Performance evaluation of an anaerobic fluidized bed reactor with natural zeolite as support material when treating high-strength distillery wastewater

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Abstract

The performance of two laboratory-scale fluidized bed reactors with natural zeolite as support material when treating high-strength distillery wastewater was assessed. Two sets of experiments were carried out. In the first experimental set, the influences of the organic loading rate (OLR), the fluidization level (FL) and the particle diameter of the natural zeolite ($D_P$) were evaluated. This experimental set was carried out at an OLR from 2 to 5 g COD (chemical oxygen demand)/l d, at FL 20% and 40% and with $D_P$ in the range of 0.2–0.5 mm (reactor 1) and of 0.5–0.8 mm (reactor 2). It was demonstrated that OLR and FL had a slight influence on COD removal, whereas they had a strong influence on the methane production rate. The COD removal was slightly higher for the highest particle diameter used. The second experimental set was carried out at an OLR from 3 to 20 g COD/l d with 25% of fluidization and $D_P$ in the above-mentioned ranges for reactors 1 and 2. The performance of the two reactors was similar; no significant differences were found. The COD removal efficiency correlated with the OLR based on a straight line. COD removal efficiencies higher than 80% were achieved in both reactors without significant differences. In addition, a straight line equation with a slope of $1.74 \text{d}^{-1}$ and an intercept on the $y$-axis equal to zero described satisfactorily the effect of the influent COD on the COD removal rate. It was also observed that both COD removal rate and methane production ($Q_M$) increased linearly with the OLR, independently of the $D_P$ used.

Keywords: Anaerobic fluidized bed reactor; Distillery wastewater; Fluidization level; Natural zeolite; Particle diameter; COD removal

1. Introduction

Anaerobic treatment of high-strength wastewaters with high biodegradable content presents a number of advantages [1–6]; for example, quite a high degree of purification with high-organic-load feeds can be achieved, low nutrient requirements are sufficient, small quantities of excess sludge are usually produced and, finally, a combustible biogas is generated. The production of biogas enables the process to generate or recover energy instead of just saving it; this can reduce operational costs by a large margin compared with the high-energy-consuming aerobic process.

However, one of the biggest problems in the anaerobic processing of liquid wastes is the loss of biomass in systems with a high hydraulic loading rate. In order to solve this problem reactors have been designed with supports, which fix the biomass and result in high loading densities and small hydraulic retention times [5–7]. With the increase of population density on the given support, there is a greater
chance of cross-feeding, co-metabolism, and interspecies hydrogen and proton transfer, which may further stimulate the growth of microcolonies [8–13]. Among the bioreactors more commonly used for this purpose are fluidized-bed reactors, where bacteria colonize particles of a support medium, thereby increasing the surface available for bacterial growth [14–21].

The anaerobic fluidized bed reactor (AFBR) is a configuration which has been demonstrated in various studies to be feasible for the treatment of different industrial wastewaters [22–24]. The use of small, porous, fluidized media enables the reactor to retain high biomass concentrations and thereby operate at significantly reduced hydraulic retention times (HRT). Fluidization also overcomes operating problems such as bed clogging and high pressure drop, which would be the case if such high-surface-area media were used in a packed bed reactor. A further advantage of using media to retain the biomass within the reactor is the possible elimination of the secondary clarifier.

The feasibility of the use of natural zeolite as a support media in AFBR for the treatment of wastewaters generated in alcohol distilleries from the fermentation of sugarcane molasses has recently been demonstrated [16]. In addition natural zeolite, with its favorable characteristics for microorganism adhesion, has been widely used as an ion exchanger for ammonia removal due to the presence of Na\(^+\), Ca\(^{2+}\) and Mg\(^{2+}\) cations in its crystalline structure. This property can also be useful for improving the anaerobic-process performance in the treatment of wastewaters with high concentrations of nitrogen compounds, such as with cattle, pig and chicken waste, with the aim of preventing process inhibition [16,23–26]. At the same time, zeolite has shown a great capacity for metal adsorption (Cu, Cd, Pb and Zn) and this property can be useful for removing toxic materials for microorganisms in anaerobic digestion [27].

