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ORIGINAL PAPER

Biodegradation of wastewater pollutants by activated sludge encapsulated inside calcium-alginate beads in a tubular packed bed reactor

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Abstract The wastewater treatment plants produce large quantities of biomass (sludge) that require about one-third of the total inversion and operation plant costs for their treatment. By the microorganisms immobilization it is possible to handle high cell concentration in the reactor, increasing its efficiency, reducing the loss of biomass and the wash out is avoided. Moreover, there is no cell growth then the sludge production is reduced. In this study, the COD removal and VSS variation were modeled in a tubular reactor with activated sludge immobilized in Ca-alginate. Moreover, two aspects that are commonly not considered in the performance of the actual reactors of this kind were introduced; the performance in non-steady state and the dispersion effect. The model was calibrated with an actual wastewater taken out from a Mexican wastewater treatment plant. The results of the performance of the tubular bioreactor at different scenarios (i.e., different residence time and VSS in the reactor) are presented. With longer residence times and higher VSS concentration in the Ca-alginate beads in the tubular bioreactor it is possible to increase the time operation of the bioreactor and to treat higher volumes of wastewater. During the process, the sludge generation was drastically reduced and it is possible to remove nitrogen form the wastewater making this process more attractive.

Keywords Biodegradation · Immobilization · Modeling · Tubular reactor · Wastewater · Activated sludge

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Introduction

The wastewater treatment plants produce large quantities of biomass (biological sludge), which must be separated from the treated wastewater in the secondary clarifier. The biological sludge must be treated and managed to comply with the Mexican environmental rules. There are different technologies applicable to treat the sludge from wastewaters, i.e., aerobic and anaerobic digestion, centrifugation, among others (Ramalho 1999). However, these methods have some drawbacks because they consume about one-third of the inversion and operation total costs of the wastewater treatment plant. The encapsulating cells technologies have been applied for different purposes: immobilization of mammal cells (Uludag et al. 2000), for the production of hydrogen (Wu et al. 2003) and compounds commercially used in food industries (Kawaguti et al. 2006). Other studies with immobilized cells have been developed

to remove malodorous gases (Park et al. 2002; Chung et al. 1997; Cha et al. 2001), and for wastewater studies have been applied to remove pollutants as phenol (Bandhyopadhyay et al. 2001) and hexavalent chromium (Humphries et al. 2005). There are relatively less applications in wastewater treatment where normally involves the immobilization of mixed-culture systems (Kawaguti et al. 2006). Therefore, there is necessary further research to obtain successful commercial-scale processes. During the immobilization it is possible to handle high cell concentration in the reactor, increasing its efficiency, the loss of biomass is reduced avoiding the wash out and the stability of the immobilized cells is increased (Park et al. 2002). Moreover, there is no cell growth, and then the sludge production is reduced (Chena et al. 2002; Adly et al. 2001). There are different immobilization methods as carrier-bonding, cross-linking, and encapsulation and the materials for the immobilization used can be natural or synthetic polymers. One of the most common materials is the alginate (Park et al. 2002) and the Calcium has been used as a gelation agent, though Ba and Sr have been used as gelation agents (Sakurai and Sakakibara 1999). To reduce the sludge produce during the wastewater treatment process, in this work is modeled in non-steady state the COD removal in a tubular reactor with encapsulated activated sludge in calcium-alginate. Moreover, in the model is introduced the dispersion effect in the reactor that is commonly not considered in the performance of the actual reactors, and the model was calibrated with an actual mixture of urban and industrial wastewater taken out from a Mexican wastewater treatment plant.

Materials and methods

Bead preparation

The activated sludge was taken out from the aerated reactor of the wastewater treatment plant, washed with saline solution two times and separated by decantation. The cell concentration (VSS) in the sludge blanket (cell suspension) was measured (Clesceri et al. 1998). The cell suspension, of known cell concentration, and the Na-alginate were mixed to obtain a suspension with cell concentration (VSS) of 6,300 mg/l and Na-Alginate of 2%. This mixture was injected into the $CaCl_2$ solution (5%) with a bead make-up apparatus to obtain Ca-alginate spheres with a VSS mean concentration of 6.3 g/l inside and a mean diameter of 5.0 mm. The gelation conditions for the immobilization were 12 h at 4°C.

