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Modeling and Performance Evaluation of a full scale Petrochemical Wastewater Treatment Process

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ABSTRACT: Evaluation and modeling of the wastewater treatment plants (WWTP) have to be based on the fact that the pollutant concentrations and flow rates change constantly. In addition, different approaches must used due to there are different processes in a WWTP. A Mexican petrochemical complex has a WWTP that processes wastewaters from several petrochemical plants, where the flow rates and pollutant concentrations change constantly. The actual WWTP has an equalization pond (EP) followed by an aerated lagoon (AL). The EP performance was evaluated by CFD tool and it was possible to evaluate the equalization pond performance. In the biological process, a more realistic dynamical model to evaluate the AL performance was developed and calibrated. The reactor was modeled as a plug flow reactor with high dispersion, due to there is no biological sludge recirculation. It was found that with an increase of 12.5% in the wastewater flow rate the Mexican regulation will not be satisfied The model improves modeling because considers different actual operational factors as lost of VOC and variations of temperature, influent COD and flow rate, which have tremendous impact on the petrochemical wastewater treatment plant performance.

Key words: CFD, Modeling, Petrochemical, Treatment, Wastewater

INTRODUCTION

La Cangrejera is one of the most important petrochemical complexes in Mexico and LatinAmerica, with a production of 500,000 ton/year of petrochemicals. The complex consists of 20 plants that produce a range of petrochemical products and feedstock. This complex produces, among others petrochemicals, ethane derivatives, low density polyethylenes and 100% of the aromatics of the country. Production processes generates nearly 8,000 m^3 of wastewater per day that are discharged to the petrochemical sewer system. Different effluents are produced due to the variety of processes and they must be treated in different ways. Some effluents require pH adjustment, in some of them separation of oils is applied and others are treated by wet oxidation to remove sulfide. Finally, the actual sewer system collects wastewater to form three different effluents. Then, all the effluents are combined in the equalization pond (EP) before reaching the biological treatment in the aerated lagoon (AL). The secondary treatment is an aerated lagoon with floating surface aerators, followed by a stabilization pond (SP), then the wastewater treated in the wastewater treatment plant (WWTP) is discharged into the river (see Fig. 1), complying with existing regulatory requirements. However, in the near future the capacity of different processes, and then their effluent flow rates, will be increased. Additionally, future environmental legislation changes will undoubtedly reduce pollutants concentration limits (SEMARNAT, 2008). In this sense, it is meaningful to know now, whether or not the WWTP will be able to deal with such varying conditions. Therefore, in order to predict its actual and future performance in different scenarios, it is vital to model current treatment processes. Proper modeling implies calibration and validation.

Unfortunately, there are few studies to evaluate the equalization systems in flow ponds by using CFD tool. In addition, most modeling studies related to this kind of biological treatment, have been performed on urban wastewater and activated sludge systems (Hulsbeek, *et al*. 2002, Gernaey et el. 2004, Koch *et al*. 2000). In few studies with aerated lagoons, quite simple modeling as has been performed because steady

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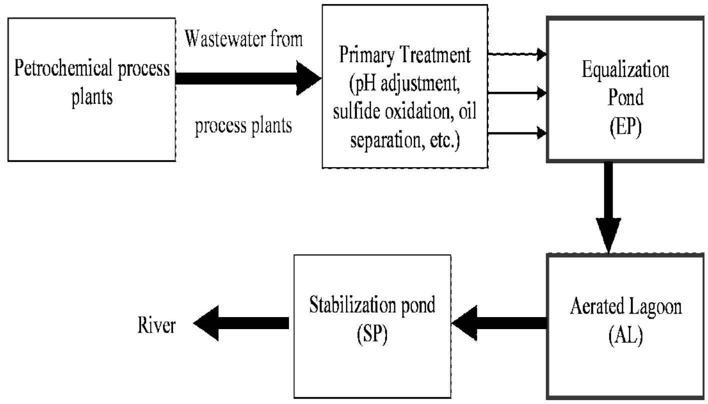

Fig. 1. Petrochemical wastewater treatment system

state conditions and first order reaction were applied (Nema, *et al*., 2005). Other studies are oriented to the hydraulics behavior inside the reactors, without considering a direct relation to the biological process (Morchain, *et al*. 2000 and Potier, *et al*. 2005).