The high organic content and degradability of the wastewater generated in alcohol distilleries from the fermentation of sugarcane molasses make it a potential source of renewable energy by using anaerobic processes. In addition, this raw material can be seen as representative of other types of distillery wastewaters. Different anaerobic reactor configurations have been previously used for purification of these wastewaters. For example, a 1 m\(^3\) fixed bed reactor showed a great stability in response to organic overloads and toxicant shocks (ammonia) with and without pH regulation in the feeding line in the anaerobic treatment of wine distillery wastewater [28]. A previous study showed that the performance of laboratory-scale fixed film reactors treating distillery wastewater was influenced by the influent pH with chemical oxygen demand (COD) removal efficiencies of 76.8% operating with alkaline influent at organic loading rates (OLR) of around 10.5 g COD/1 d [29]. An inverse turbulent bed reactor with extendospheres as carrier particles was tested with distillery wastewater and presented promising performances after 90 days of operation: 75–85% carbon removal with an OLR of 15 g COD/1 d [30]. The performance observed during the start-up of this reactor was similar to that of other previously tested fluidized bed technologies treating the same wastewater [30]. A down-flow (or inverse) fluidized bed reactor with ground perlite as carrier was also used for distillery wastewater treatment achieving 85% total organic carbon (TOC) removal at an OLR of 4.5 g TOC/1 d [31].

The aim of the present work was to study the influence of both operational and design parameters on the performance of two AFBRs using natural zeolite as support material when treating high-strength distillery wastewater. Two experimental runs were carried out. In the first one, the effects of the OLR, the fluidization level (FL) and the particle diameter of the zeolite (\(D_p\)) on the process performance were assessed, operating at low OLR values (<5 g COD/1 d). In the second run, the performance of the AFBR and the effect of \(D_p\) were also evaluated operating at a fixed FL (25%) and at medium and high OLR values (5–20 g COD/1 d).

2. Materials and methods

2.1. Equipment

Two AFBRs consisting of two acrylic plastic cylindrical columns of 5.90 and 1.65 l of total and effective volumes, respectively, denoted as R-1 and R-2, were used. Each reactor was composed of a fluidization section 6.5 cm in diameter and 74 cm high, where the fluidization took place, and a decantation section located at the top of the reactor 14.4 cm in diameter and 20 cm high. The original height of the support within the reactor and without fluidization was 24 cm. The change of column diameters was achieved by a truncated cone situated at the top of the cylindrical section. The increase in the diameter determined the decrease in fluid velocity, facilitating the settling of the support particles. A liquid–gas separator was placed at the top of the decantation section in order to guarantee the separation of solid, liquid and gas fractions. The gas produced in the process was bubbled in a NaOH solution at 15% to remove the CO\(_2\), and was measured by water displacement in gas-collecting tubes. The operating temperature of the reactors (30 ± 2°C) was maintained virtually constant by placing them in a room with controlled temperature. Fig. 1 shows a schematic diagram of the experimental set-up used.

2.2. Characteristics of the zeolite used

The natural zeolite used as biomass support was obtained from a deposit located in the Province of Villaclara, Cuba. The chemical composition (% w/w) of the zeolite used was 66.62% of SiO\(_2\), 12.17% of Al\(_2\)O\(_3\), 2.08% of Fe\(_2\)O\(_3\), 3.19% of CaO, 0.77% of MgO, 1.53% of Na\(_2\)O, 1.20% of K\(_2\)O and 11.02% of ignition wastes, its phase composition being 35% Clinoptilolite, 15% Mordenite, 30% Montmorillonite and 20% others (calcite, feldspate and quartz). Finally,
other characteristics of the zeolite used were framework density (FD) 20.6 T-atoms per 1000 Å³, 32.03% porosity and grain density \( (\rho_A) \) 2.12 g/cm³. Zeolite particles between 0.2–0.5 mm in diameter were used in R-1, whereas in R-2 the zeolite particles used were between 0.5–0.8 mm in diameter.

2.3. Characteristics of the inoculum used

Each reactor was inoculated with 330 ml of methanogenically active biomass from an anaerobic batch reactor processing pig manure after a digestion period of 45 days. The inoculum had a concentration of volatile solids (VS) of 104 g/l.

