Kinetics and Effect of Temperature in Anaerobic Fluidised Bed Reactors with Clayey Supports

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An anaerobic treatment in batch regime of swine wastewater was carried out. Five stirred tank reactors were used, one of them containing suspended biomass for reference, and the other four with various suspended micronised clay supports of different chemical composition (saponite, zeolite, calcined sepiolite and esmectite). The experimental device was maintained at three different temperatures: 25, 35 and 47 °C.

The obtained removal efficiency (η_{COD}/%) was about 80 % at 25 °C, in reactors containing esmectite, saponite and calcined sepiolite support. The reactor with zeolite support showed the minimum mean concentrations in NH_4^+–N and volatile acids in the effluents, at any temperature.

The Romero methane production kinetic model has been applied obtaining the value of the maximum specific growth rate of microorganisms, μ_{max}, and the specific kinetic constant, k, for each temperature studied. The highest mean μ_{max} was obtained at 25 °C and a decrease was observed as the temperature applied increased.

Key words:
Anaerobic digestion, kinetics, mesophilic process, support, swine wastewater, thermophilic process

Introduction

Spain has around 20 million pigs. These are mainly on intensive farms, where high animal concentration implies an increase in waste production that makes its traditional use as fertilisers or soil conditioners on agricultural lands practically impossible.

These changes have affected the volume and the composition of the residues, which contain products that induce growth, medicines, heavy metals (zinc and copper), etc. The presence of these compounds can cause unexpected problems in the utilisation and subsequent application of the wastes.[1]

Swine wastewater is the residual water collected from the pigsty, without previous separation of the solid fraction. The disposal of pig waste ranges between 6 and 8 L/animal (70 kg mass), including the water used for cleaning and draining of residues. Its principal characteristic is high content of total solids, 25–50 kg m^{-3}, with 80 % as suspended solids and up to a 30 % of the dried matter as mineral solids.[2]

Among the treatments of this kind of wastewater, anaerobic digestion has been shown to be the most appropriate in comparison with other possible technologies.[3] The low growth rate of anaerobic microorganisms has encouraged the development of various techniques for their immobilisation in order to avoid biomass loss in the effluent stream and hence diminish process rates. Among the reactors more commonly used for this purpose are stirred tank reactors, where bacteria colonize particles of support materials, thereby increasing the surface available for bacterial growth. These reactors also cope with the greatest volumetric loads, which makes them suitable for the treatment of wastewaters at either high or low organic loads. At the same time, as population density on the supports increases, so do: a) the possibility of both hydrogen and proton transfer between the different species and b) the successive reactions.[4,5]

The aim of this work is to carry out a kinetic study of the anaerobic digestion of swine wastewater in four reactors, containing microorganisms adhered to saponite, zeolite, calcined sepiolite and esmectite supports, plus a reactor without support. The influence of these supports on the biokinetic parameters of the digestion process will be studied.

Three experiments have been carried out at different temperatures, in order to compare the yield of methane and the organic matter degradation rate, in batch regime: at 25 °C-mesophilic range-, at 35 °C-optimum temperature of the anaerobic microorganisms in the mesophilic range- and at 47 °C-thermophilic range-.

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Materials and methods

Equipment – The experimental set-up used consisted of 1 litre magnetically stirred batch anaerobic reaction units, at a constant temperature.[6] The biogas generated was passed through a solution of sodium hydroxide to retain carbon dioxide. The volume of methane produced throughout this process was measured daily in Boyle-Mariotte's bottles and measured indirectly from the amount of water displaced by the gas.

Swine wastewater – The wastewater used was collected from the farm "El Cerro", in Seville (Spain). The average features of this wastewater are summarized in Table 1. These values are an average of 30 determinations; the differences between the observed values were less than 5 % in all cases.

Table 1 – *Composition and features of the wastewater used*

pH	8.0	Alkalinity ($CaCO_3$)	4.6 g L^{-1}
COD_T	21.0 g L^{-1}	V. A. (HAcO)	0.7 g L^{-1}
COD_S	4.8 g L^{-1}	TS	19.8 g L^{-1}
N_{kj}	4.3 g L^{-1}	MS	7.1 g L^{-1}
NH_4^+–N	0.8 g L^{-1}	VS	13.1 g L^{-1}
NO_3^-	40.6 mg L^{-1}	TSS	14.7 g L^{-1}
NO_2^-	3.6 mg L^{-1}	MSS	5.2 g L^{-1}
PO_4^{3-}	46.2 mg L^{-1}	VSS	9.8 g L^{-1}

Inoculum – The reactors were inoculated with biomass from an anaerobic pond of swine wastewater, at the same farm "El Cerro". Its composition is detailed in Table 2.