Tubular reactor

The experiments were performed with an actual wastewater sampled from the exit of the primary settler of a wastewater treatment Mexican plant. This wastewater is a mixture of domestic and industrial wastewater. The tubular packed bed reactor of 2.0 l of total capacity and volume operation of 1.3 l was filled with the Ca-alginate-activated sludge spheres (Fig. 1) and it was operated in the up-flow mode. The reactor was aerated by an air injection in the bottom during the process. Samples were taken out from each sampling port of the reactor at different heights ($z = 0.55, 0.7, 0.85$; port A, B, C, respectively) and at the effluent ($z = 1$), then the chemical oxygen demand (COD), total organic carbon (TOC), nitrogen and phosphorous were measured in each sampled (Clesceri et al. 1998).

Model

The model applied to describe the COD (S) removal in the packed reactor with the Ca-alginate spheres with the immobilized activated sludge cells in non-steady state, is shown in the Eq. 1. As seen, the dispersion effect, Monod kinetic was introduced in the equation (Dochain and Vanrolleghem 2001)

$$th\,\frac{\partial S}{\partial t} = \frac{D}{uL}\cdot\frac{\partial^2 S}{\partial z^2} - \frac{\partial S}{\partial z} + th\cdot\left(\frac{1-\varepsilon}{\varepsilon}\right)\cdot\frac{1}{Ys}\cdot\frac{\mu_{\max}\,XS}{K_s + S}. \tag{1}$$

The most largely used boundary conditions are (Dancwerts 1953):

$$S - \frac{D}{uL}\cdot\frac{\partial S}{\partial z} - S_o = 0 \quad \text{at } z = 0 \tag{2}$$

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

Due to there is no net cell growth (Ibrahim et al. 2001), the volatile suspended solids (VSS) concentration (X) as function of the reactor length (z) was estimated and is described by Eq. 4.

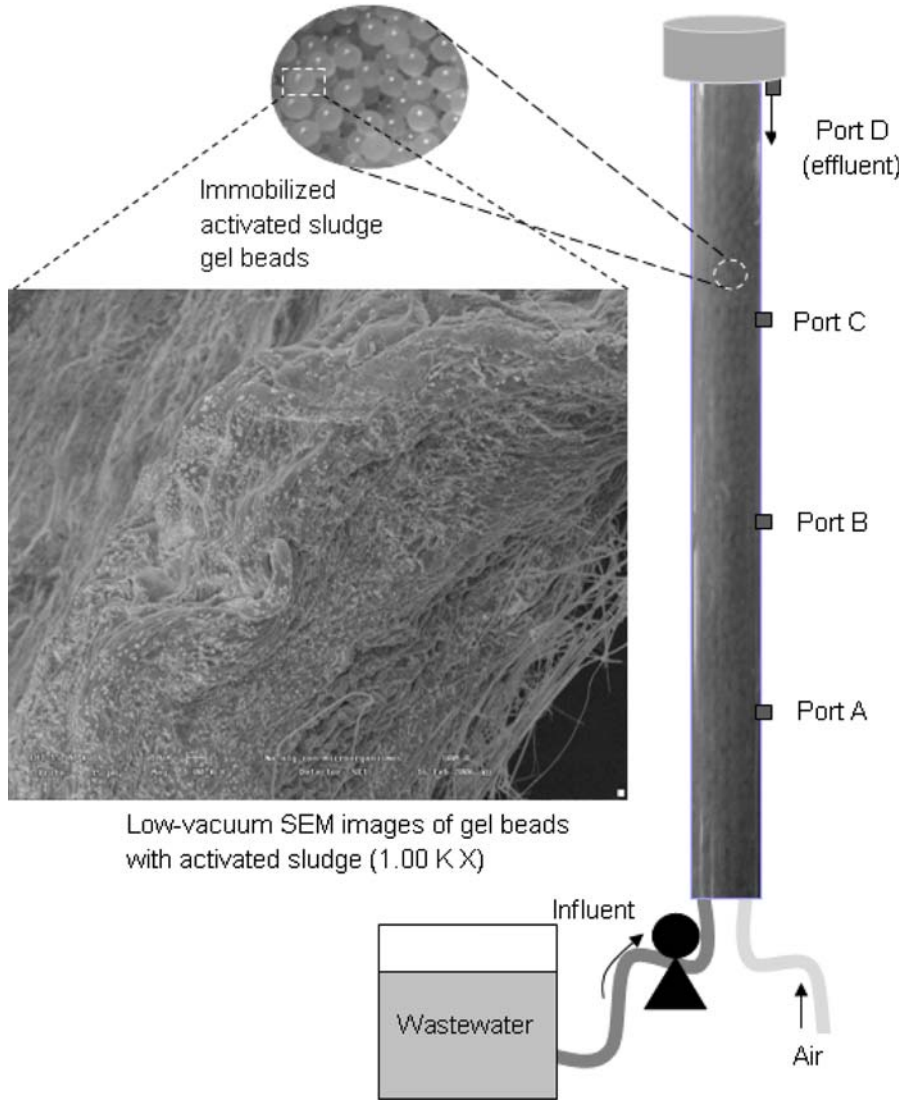

Fig. 1 Tubular packed bed reactor filled with the Ca-alginate-activated sludge spheres