In this work, the evaluation of the wastewater treatment was performed accounting for the equalization pond (EP), because the biological treatment performance depends on the good equalization. Its performance was evaluated using computational fluid dynamics (CFD, which is a powerful tool to obtain the hydraulics behavior of ponds (Persson, 2000, Salter *et al*., 2000, Abbas, *et al*., 2006, Alvarado, *et al*., 2012). The EP receives three influents from the petrochemical complex that must be mixed and equalized, before reaching the biological reactor. After the evaluation of the EP the biological treatment major dynamics, were modeled. The biological treatment was modeled using ASM1 kinetic equations and its performance was simulated to evaluate if it was possible to conform to future concentration limits. The non-steady state model proposed considers the dispersion in the reactor (hydraulics) due to the reactor sizes makes it has a non ideal plug flow reactor, and the rate flow and chemical oxygen demand (COD) fluctuation in the reactor influent, as for current operating conditions. The biodegradation kinetics of the ASM1 model were used (Henze, *et al*. 2000 and Orhon, *et al*., 2009), which is an important difference with respect to the first order model.

MATERIALS & METHODS

The equalization pond mesh was built with the same dimensions of the actual pond as shown in figure 2.The inlet (three pipes, from different processes) was defined as velocity inlet and the velocity magnitude of the wastewater was 0.08 m/s. A pulse of nonreactive tracer of 100 s, with the same properties of the wastewater, was introduced into the fluid entering in the pond and the concentration-time of tracer leaving the equalization pond was recorded to evaluate the residence time (Levenspiel, 1999). Fluent version 6.3 has been used to perform the CFD simulations at laminar flow conditions ($N_{Re} < 500$) and unsteady state fluid flow (species transport); a pressure-based segregated algorithm solver has been used, where the governing equations are solved sequentially. For the pressure–velocity coupling a non linear procedure called semi-implicit pressure-linked equation (SIMPLE) algorithm was used, for pressure discretization the standard scheme was selected, and for the momentum discretization, first-order was used for the initial solution and second order discretization was used for the final solution.

Experimental data were obtained from the actual aerated lagoon of the petrochemical complex. The volume is about 49,545 m^3 and it has 20 surface aerators located along the lagoon to transfer oxygen. The substrate removed (Ss evaluated as COD), biomass concentration (VSS) and the different parameters were evaluated based on standard methods (Clesceri, *et al*., 1998) and measured at the reactor influent and effluent. Considering that nutrients content (N and P) in petrochemical wastewaters is very low, only carbon degradation was taken into account, then the model was simplified (Costa, *et al*. 2009 and Henze, *et al*. 2000). In fact, for the actual process, they are added into the influent to avoid a nutrient deficiency. The applied model considers a non-steady state plug flow reactor due to the daily flow rate and COD fluctuations in the influent, which is inherent to the petrochemical complex operation. High longitudinal dispersion in the reactor is considered as well because of the mixing effect caused by the surface aerators distributed along the aerated lagoon. The effect of the dispersion was introduced in the model as the dispersion number ($Nd = D/uL$). Nd values from 0.1 to 4 have been reported in other studies (Nema, *et al.,* 2005). In this