2.4. Characteristics of the wastewater

The substrate used in the experiments was the wastewater generated in the distillation process from the alcoholic fermentation of sugarcane molasses. The average characteristics of this wastewater with their corresponding standard deviations were soluble COD: 63.0 ± 3.1 g/l; total nitrogen: 735 ± 40 mg/l; total phosphorus: 335 ± 15 mg/l; sulfates: 3.5 ± 0.2 g/l; and pH: 4.7 ± 0.3.

2.5. Start-up of the AFBRs and acclimatization stage

The start-up of the reactors was carried out in the batch mode with 20% of FL or bed expansion. The biomass of each reactor was initially acclimatized by batch feedings of 20–100 ml of diluted wastewater (1:50) over a period of 45 days. The loaded volume was changed successively after methane was found to have finished. After this acclimatization stage, the reactors operated in continuous mode, initially at an OLR in the range of 2–3 g COD/l d.

2.6. Experimental procedure

After this preliminary step, two sets of experiments were carried out in continuous mode:

(a) In the first experimental set, three variables were evaluated: the OLR, the FL and the \( D_p \). The reactors operated at two ranges of OLR, from 2 to 3 g COD/l d and from 4 to 5 g COD/l d, and FL of 20% and 40%. Reactor R-1 operated with zeolite particles between 0.2 and 0.5 mm in diameter \( (D_p) \), while reactor R-2 used zeolite as the support media with \( D_p \) from 0.5 to 0.8 mm. These values have been previously recommended by different researchers as adequate for various anaerobic processes [1,2,5,6,9,10,12,20]. The experiment was carried out by a factorial plan design \( (2^3) \). Table 1 summarizes the experimental design and the arrangement carried out in this first experimental set. The HRT was maintained constant at 11 h throughout the experimental set. As a consequence, the raw wastewater was diluted 1:50 and 1:25 with distilled water until OLR values in the ranges of 2–3 and 4–5 g COD/l d, respectively, were reached. The steady-state conditions were assumed to be achieved after a period equivalent to 4–5 times the HRT value (11 h), which means 44–55 h after starting the experiment. The total duration of this first experimental set was 84 days.

(b) In the second experimental set, the following OLRs were studied: 3, 6, 8, 10, 12, 14, 18 and 20 g COD/l d. Taking into account that the HRT was also kept constant at 11 h throughout the second experimental set, the above values of OLR corresponded to influent concentrations \( (S_I) \) of 1.4, 2.8, 3.7, 4.7, 5.6, 6.5, 8.4 and 9.3 g COD/l, respectively. In order to achieve these influent concentrations, dilutions of 1:45, 1:22.5, 1:17, 1:13, 1:10, 1:8 and 1:7, respectively, were prepared. In this case, the reactors were fluidized to obtain a bed expansion of 25% for which an effluent recycling ratio of 40:1 was used (equivalent to a recycling flow rate of 147 l/d). The steady-state conditions were also assumed to be reached after a period equivalent to 4–5 times the HRT value. This second experimental set had a total duration of 45 days.

2.7. Sampling and analytical determinations

The control of the fluidized beds operation in both experimental sets was carried out daily by measuring the FL, the influent and effluent pH, the raw waste feeding rate
(Q_f), the recycling flow rate (Q_R) and the methane production (Q_M). Once steady state was achieved, triplicate samples were taken three times a week from the influent and effluent of each AFBR. The steady-state value of a given parameter was taken as the average of these consecutive measurements for that parameter when the deviations between the observed values were less than 5% in all cases. The samples obtained were analyzed for determining the COD and pH according to the Standard Methods for the Examination of Water and Wastewater [32]. For the processing of the experimental data the Stat graphics plus 5.0 program was used.

3. Results and discussion

3.1. First experimental set

Fig. 2 shows the variation of effluent pH with the OLR and FL throughout the operation time for the two reactors studied during the first experimental set. As can be seen, this parameter was not significantly affected by the increase in the OLR, FL and D_p, and remained in the range of 6.9–7.5 as extreme values. This pH interval can be considered as optimum for the anaerobic process [33]. This high stability can be attributed to the carbonate/bicarbonate buffering, which guards against possible acidification of the reactors, giving a pH of the same order as the optimal for methanogenic bacteria [33]. In the present work, total alkalinity values higher than 3500 mg/l (as CaCO_3) (data not shown) were sufficient to prevent the pH from dropping to below 6.9 at OLR of up to 5 g COD/l d. 