$$\frac{\partial X}{\partial t} = -bX. \quad (4)$$

Where S = reactor COD (mg/l), S_o = influent COD (mg/l) = 550 mg/l, ε = void fraction, x = reactor height (m), L = reactor length (m), th = hydraulic residence time (h), z = x/L (dimensionless).

Biokinetic parameters used (Ramalho 1995; Bailey and Illis 1986): μ_{max} = specific growth rate (h^{-1}) = 0.15 h^{-1}, Ks = substrate saturation coefficient (mg/l) = 122 mg/l, b = death coefficient = 0.001 (h^{-1}), Ys = yield coefficient (mg biomass/mg substrate, dimensionless) = 0.3.

Dispersion tests

The dispersion in the reactor, experiments were performed (Levenspiel 1999), to obtain the exit age distribution function (**E**) as a function of *t/th*. Based on these results, the dispersion number (Nd) was calculated.

$$Nd = \frac{D}{uL}$$

Where D = dispersion coefficient (m^2/s), u = flow velocity (m/s), L = reactor length (m), th = hydraulic time, t = time.

During the tests, the reactor was filled with the spheres of Ca-alginate and tap water was used. A pulse input of a no reactive tracer (KCl) was instantaneously introduced into the liquid entering (influent) into the reactor and recorded the concentrations of the tracer in the exit liquid leaving the reactor (effluent), with a conductivity meter.

Results and discussion

The exit age distribution function (**E**) as a function of *t/th* obtained from the dispersion tests is shown in Fig. 2.

It was considered the tubular reactor was a closed vessel and a $Nd = 0.1$ was obtained, which means that the reactor has a high dispersion because $Nd > 0.01$ (Levenspiel 1999). The high dispersion is due to the air flow injection that was considered in the model because affects the performance of the reactor. In addition, mean residence time in the reactor of 45.3 min, was obtained.

Figure 3 shows the experimental COD concentration data (points)and the COD concentration obtained with the model (lines) as a function of the time, at different reactor heights (ports) with a residence time in the reactor of 0.75 h.

The experimental results and the model show that the COD trends to increase as the treatment proceeds; this is because there was a reduction in the microorganisms activity, supported for the reduction in the oxygen uptake rate (OUR), which is reduced from 0.536 mg l^{-1} min^{-1}, at the beginning of the test (time = 0 h) to 0.146 mg l^{-1} min^{-1} at 72 h of time process, as it is shown in Fig. 4.

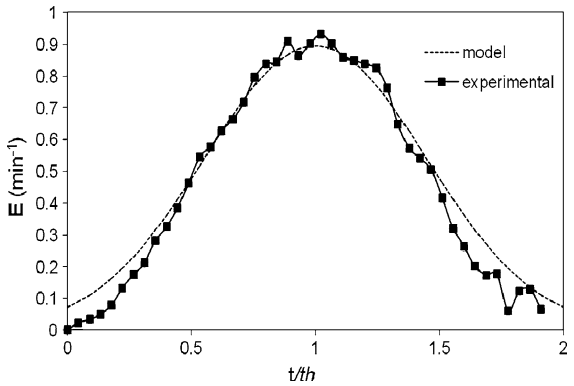

Fig. 2 Exit age distribution in the tubular bioreactor at a residence time of 45 min

