank, a single tank was used for the biological processes. The wastewater entering the biological tank undergoes some biological processes. The water and sludge mixture, which is known as activated sludge, leaving the biological tank enters the settler where sludge settles down and water is discharged to the receiving medium. Most of the sludge settled down is recycled to the biological tank in order to increase the quantity of the biological mass and maintain the appropriate substrate-to-biomass ratio. In the present study ASM3 was considered as an appropriate choice for the time being especially in dealing with the aerobic and anoxic processes in a single tank. Mass balances in the aeration tank result in:

$$\frac{dXat}{dt} = \frac{QinXin + Qrs\,\mathrm{Xrs} - (Qin + Qrs)Xat}{Vat} + Ri \tag{5}$$

Where X_{at}, X_{rs} and X_{in} are 13-dimensional vectors consisting of ASM3 components in the activated sludge tank, recycle, and inlet wastewater, respectively. Ri is the component conversion rate of xi, V_{at} is the aeration tank volume, and Q denotes the flow rate.

The mass balance related to the dissolved oxygen (S) includes an additional term on the right-hand side $k_L\,a\,(\mathrm{S_O}^{sat} - \mathrm{S_O}^{at})$ where $k_L\,a$ and $\mathrm{S_O}^{sat}$represent liquid phase volumetric mass transfer coefficient and saturation of the dissolved oxygen, respectively.

$$\frac{dXat}{dt} = \frac{QinXin + Qrs\,\mathrm{Xrs} - (Qin + Qrs)Xat}{Vat} + Ri + k_L\,a\,(\mathrm{S_O}^{sat} - \mathrm{S_O}^{at}) \tag{6}$$

In the activated sludge model (ASM3), there are 13 components and 12 microbiological transformation processes in the original model and kinetic rate expressions for each process are given in the model as a function of 13 model components. The inlet wastewater composition, stoichiometric matrix and kinetic parameters (at 20°C) were taken from ASM3. The stoichiometric matrix was used to write the conversion rate of each component. The process rates, formation/disappearance rates of model compounds, the mass balances around each layer of settler were applied. As mentioned before, the ASM3 model allows us to describe phenomena of organic matter, nitrogen removal and suspended solids. In fact, the main classification in the model state variables is in organic matter, expressed in terms of COD, nitrogen compounds and suspended solids. The state variables included in the ASM3 are the fundamental components that act upon the process, but they are not always measurable or interpretable in many practical applications. Therefore, some composite variables can be calculated from the state variables in order to combine them into forms that are typically measured in reality, such as MLVSS (mixed liquor volatile suspended solids), COD (chemical oxygen demand), TSS (total suspended solids) and TN (total nitrogen), as reported below:

$$MLVSS = 0.75 \times (X_1 + X_S) + 0.90 \times (X_H + X_A) + 0.60 \times X_{STO} \tag{7}$$

$$COD = S_I + S_S + X_I + X_S + X_H + X_{STO} + X_A \tag{8}$$

$$SS = X_{SS} \tag{9}$$

$$TN = S_{NH} + S_{NO} + 0.01 \times S_I + 0.03 \times S_S + 0.02 \times X_I + 0.04 \times X_S + 0.07 \times (X_H + X_A) \tag{10}$$

2.3. Secondary Settler Model

Activated sludge plants transform organic matter into biomass. The effective operation of the process requires the biomass to be removed from the liquid stream (in the secondary settler) prior to being discharged in the receiving waters. The sedimentation of the particles in the liquor is achieved by gravity along with the density differences between the particles and the liquid. Part of the biomass is purged, while a large fraction is returned to the biological reactor to maintain the appropriate substrate-to-biomass ratio.

In order to solve the mass balances around the biological tank the concentrations of compounds in the recycled stream are needed. Furthermore, the concentrations in the discharged water are also necessary to know whether the treatment is sufficient or not. Settling tank is modeled as a cylindrical tank with 10 layers and Takács Model [17] is adapted to ASM3 compounds. No biological processes in the settler and no change in the concentrations in radial direction are assumed in the modeling. According to the flux theory; total flux is equal to the sum of the bulk and gravity fluxes. The soluble components of ASM3 which are denoted as '*S*' are assumed to follow the water flow and gravity fluxes for them are set to zero. Hence, the concentrations of soluble components of ASM3 are taken as equal in the inlet and outlet of the settling tank. For the particulate components of ASM3 which are represented by '*X*', the settling velocity is derived from Takács' expression as follows:

$$v_{sj}\left(X_j^{set}\right) = \max(0, \min(v_0', v_0(e^{-rh\left(X_j^{set} - f_{ns}X_{in}^{set}\right) - e^{-re\left(X_j^{set} - f_{ns}X_{in}^{set}\right)})))} \tag{11}$$

$$0 \leq v_{sj} \leq v_0'$$

Where v_0, v_0', *rh*, *rp*, and f_{ns} are model parameters defined in Takács et al., $X_{in}{}^{set}$ is the suspended solids concentrations entering the settler, $X_j{}^{set}$ concentration of the suspended solids calculated for each layer of the settler based upon ASM3 as follows:

$$X_j^{set} = 0.75(X_1^{set} + X_S^{set}) + 0.90(X_H^{set} + X_A^{set}) + 0.60X_{STO}^{set} \tag{12}$$

2.4. Extending ASM3 Model

In this study, the above mentioned model which is a combination of ASM3 and settler models is improved by adding novel inhibitory models obtained from batch experiments with growth and decay of heterotrophic biomass processes to respond to changes in the heavy metals concentrations. The simulation of the ASM3 model is achieved under unsteady conditions. The model is simulated by modifying only two parameters: maximum growth rate and lysis rate, which vary depending on the change in heavy metal concentration as well as the composition of industrial waste water, are not considered in the ASM3 default values. All kinetic and stoichiometric parameters regarding the twelve processes are the default values, except the aerobic growth and decay processes of heterotrophic biomass which are already included from the experimental results with the presence of Cu and Cd [14].

According to linear regression models for copper and cadmium observed in batch experiments for heterotrophic process, the values of growth and lysis rate constants in the absence of copper and cadmium are found to be 4.5197 and 0.3122 d^{-1}, respectively; whereas, these values are calculated as 0.1338 d^{-1} and 0.0143 d^{-1}, respectively in the presence of 0.7 mgL^{-1} of Cd and 0.1192, 0.0179d^{-1}, respectively in the presence of 0.7 mgL^{-1} of Cu.

2.5. Designed Parameters for the Activated Sludge Process Plant

The design parameters related to the activated sludge plant were chosen according to the basic principles of wastewater treatment plant design [18] as shown in Table 1.

Table 1. Designed parameters for activated sludge process plant [19]

Design parameters	Symbol	Unit	Value
The influent average flow	Q_{in}	m^3 day^{-1}	1000
Average flow of recycle	Q_{rs}	m^3 day^{-1}	800
Volume of Aeration tank (m^3)	V_{at}	m^3	450
Volume of settling tank (m^3)	V_{set}	m^3	400
Height of the settling column	h_{set}	*m*	3.5
Oxygen mass transfer coefficient	*kla*	h^{-1}	4.5
Effluent average flow	Q_{eff}	m^3 day^{-1}	980
Waste sludge rate	Q_w	m^3	12
Waste sludge ratio	Q_w/Q_{in}	-	0.012
Recycle ratio	Q_{rs}/Q_{in}	-	0.80
Area of the settler	As	m^2	113
Length of start-up period	tp1	*h*	480
Length of conditioning period	tp2	*h*	480
Length of normal operation period	tb3	*h*	100

2.6. Effluent Requirements of Activated Sludge Plant

The main aim of the WWTP plant is to maintain sufficient concentrations of organics, nitrogen, and other pollutants. In order to avoid both infeasibility and failure in such plants, the effluent should be restricted by law. According to EU Commission Directives 1991 [20], on the effluent of wastewater treatment plants, the maximum concentrations in terms of COD, SS, and TN are given by:

COD_{max} = 125 mg/L

SS_{max} = 30 mg/L

TN_{max} = 20 mg/L

3. Results and Discussion

To represent the process, model ASM3 has been adopted with regard to activated sludge system to characterize the removal of organic and nitrogen pollutants, and a novel inhibitory kinetic model has been used to characterize the growth and lysis rate constants. Using MATLAB code, the activated sludge process has been modeled with respect to ASM3 coupled with novel inhibitory kinetic models and settler model.

During simulations the results shows the changes in the concentrations of heterotrophs with respect to time at the end of start-up period, conditioning period and operating period are given in the Figures 1 and 2 with or without heavy metals (cadmium and copper) having a concentration of 0.7 mgL^{-1}.