Fig. 3 shows the effect of the variables evaluated on COD removal. The increase in OLR, FL and D_p produced a slight increase in COD removal. The increase in the OLR at a constant value of HRT determined the increase in the concentration gradient between the liquid and the biofilm. This fact favored the organic matter removal, as was reported by other researchers [1,3,5,10,19]. The increase in FL determined the improvement of the contact between the microorganisms adhered to the support and the substrate, which caused an enhancement in the process performance, as was also previously reported in the literature [9,10,16]. Finally, reactor R-2 which used zeolite support with D_p of 0.5–0.8 mm, operated with slightly higher COD removal when compared with R-1. The increase in D_p was favorable for a better separation of the support in the separation or

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**Table 1**

Experimental design and arrangement of the first experimental set

<table>
<thead>
<tr>
<th>Experimental design</th>
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<td>Variables</td>
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<tr>
<td>OLR (kg COD/m³ d)</td>
<td>2–3</td>
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<tr>
<td>FL (%)</td>
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<td>D_p (mm)</td>
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<th>Experimental arrangement</th>
<th>OLR (kg COD/m³ d)</th>
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<td></td>
<td>2–3, FL (%)</td>
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<td>Experiment duration (d)</td>
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<td>R-1</td>
<td>1–21</td>
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<tr>
<td>R-2</td>
<td>1–21</td>
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Fig. 2. Effect of OLR, FL and D_p on the effluent pH in the first experimental set.
decanting zone of the reactor, which reduced the possibilities of biomass escaping from the reactor.

Fig. 4 shows the variation of the methane production throughout the operation time in both reactors at different operational conditions. $Q_M$ appeared to be influenced by the OLR and FL, mainly at the highest OLR range studied in this first experimental set (4–5 g COD/l d). The increase of both parameters caused the rise of $Q_M$. As the amount of organic matter treated in the AFBRs increased, $Q_M$ also increased. Apparently, the value of $Q_M$ increased slightly when the FL increased from 20% to 40%. However, no significant effect of $D_p$ on $Q_M$ could be observed.

Taking into account the experimental results obtained, a statistical analysis was carried out. Fig. 5 shows the effect of the variables evaluated on the COD removal and $Q_M$ according to the experimental design (Table 1). In the case of COD removal, it can be observed that none of the aforementioned factors had a significant influence for a confidence limit of 95%. However, in contrast to this, there was a significant influence of OLR and FL on $Q_M$. The variance analysis (ANOVA) confirmed the significant influence of both variables on $Q_M$ with a significance level of 95% ($p \leq 0.05$).

3.2 Second experimental set

3.2.1 Effect of the organic loading on the effluent pH

Fig. 6 shows the variation of the effluent pH throughout the operation time at different OLRs in both reactors. As can be seen, the values of pH during the experiment remained in the range of 6.7–7.6 in reactors R-1 and R-2, showing that the process was in equilibrium despite the fact that the OLR increased considerably from 3 to 20 g COD/l d and influent pH was not controlled during the process.

Therefore, the activity of methanogenic microorganisms was not impaired even at OLR as high as 20 g COD/l d again, because of the adequate buffering capacities provided in the two reactors studied, for which total alkalinity values higher than 3800 mg/l (as CaCO₃) were observed. In addition, it can be observed that there were no significant differences between the effluent pH values of R-1 and R-2, indicating that $D_p$ had no influence on the process equilibrium.