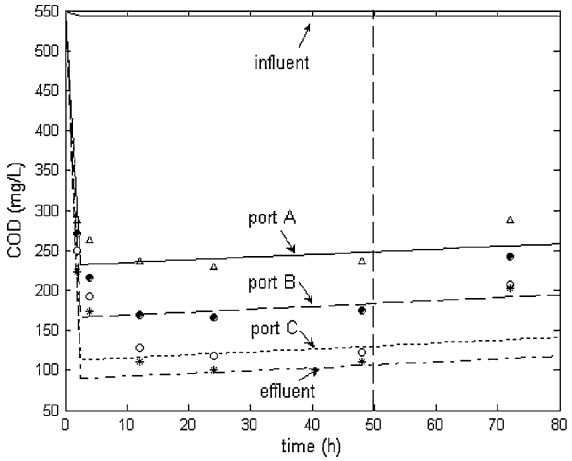

Fig. 3 Experimental COD (*dots*) and model COD (*lines*) variation as a function of the time at different reactor heights (*ports*) with $th = 0.75$ h

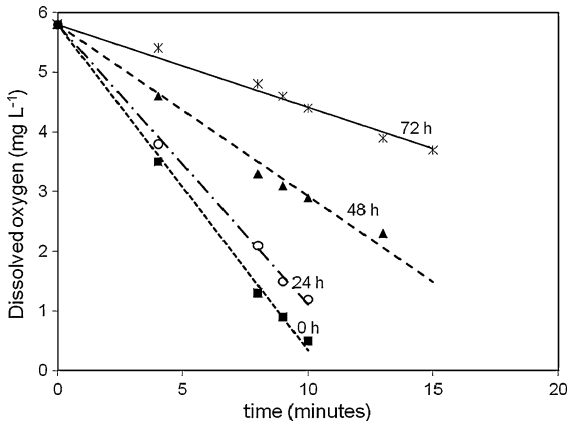

Fig. 4 Oxygen variation as function of rime at different process times to evaluate the oxygen uptake rate (OUR)

In addition, as shown, the model describes adequately well (95% of confidence) the experimental results until 50 h of the process. However, after 50 h the experimental data show an important deviation from the model. This deviation is explained because due to the agitation caused by the injection of air at the bottom of the reactor, caused that the spheres broke up and part of them were partially damaged. Perhaps the gelation conditions produced a low mechanical strength of the spheres, causing the loose of Ca-alginate-sludge activated tiny parts into the liquid, increasing the total COD of the sample. As is well known, the reported gelation conditions for the immobilization of cells using alginate are very

different; the gelation temperature range goes from 0°C to a room temperature and the gelation time varies from 10 min to 24 h (Sakurai et al. 1999). In our case, gelation was performed during 12 h at a temperature of 4°C. Based on the results, the gelation period should be increased or the temperature changed to avoid the erosion of the calcium-alginate beads. Other alternative to increase the mechanical strength of the spheres could be use Sr_2, because both, the chemical strength and the mechanical strength of Sr-alginate are known to be superior to those of Ca-alginate (Tanaka and Irie 1988; Sakurai et al. 1999).

Figure 5, shows the COD variation as a function of the time and distance (ports) in the reactor. As seen, the model shows that as the time of the process increase the COD in all the ports increase, also in the effluent. It is due to the activity of the microorganism decrease over the time as is described by Eq. 4 and supported by the reduction in the OUR, as before was discussed. Based on the model, simulations related to the SSV were performed to evaluate their behavior at different scenarios.

Figure 6 shows that the concentration of active microorganism (VSS) decreases as a function of time. Moreover, as the residence time in the reactor (*th*) increases, the death rate decreases. On the one hand, at a the residence time of 1.5 h the VSS concentrations decreased from 6,300 mg/l to about 4,500 mg/l, on the other, at 0.75 h the VSS reached <3,400 mg/l. This produce that the VSS last longer active at higher

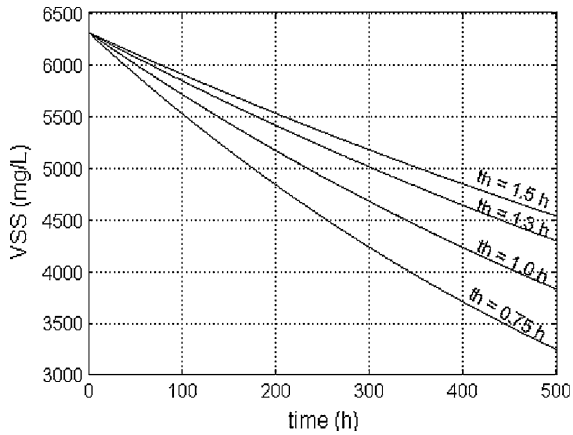

Fig. 6 Variation of the active VSS concentration as a function of time for different residence times in the reactor

th as shown in the same figure. At the same time, the increase in the residence time causes that the COD in the effluent reaches lower values than at low residence times.