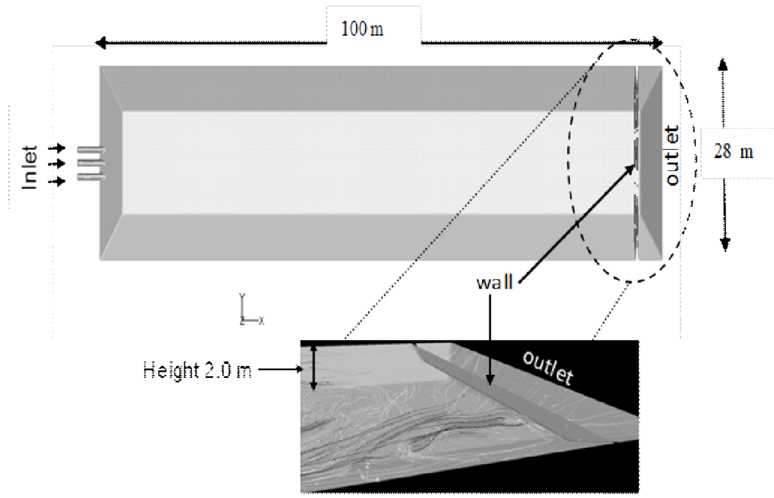

Fig. 2. Equalization pond of the CPQ la Cangrejera

work, in the aerated lagoon a dispersion number of 2.6 were used to calibrate the model. The model, also ponders the effect of substrate removal due to the VOCs stripped to the atmosphere during the process, as shown in the last term of the equation 1 (Martinez *et al*. 2005). The model and their most widely used boundary conditions (Dancwerts, 1953) are shown in equations 1 to 12. The kinetic parameters used to calibrate the model, in order to fit the experimental data, were obtained from other researches (Henze, *et al*. 2000 and Orhon, *et al.*, 2009).

Soluble (COD) substrate (S_S):

$$th \cdot \frac{\partial S_S}{\partial t} = \tag{1}$$

$$\frac{D}{uL} \cdot \frac{\partial^2 S_S}{\partial z^2} - \frac{\partial S_S}{\partial z} - th \cdot \left(\frac{\mu_H}{Y_H} \cdot \left(\frac{S_S}{K_S + S_S}\right)\right.$$

$$- k_h \cdot \left(\frac{X_S}{K_X X_{BH} + X_S}\right) \cdot \left(\frac{S_O}{K_{OH} + S_O}\right)$$

$$\cdot \left(\frac{S_O}{K_{OH} + S_O}\right) X_{BH}$$

$$\left. X_{BH} + k_{ev} \cdot S_S\right)$$

$$S_S - \frac{D}{uL} \bullet \frac{\partial S_S}{\partial z} - S_{Si} = 0 \quad \text{at} \quad z = 0 \tag{2}$$

$$\frac{\partial S_S}{\partial z} = 0 \quad \text{at} \quad z = 1 \tag{3}$$

Heterotrophic biomass (X_{BH}):

$$th \cdot \frac{\partial X_{BH}}{\partial t} = \frac{D}{uL} \cdot \frac{\partial^2 X_{BH}}{\partial z^2} - \frac{\partial X_{BH}}{\partial z} - th \cdot \left(\mu_H \cdot \left(\frac{S_S}{K_S + S_S}\right) \cdot \left(\frac{S_O}{K_{OH} + S_O}\right) \cdot X_{BH} - b_H \cdot X_{BH}\right) \tag{4}$$

$$X_{BH} = 0 \quad \text{at} \quad z = 0 \tag{5}$$

$$\frac{\partial X_{BH}}{\partial z} = 0 \quad \text{at} \quad z = 1 \tag{6}$$

Slowly biodegrad

$$th \cdot \frac{\partial X_S}{\partial t} = \frac{D}{uL} \cdot \frac{\partial^2 X_S}{\partial z^2} - \frac{\partial X_S}{\partial z} + th \cdot ([1 - f_p] \cdot b_H - k_h \cdot \left(\frac{X_S}{K_X X_{BH} + X_S}\right) \cdot \left(\frac{S_O}{K_{OH} + S_O}\right) \cdot X_{BH}) \tag{7}$$

$$\frac{\partial X_S}{\partial z} = 0 \quad \text{at} \quad z = 0 \tag{8}$$

$$X_S - \frac{D}{uL} \bullet \frac{\partial X_S}{\partial z} - X_{Si} = 0 \quad \text{at} \quad z = 1 \tag{9}$$