3.2.2 Effect of the organic loading rate on the process performance

Fig. 7 shows the effect of the OLR on the COD removal efficiency ($E$) throughout the operation time for the two reactors studied. An increase in the process efficiency was observed as the OLR increased in both reactors. The removal efficiency was similar in R-1 and R-2 showing that $D_p$ had no significant influence on the organic matter removal for this substrate. It can be seen that the COD removal efficiency increased from around 60% to 80% when the OLR rose from 3 to 20 g COD/l d, in both reactors. Eighty percent of the feed COD could be removed at an OLR of 20 g COD/l d, which indicates that the anaerobic fluidized bed system is very effective. COD removals of 76.8% were achieved in fixed-film anaerobic reactors treating this same wastewater at an OLR of 10.5 g COD/l d and HRT of 4.04 days [29], values lower and higher, respectively, than those studied in the present work. Carbon removals of 75–85% were obtained in an inverse turbulent bed with extendospheres as carrier particles treating distillery wastewater at an OLR of 15 g COD/l d after 90 days of operation [30]. These carrier particles were chosen for their large specific surface areas (20000 m²/m³) and their low-energy requirements for
fluidization. The performance observed during the start-up of this reactor configuration was similar to that of other previously tested fluidized bed technologies treating the same wastewater [30]. TOC removal of 85% was reported in the anaerobic digestion of distillery wastewater using a down-flow (or inverse) fluidized bed reactor operating at an OLR of 4.5 g TOC/l d [31], OLR value lower than that achieved in the present work. Perlite, an expanded volcanic rock, was used as carrier particle in the down-flow fluidized bed reactor on the basis of its adequate physical and fluidization properties (diameter of 0.968 mm, specific density of 280 kg/m³ and minimum fluidization velocity of 2.3 m/h) [31]. COD removal efficiencies of 68.6% and 63.5% were achieved in the anaerobic treatment of untreated distillery wastewater and distillery wastewater previously fermented with Penicillium decumbens using laboratory-scale suspended cell bioreactors operating at an OLR of 7.5 g COD/l d in both cases and HRTs of 10.6 and 3.1 days, respectively [34].

The average biomass values (with their corresponding standard deviations) attached to the zeolite for reactors R-1 and R-2 measured after 45 days of operation time were 44 ± 1 and 45 ± 1 g/l for reactors R-1 and R-2, respectively [35]. These values are similar to those reported by Enger et al. [36] in two-stage anaerobic digestion processes of wastewaters carried out in full-scale AFBRs. The values of biomass also supported the high COD removal efficiencies obtained in both reactors. However, no significant differences between the biomass values in reactors R-1 and R-2 were observed. The attainment of high reactor biomass hold-up in the anaerobic fluidized bed system, via the immobilization of the microorganisms on the small fluidized particles, contributed to such a good system efficiency. In addition, the production and subsequent release of methane from the biofilms could have had a profound effect on the equilibrium biofilm thickness (and, therefore, equilibrium biomass hold-up) in the reactor, because the resulting effervescence might have sloughed the biofilms off the zeolite particles [37]. On the other hand, no clogging was observed throughout the reactor operation.

Fig. 5. Pareto diagrams of the standardized effect on response variables in the first experimental set.

Fig. 6. Variation of pH and OLR throughout the operation time in the second experimental set.

Fig. 7. Variation of COD removal efficiency (E) and OLR throughout the operation time in the second experimental set.
despite the high OLR values achieved (20 g COD/l d) at the end of the study.

Fig. 8 shows the influence of the OLR on the COD removal efficiency \( E \) for reactors R-1 and R-2. As can be seen, differences between the two reactors were not significant and it may be observed that a straight line fitted well to the experimental data for both reactors. The regression coefficient \( R^2 \) obtained in the linear fit was equal to 0.95 and the differences between experimental data and theoretical values were lower than 6% in all cases. Therefore, in the range of OLRs used (3–20 g COD/l d) in the second experimental set, the COD removal efficiency increased linearly with the OLR according to the following equation:

\[ E = 58.2 + 1.3 \text{OLR} \]  

(1)

where \( E \) is the removal efficiency (% of COD removed).

Taking into account that the OLR is directly proportional to the influent concentration:

\[ \text{OLR} = \frac{Q_I S_I}{V} = \frac{S_I}{\text{HRT}} \]  

(2)

where OLR is the organic loading rate (g COD/l d), \( Q_I \) is the influent flow rate (l/d), \( S_I \) is the influent concentration (g COD/l), \( V \) is the volume of the reactor (l) and HRT is the hydraulic retention time (d). As a consequence, the value of OLR is equivalent to the quotient between the influent concentration and the HRT. Therefore, the increase in the influent concentration determined the increase in the COD removal efficiency and in the COD removal rate. In addition, the effect of the influent substrate concentration on the COD removal rate can be described by the following equation:

\[ R_S = K(S_I)^n \]  