The Fig. 7 shows simulations related to the COD in the effluent at different residences times and SSV (6,300 mg/l) to obtain a maximum COD effluent concentration of 20 mg/l. As shown, with a residence times of 0.75 h or 1.0 h it would not be possible to reach 20 mg/l concentration in the effluent. Conversely, when the residence time in the reactor is 1.3 h a COD concentration $\leq$20 mg/l would be reached during 220 h continuous operation of the reactor, but after this time the effluent COD would be

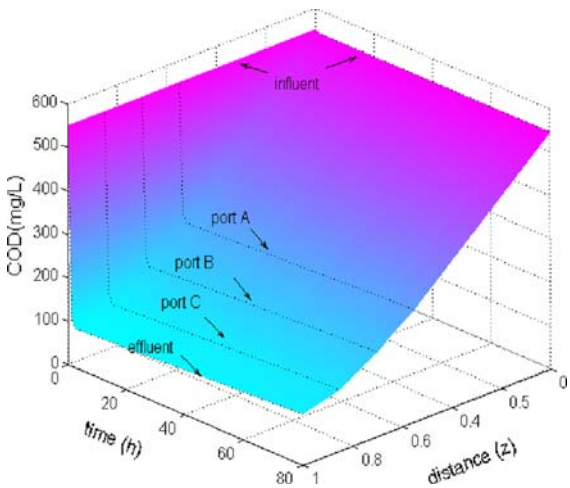

Fig. 5 COD variation as a function of the time and distance (*ports*) in the reactor at $th = 0.75$ h

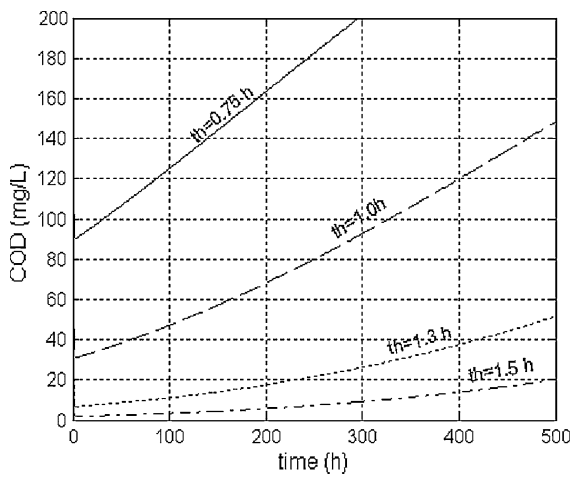

Fig. 7 COD variation as a function of time at 6,300 mg/l of VSS concentration at different residence times in the reactor

above de limit. Equally, if the residence time in the reactor were 1.5 h, the reactor could be in continuous operation during about 500 h. It means that at a residence time of 1.5 h and 6,300 mg/l of SSV, it could be possible to treat about twice volume of wastewater of that reactor of 1.3 h of residence time. Simulations based on the calibrated model were carried out to evaluate the effect of the increase of the VSS concentration in the Ca-alginate beads.

Figure 8, shows the results if the VSS concentration in the Ca-alginate beads with 6,300 and 8,000 mg/l. Clearly, the increase in the biomass produces a higher COD removal. However, in both cases, 6,300 and 8,000 mg/l of SSV and at a residence time of 0.75 h, it is not possible to reach a COD concentration <20 mg/l. In contrast, the reactor performance at $th = 1.3$ h and 8,000 mg/l of VSSs similar to the reactor at $th = 1.5$ h and 6,300 mg/l. In addition, it can be seen that at a $th = 1.5$ h and 8,000 mg/l, the time operation can be increased until more than 800 h that is in agreement with other studies that report (Parameswarappa et al. 2006) that cells entrapped in alginate and polyacrylamide could efficiently biodegrade for 824 h (36 days) to 1,008 h (42 days) It means that higher VSS concentrations in the encapsulated calcium-alginate beads, higher will be wastewater volume treated with COD concentration <20 mg/l.