Dissolved oxygen (S_O)

$$th \cdot \frac{\partial S_O}{\partial t} = \frac{D}{uL} \cdot \frac{\partial^2 S_O}{\partial z^2} - \frac{\partial S_O}{\partial z}$$
$$- th \cdot (kla \cdot [S_{Osat} - S_O] + \frac{Y_H - 1}{Y_H} \cdot \mu_H$$
$$\cdot \left(\frac{S_S}{S_S + K_S} \right) \cdot \left(\frac{S_O}{K_{OH} + S_O} \right) \cdot X_{BH}) \qquad (10)$$

$$S_O = 0 \qquad \text{at } z = 0 \qquad (11)$$

$$\frac{\partial S_O}{\partial z} = 0 \qquad \text{at } z = 1 \qquad (12)$$

Where:
D = dispersion coefficient (m^2/s)
u = flow velocity (m/s)
L = reactor length (m)
x = lagoon length (m)
z = x/L (dimensionless)
t =time (day)
V =49545 (reactor volume m^3)
th= hydraulic time (V/Q) (day)
b_H = 0.25 (decay coefficient for heterotrophic biomass/ day)
f_p = 0.08 (fraction of biomass leading to particulate products)
k_h =1.0 (hydrolysis rate constant/day)
K_{OH} = 0.2 (oxygen half-saturation coefficient for heterotrophic biomass , mg/L)
K_S = 170 (half-saturation coefficient for readily biodegradable substrate, mg/L))
K_X =0.017 (half-saturation coefficient for particulate biodegradable substrate, mg/L)
Y_H =growth yield of heterotrophic biomass
X_{BH} = active heterotrophic biomass (mg/L)
X_S= slowly biodegradable (COD) substrate (mg/L)
S_S = readily biodegradable (COD) substrate (mg/L)
S_O =dissolved oxygen (mg/L)
X_{Si} =influent slowly biodegradable substrate (mg/L)
T_W =lagoon temperature (°C)
μ_H = specific growth rate for heterotrophic biomass/d
kla = mass transfer coefficient/d
k_{ev} = empirical mass transfer coefficient of VOC/d

Due to the temperature (T_W) changes along lagoon length, as presented in Fig. 3, its effect was introduced in parameters as μ_H , kla and k_{ev} as it is shown in equations 13 to 16.

$$T_W = 12.564*x^2 - 25.819*x + 40.7213 \qquad (13)$$

$$\mu_H = 2.74*\exp(-(((Tw-25.75)/30)^2)) \qquad (14)$$

$$kla = kla_{20}*1.02^{(Tw-20)} \qquad (15)$$

$$k_{ev} = 0.01*Tw - 0.15 \qquad (16)$$

Flow rate (Q) and (COD) substrate (S_{Si}) fluctuations in the influent were modeled as sinusoidal functions to fit the experimental data. The variations of both parameters were described as shown in equations 17 and 18.

$$Q = 1600*\sin(((2*pi)/-200)*(t-10))+8000 \qquad (17)$$

$$S_{Si} = 110*\sin(((2*pi)/-450)*(t-2))+550 \qquad (18)$$

Where:
Q =influent flow rate (m^3/day)
S_{Si} = influent readily biodegradable (COD) substrate (mg/L).