(3)

where \( R_S \) is the COD removal rate (g COD/l d), \( K \) is the reaction constant (d\(^{-1}\)), \( S_I \) is the influent substrate concentration (g COD/l) and \( n \) is the reaction order (non-dimensional). In the case of first-order kinetics, the value of \( n \) is equal to unity. In this case, a straight line with a slope equal to \( K \) and an intercept on the \( y \)-axis equal to zero expresses the effect of the influent concentration on the substrate removal rate. Fig. 9 illustrates the effect of the influent concentration on the removal rate for R-1 and R-2, and the theoretical straight line obtained with the intercept equal to zero indicates that a first-order model satisfactorily described the experimental data. The slope obtained, which represents the value of the reaction constant, was equal to 1.74 d\(^{-1}\), while \( R^2 \) was equal to 0.98. This first-order model predicted the behavior of the reactors very accurately, showing deviations lower than 5% between the experimental and theoretical values of substrate removal rates.

3.2.3. Effect of the organic loading rate on the methane production

Fig. 10 shows the variation of \( Q_M \) with the applied OLRs during the entire experimental period in both reactors used. Differences between the values of \( Q_M \) for R-1 and R-2 were not found, which highlighted the fact that particle size, in the ranges studied, did not influence process performance (process equilibrium, removal efficiency and methane gas production). It was observed that the increase in OLR
determined the increase in $Q_M$ in the same way in both reactors as was previously found with respect to the COD removal efficiency. Apparently, the activity of methanogenic bacteria was not impaired during the OLR range tested in this study because of the adequate buffering capacities provided in the experimental systems. The experimental data of $Q_M$ and COD removed were used to determine the methane yield coefficient, $Y_P$, taking into account that the volume of gas produced per day is assumed to be proportional to the amount of substrate consumed [37]. From these data, a value of $0.29 \pm 0.03 \text{CH}_4$ (at standard temperature and pressure conditions, STP)/g COD consumed (95% confidence limits) was obtained over the substrate concentration range used. This methane yield value is virtually coincident with other values reported in the literature [8,9,15,37]. The theoretical methane yield expressed in liters per gram of COD consumed should be 0.35, when assuming that all of the incoming COD is transformed into methane, and considering that the biomass growth and cell maintenance is null [33,37]. During anaerobic digestion, in the absence of any other oxidizing agent, the COD removed due to reactants removal should be equal to the COD of the products (methane). Therefore, a theoretical methane yield of $0.351 \text{CH}_4$/g COD removed is calculated. The methane yield value obtained in the present work ($0.291 \text{CH}_4$/g COD removed) could be explained by the presence of important concentrations of sulfates (3.5 g/l) in the substrate among other agents that would consume COD without producing methane. However, lower values of $Y_P$ were achieved in semi-continuous well-stirred reactors with microorganisms immobilized on sepiolite support (0.281 methane STP/g COD removed) and on waste tyre rubber (0.251 methane STP/g COD removed) treating the same type of wastewater [38,39]. This fact demonstrates that the system reported in the present work promoted methanogenesis more over other processes (as sulfate reduction).

4. Conclusions

The results of the first experimental set demonstrated that the pH of the effluents obtained and COD removal efficiency were not significantly affected by OLR, FL and $D_P$. However, $Q_M$ was significantly influenced by OLR and FL, but the effect of $D_P$ was not relevant. The feasibility of using natural zeolite as microorganism support in AFBR was shown.

The second experimental study revealed that the values of pH throughout the operation time remained within the optimum range for methanogenic bacteria despite the fact that OLR increased from 3 to 20 g COD/l d and influent pH was not controlled. In addition, no significant differences were observed in the quality of the effluents of reactors R-1 and R-2, indicating that $D_P$ had no influence on process equilibrium. COD removal efficiency rose with an increase in OLR in both reactors. A linear relationship determined the influence of the OLR on COD removal efficiency according to the range of OLR studied. It was found that a first-order kinetic model satisfactorily described the effect of influent substrate concentration on the organic matter removal rate. At the same time, $Q_M$ also increased linearly with OLR. Depending on the range of OLRS studied the behaviors of R-1 and R-2 were very similar, indicating no effect of the particle diameter on the process performance.

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References


Fig. 10. . Variation of methane production $(Q_M)$ throughout the operation time in the second experimental set.