The total organic carbon (TOC) was measured at different times and a there was an important variation of the COD/COT ratio at different treatment times with a mean of 4.2, agree with the reported

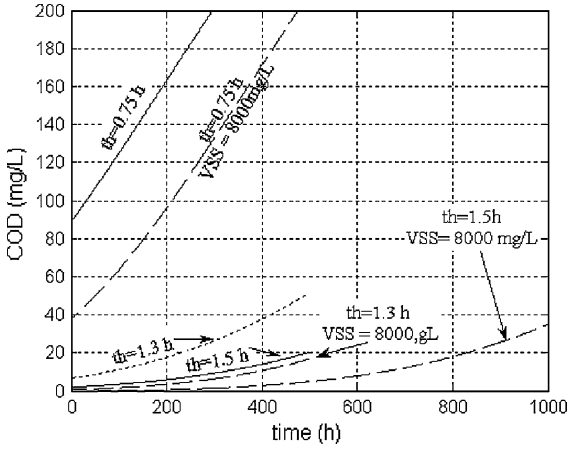

Fig. 8 COD concentration in the effluent at the different residences times and VSS concentrations

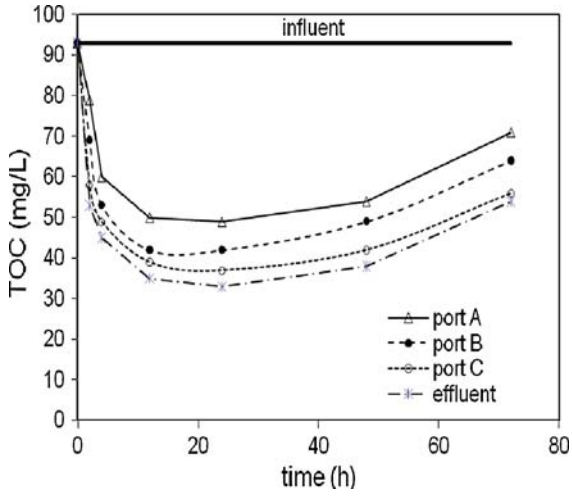

Fig. 9 Experimental TOC concentration data variation as a function of the time at different reactor heights (*ports*) with $th = 0.75$ h

(Eckenfelder 2000). Figure 9 shows the results of the experimental TOC concentration data (points) as a function of the time, at different reactor heights (ports) with a residence time in the reactor of 0.75 h. As seen, the trend of the experimental data is similar to those experimental data of the COD concentration, shown in Figs. 3 and 5. In the case, of the N–NH^{4+} concentration in the bioreactor, the behavior also is the same as the COD and TOC, as shown in Fig. 10. In addition, it is possible to see that the removal of N–NH^{4+} reached about 70% in the effluent (from 65 mg to about 20 mg of N–NH^{4+}/l) at processing times lower than 50 h.

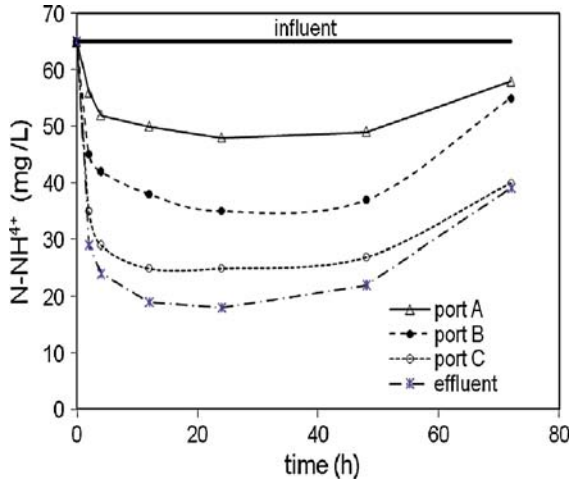

Fig. 10 Experimental N–NH^{4+} concentration data variation as a function of the time at different reactor heights (*ports*) with $th = 0.75$ h

After this time, the $N–NH^{4+}$ concentration increased due to the same effect of erosion of the calcium-alginate beads due to their low strength. This must be studied in more detail to complement the model. Finally, it is important to say that the formation of sludge was reduced drastically that will reduce its treatment, management, and disposal.

Conclusions

The experimental results showed the actual tubular reactor presents a high dispersion that must be considered in the modeling of this kind the reactors because it affects its performance. The model was calibrated with an actual wastewater and describes adequately the removal of the COD in the reactor in non-steady state with calcium-alginate beads with immobilized activated sludge. However, deviations are presented due to the low strength of the calcium-alginate beads, which could be improved with other gelation agent as Sr_2. With longer residence times and higher VSS concentration in the alginate beads reactor, it is possible to increase the time operation of the bioreactor and treat higher volumes of wastewater than at short residence time where the microorganisms' death rate is higher than at longer residence times. The sludge generation was drastically reduced and it is possible to remove nitrogen from the wastewater.

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