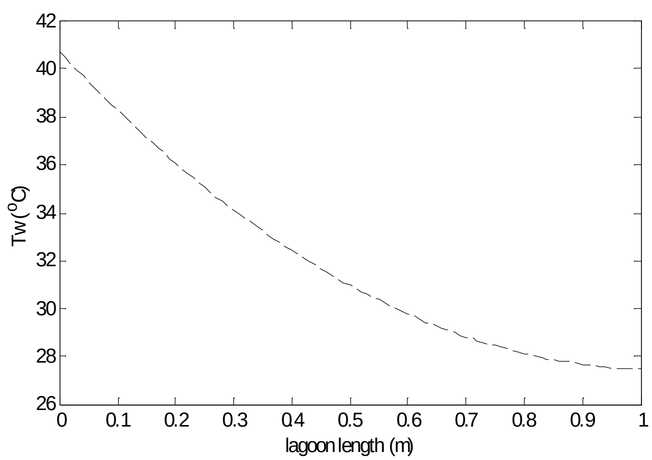

Fig. 3. Variation of the temperature as a function of the lagoon length

RESULTS & DISCUSSION

Fig. 4, shows the path lines colored by velocity magnitude (m/s) in the equalization pond. As can be seen, there are channeling of the fluid and parallel paths inside the pond. There is an important internal fast flow (colored in white), which reaches the outlet before other fluid elements. On the other hand, strong internal recirculation and stagnant backwaters can be observed (path lines colored in black) with low fluid velocity and poor mixing. The faster wastewater stream carries the pollutants without mixing, which produces very poor equalization performance. A tracer pulse injection was simulated by CFD, at the inlet of the equalization pond to evaluate its performance. The mass fraction tracer profile as a function of the outlet position was obtained, after 4.5h of the tracer pulse injection, as shown in Fig. 5. It is noticeable, that it is not uniformly distributed over the whole outlet surface, because the channeling causes that the tracer leaves the pond mainly through the central part of the outlet. In fact, the tracer concentration near both sides of the outlet is zero, because in these zones, the tracer has not reached the outlet yet. The central fluid with higher velocity and channeling in the pond, explains the peaks (I, II and III) shown in the mass fraction tracer at the outlet as a function of time in Fig. 6. The high tracer concentrations at the outlet shown in the peaks, explains why the influent wastewater of the aerated lagoon, following process (Fig. 1), presents important variations and why several times enters at high COD concentrations (> 65O mg/L), as shown in Fig. 7, showing the poor equalization performance of the actual full scale pond. The slower fluid motion and stagnant backwater regions explain the long tail of tracer concentration shown in Fig. 6. The mean residence time estimated with the results of curve 5 was 13.9 h, while the calculated with the ratio of the pond volume to the inlet flow rate was 12.8 h. The difference is about 1 h, which is due to the different effects mentioned above. The actual behavior of the pond is as a plug flow vessel with high dispersion and its behavior is far from an efficient equalization pond. Therefore, it is necessary to introduce mixers in the lagoon to improve its equalization function and by doing so; variations in substrate concentration, as the ones shown Fig. 7, will be reduced, which would have lower negative impact on biological process carried out in the aerated lagoon. A more stable EP outlet (influent flow rate to the aerated lagoon), will positively impact the biological treatment, showing that the CFD is an important tool to evaluate the hydraulics of the equalization pond. As shown by the analysis carried out *in situ*, important fluctuations in the substrate (COD) concentration are presented in the aerated lagoon influent, due to the inherent operation conditions in the

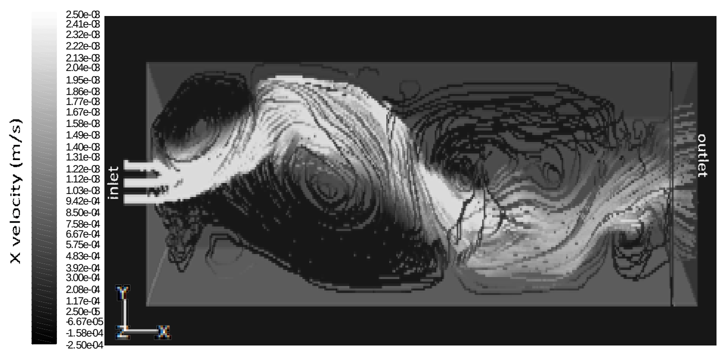

Fig. 4. Path lines colored by velocity magnitude (m/s) in the equalization pond

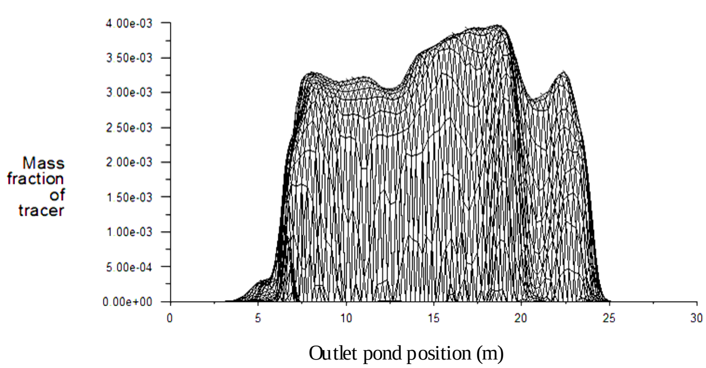

Fig. 5. Mass fraction tracer as a function of the outlet position in the equalization lagoon after 4.5h of the application of the tracer pulse