It is evident from this simulation that the presence of heavy metals (Cu, Cd) at concentration 0.7 mgL^{-1} in the biological system effects on growth of bacteria. In the case of cadmium, the decrease in heterotrophic bacteria concentration is 8.76 %, whereas 25.00 % for copper case.

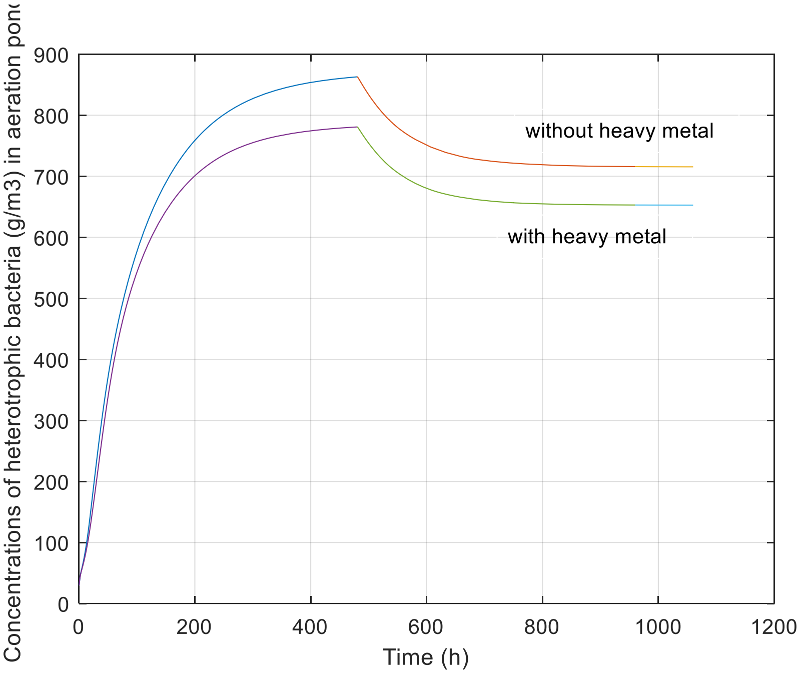

Figure 1. Changes in growth of heterotrophic bacteria in activated sludge system (with and without heavy metal Cd)

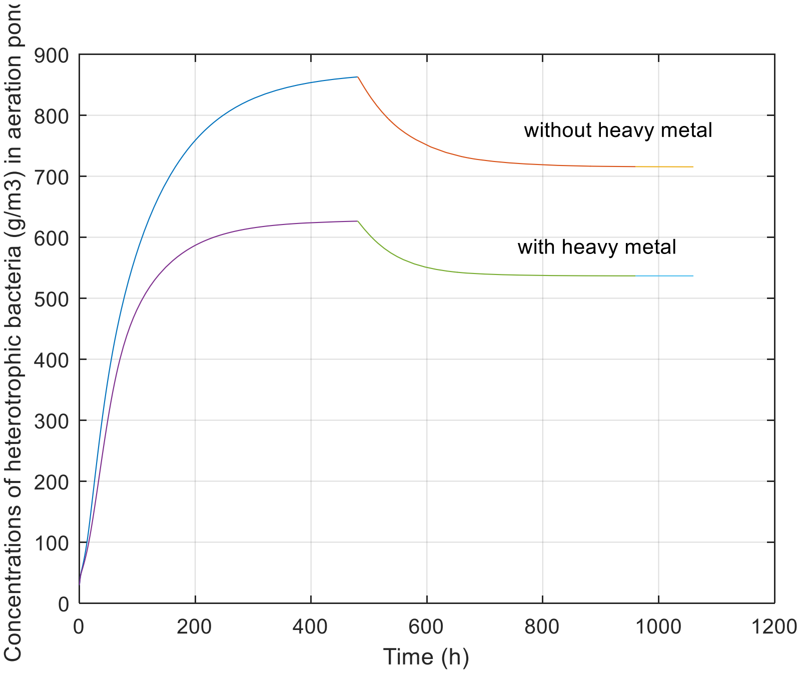

Figure 2. Changes in growth of heterotrophic bacteria in activated sludge system (with and without heavy metal Cu)

In the meantime, slight changes in COD (chemical oxygen demand), SS (total suspended solids), and TN (total nitrogen) have happened in final effluent. Total suspended solids and mixed liquor volatile suspended solids have decreased, in the same time, chemical oxygen demand and total nitrogen have increased as shown in Table 2 in the final effluent of the plant. MLVSS, COD, TSS, and TN are calculated according to the state variables included in the ASM3 using Equations 7 to 10.