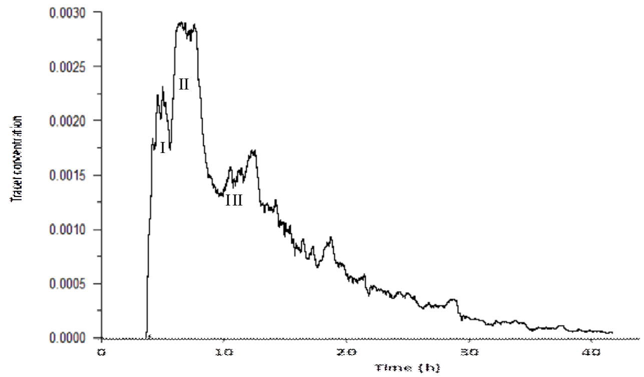

Fig. 6. Tracer concentration as a function of time at the pond outlet

petrochemical process. Those variations are not reduced by the deficient performance of the equalization pond, as it was demonstrated before. In addition, in the same period of time, important changes in the influent flow rate also are presented due to the process operation, in the petrochemical plants. Both effects, influent COD and flow rate fluctuations, were considered (equations 17 and 18) to model the biological dynamics in the aerated lagoon (AL). Fig. 7 shows the actual experimental data and model results of: (a) influent flow rate and (b) influent and effluent substrate fluctuations (S_S) in the AL. As seen equation 17 and 18, describe in good agreement the actual behavior in the plant for both parameters. There are important variations of the measured flow rate (Fig. 7a) and substrate concentration (Fig. 7b) in the influent to the biological treatment. Due to the deficient performance of the equalization pond, the Ss concentration after equalization reached values higher than 850 mg/L (lagoon aerated inlet in Fig. 7b). However, if the performance of the pond is improved with mixers, the maximum of 650 mg/L could be reached at the pond exit, with a mean value of 530 mg/L, improving also the biological treatment performance. As can be seen, in spite of the fluctuations, the model fits adequately the experimental data and describes the behavior of the aerated lagoon exit (dashed curve in Fig. 7b). The S_S at the exit of the biological treatment is lower than 230 mg/L. The Xs in the treated effluent from the aerated lagoon, reaches a concentration lower than 5.0 mg/L most of the time, and only from the 130d to 160d, the concentrations was higher than 10 mg/L, which does not have an important impact in the total concentration in the treated effluent. As can be seen in Fig. 1, the effluent from AL goes to the stabilization pond, where the COD is reduced in an additional 30% therefore; at the current conditions the wastewater treated in the petrochemical wastewater treatment plant complies with the Mexican environmental regulations. In addition, the model describes the experimental variations in biomass, as seen in Fig. 8a. The 20 surface aerators maintain the dissolved oxygen concentration in the lagoon above 2 mg/L, not limiting carbon degradation, as seen in Fig. 8b. Based on the validated model, two future possible scenarios were simulated to evaluate if the S_S in the aerated lagoon could reach values lower than 230 mg/L, which would guarantee compliance to environmental regulation. The first simulation was carried out supposing an increase in the flow rate (Q) at constant S_{Si}. In the second one, the S_{Si} was increased maintaining the flow rate constant. The results obtained are presented as contours along the lagoon, which are presented in Figs. 9 and 10, respectively. Fig. 9 illustrates the contours of S_S for current conditions (a) to compare them with the simulation if the plant was operated increasing the Q by 12.5%. As can be seen, the model describes that in the first part of the lagoon the S_S is high, along the 360 d, but decreases along the lagoon length in all cases, showing the plug flow behavior of the biological reactor. At the current conditions (Fig. 9a), the S_S at the effluent does not reach values higher than 230 mg/L at any time. However, increasing Q by 12.5% the S_S lagoon effluent reaches values higher than 230 mg/L from 150 d to 325 d. Therefore, if the Q in the petrochemical complex is increased by more than 12.5%, then the Mexican regulation will not be satisfied. The stabilization pond (SP) must also be evaluated under different operation conditions and study its impact on the greenhouse gas generation. On the other hand, when the S_{Si} is increased by 75%, the effluents S_S will reach values lower than 230 mg/L, as shown in Fig. 10a. However, in this case it would be necessary to increase the aeration 65% to maintain oxygen dissolved in concentrations greater than 2.0 mg/L (Fig. 10b). Moreover, contours in Fig. 10 show lower S_S values than in current conditions, due to increasing biomass (almost doubled), as shown in Fig. 9a (dashed curve), but higher X_{BH} will affect the stabilization pond performance, discharging a final petrochemical effluent that could not comply with future environmental regulations. The model improves modeling because considers different actual operational factors as lost of VOC and variations of

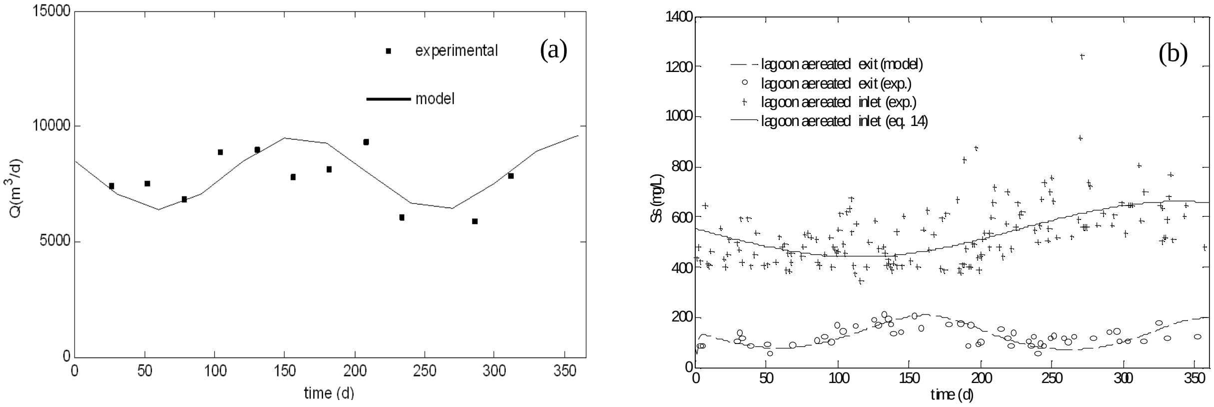

Fig. 7. (a) Flow rate (Q) and (b) substrate (COD) fluctuations (S_S), as a function of time

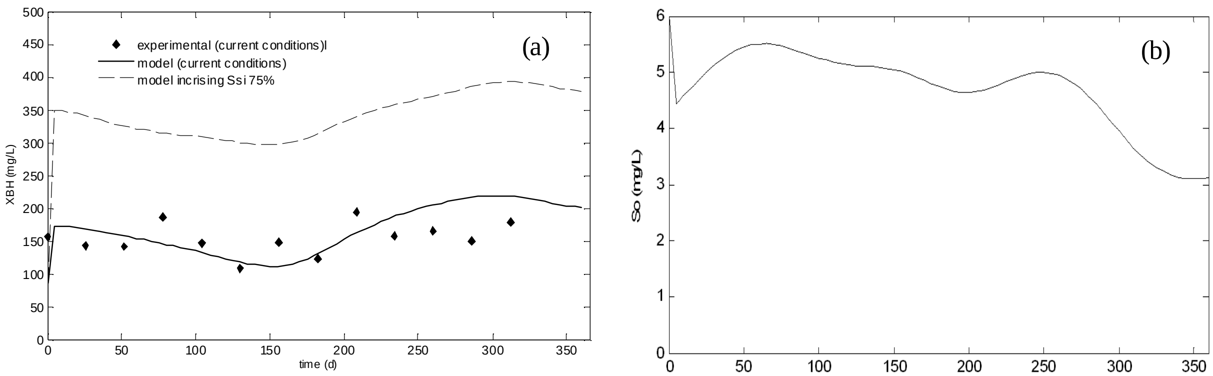

Fig. 8. Variation of (a) X_{BH} and (b) dissolved oxygen (S_O) in the lagoon effluent, as a function of time.