Table 2. Results of simulation for effluent quality in a conventional system with heavy metals (cadmium, copper) and without heavy metals

Parameters	Initial	Normal operation period		
		No heavy	Cadmium (0.7 mgL^{-1})	Copper (0.7 mgL^{-1})
COD_{eff} (g/m^3)	260.1000	37.2243	37.2418	37.2700
TN_{eff} (g/m^3)	24.9070	20.7322	20.8705	21.1207
SS_{eff} (g/m^3)	125	7.7925	7.7858	7.7762
MLVSS (g/m^3) (Before settling tank)	102.0900	1928.5	1885.0	1797.2

The simulations of results of state variables of ASM3 in the aeration tank and final effluent of wastewater plant have shown that X_I, X_S, X_{STO}, and X_A are slightly increased by these heavy metals, while X_{SS} and X_H are decreased, in addition, no change in concentration of soluble compounds (S) as shown Table 3.

Table 3. Simulation results of state variables of ASM3 in output of aeration tank and final effluent

State variables	Initial (untreated)	AERATION TANK			Final effluent of wastewater plant (Effluent)		
		No heavy	Cadmium (0.7 mgL^{-1})	Copper (0.7 mgL^{-1})	No heavy	Cadmium (0.7 mgL^{-1})	Copper (0.7 mgL^{-1})
S_O (g/m^3)	0.00	3.3	3.3	3.2	3.3	3.3	3.2
S_I (g/m^3)	30.00	30	30	30	30	30	30
S_S (g/m^3)	100.00	0.2	0.3	0.3	0.2	0.3	0.3
S_{NH} (g/m^3)	16.00	0.4	0.4	0.4	0.4	0.4	0.4
S_{N_2} (g/m^3)	0.00	1	1	1	1	1	1
S_{NO} (g/m^3)	0.00	19.8	19.9	20.2	19.8	19.9	20.2
S_{HCO} (gmole/m^3)	5.00	2.5	2.5	2.5	2.5	2.5	2.5
X_I (g/m^3)	25.00	1546.1	1545	1556.5	4.4446	4.5120	4.6992
X_S (g/m^3)	75.00	58.7	59.1844	60.3328	0.1688	0.1728	0.1821
X_H (g/m^3)	30.00	715.5	652.7924	536.6389	2.0565	1.9062	1.6200
X_{STO} (g/m^3)	0.00	50.3	72.1771	83.4754	0.1447	0.2108	0.2520
X_A (g/m^3)	0.10	56.4	56.7180	57.1971	0.1622	0.1656	0.1727
X_{SS} (g/m^3)	125.00	2710.8	2666.2	2575.7	7.7925	7.7858	7.7762

4. Conclusion

The developed model ASM3 was extended to examine the influence heavy metals by novel inhibitory kinetic models upon the waste water treatment system performance. The inhibitory kinetic models are used for the values of growth and lysis rate constants achieved from the batch experimental results in the presence of heavy metals under aerobic growth of heterotrophic biomass process. The main contribution of this study is to improve ASM3 by combination with novel inhibitory kinetic models to assess the impact on the operation of an activated sludge wastewater treatment plant that receives the effluent of an industrial plant.

Using MATLAB code, the activated sludge process has been simulated with respect to ASM3 coupled with novel inhibitory kinetic models and settler mode. We can conclude from this simulation that the presence of heavy metals (Cu, Cd) at the concentration 0.7 mgL^{-1} in the biological system has negative effect on growth of heterotrophic bacteria. In the case of cadmium, the decrease in heterotrophic bacteria concentration is 8.76 %, whereas 25.00 % for copper case and consequently, on effluent quality [COD, TN, MLVSS, TSS and particulate compounds (X)]. However, all these parameters are acceptable and consistent with EU Commission Directives. Finally, one can say that ASM3 can predict and evaluate the operation of an activated sludge wastewater treatment plant that receives the effluent of an industrial plant

5. Conflicts of Interest

The authors declare no conflict of interest.

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