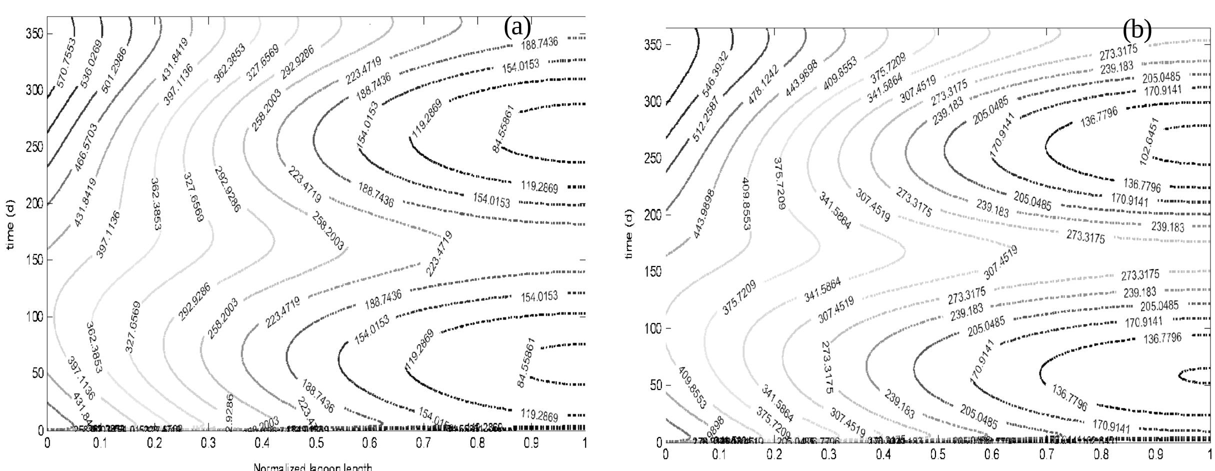

Fig. 9. Contours of S_S along the aerated lagoon length during a year (365d): (a) current operation and (b) increasing Q in 12.5%.

temperature, influent COD and flow rate, which have tremendous impact on the petrochemical wastewater treatment plant performance. In addition, due to it is not an activated sludge treatment, variations in time and reactor position are evaluated adequately by the model proposed.

CONCLUSIONS

CFD simulation was useful to obtain better insight of the flow distribution in the equalization pond and showed its deficient performance. Based on this, it is necessary to introduce mixers in the pond in order to improve the equalization function and then the biological

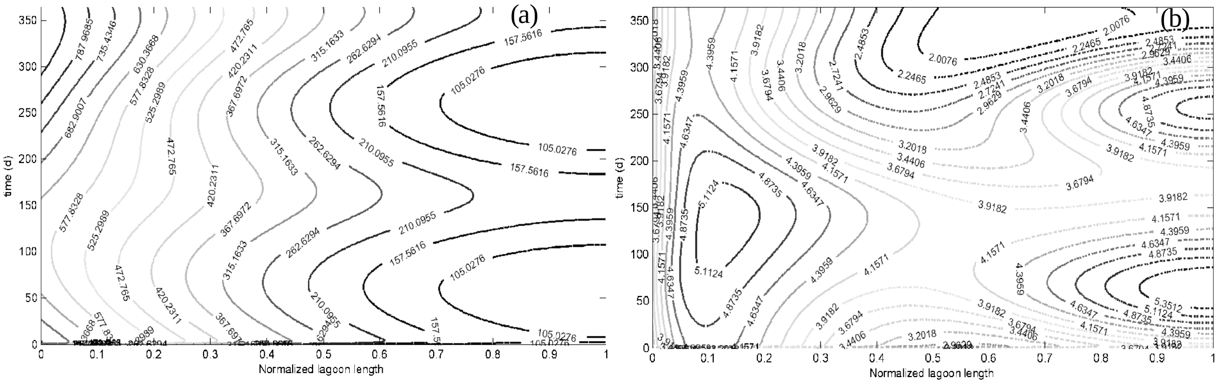

Fig. 10. Contours of (a) Ss and (b) S_O along the aerated lagoon length during an operation of 365 d, increasing the influent substrate concentration (S_{Si}) in 75% and aeration in 50%

treatment. The model applied to the biological treatment was calibrated and it was possible to evaluate the lagoon performance at full scale in non-steady state under different conditions. The obtained model also enables WWTP tuning with the aim of complying with future environmental regulations. Fluctuations of influent concentration were modeled and its adverse influence on biological treatment was demonstrated, so that the importance of an integral research of the WWTP is established.

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