Table 2 – *Composition of the biomass used as inoculum*

pH	7.6
TS	70.5 g L^{-1}
MS	17.5 g L^{-1}
VS	53.0 g L^{-1}
TSS	62.7 g L^{-1}
MSS	14.4 g L^{-1}
VSS	48.3 g L^{-1}

Supports – The materials used as supports for the bacteria were commercially available micronised calcined sepiolite (at 500 °C), esmectite, saponite and zeolite with 2–5 μm diameter pore, supplied by Tolsa, S.A. (Madrid, Spain). These clayey supports were selected on account of their favourable kinetic behaviour from previous experiment. Their chemical composition and features are summarised in Table 3, where it can be seen that zeolite and esmectite present higher concentration of Al_2O_3 and saponite and sepiolite of MgO.

Table 3 – *Composition of the supports used*[a]

	Saponite	Zeolite	Sepiolite	Esmectite
SiO_2	57.3	6.9	65.6	60.0
Al_2O_3	4.4	11.9	3.4	17.3
Fe_2O_3	2.0	2.1	1.1	5.3
TiO_2	0.2	–	–	0.2
MgO	25.4	1.2	23.5	6.0
CaO	0.6	2.8	1.7	0.5
Na_2O	0.2	1.5	0.4	1.2
K_2O	1.0	1.1	1.0	2.3
calcination loss (1000 °C)	8.3	11.5	3.3	7.4
moisture content (%)	9.0	–	< 2.0	10.0
bulk density (g mL^{-1})	0.84	–	0.49	0.86

[a]Typical chemical analysis (% sample dried at 105 °C)

Experimental procedure – Five reactors were used: a reference and four reactors with 15 g L^{-1} of the support above mentioned. While larger amounts of support provided increased amounts of biomass, they could also increase the apparent viscosity of the medium, and thus hinder mass transfer and decelerate the process of biodegradation. Each reactor contained 750 mL of distilled water, 250 mL of the above-mentioned inoculum at a final concentration of 9 g L^{-1} VSS of biomass. The biomass was adapted by feeding it with gradually increasing volumes of the wastewater in question for four months at each working temperature with subsequent additions of methanol (1.0 g L^{-1} COD) and wastewater in a decreasing ratio to allow the growth of methanogenic flora.[7]

Successive loads of 0.6; 1.2; 1.8; 2.4; 3.0; 3.5; 4.5; 5.0; 6.0 and 7.0 g L^{-1} as COD in batch regime, were added. The duration of each experiment corresponded to a complete biomethanation. In each load, the daily volume of methane produced and the initial and final COD were determined. After settling (2 h), the wastewater volumes were added after separating the same volume of liquid from the reactor in order to avoid biomass losses. All experiments were conducted in duplicate.

Chemical analyses – The following parameters were analysed: pH, total chemical oxygen demand (COD_T), soluble chemical oxygen demand (COD_S), ammonium nitrogen (NH_4^+–N), volatile acidity (VA), alkalinity, total solids (TS), mineral solids (MS), volatile solids (VS), total suspended solids (TSS), mineral suspended solids (MSS) and volatile suspended solids (VSS). These analytical measurements were determined according to the recommendations of the Standard Methods for the Examination of Water and Wastewater.[8]

Results and discussion

Methane production accumulated in function with the load

Evolution of the accumulated volume of methane

Figs. 1, 2 and 3 show the variation of the accumulated methane volume at different times (days) for each feeding and temperature studied, in the reactor containing esmectite as support. All the curves present an exponential growth in the mesophilic range. However, at 47 °C the slopes of the curves are sigmoid, which indicates the existence of an inhibition phenomenon.

Initial relative yield (48 h)

It has been observed that the methane production accumulated is maximum in the first two days, mainly for medium and high loads. In order to compare the yields in methanation at the different working temperatures, the ratio between the volume of methane accumulated in the first two days and the total volume % $CH_{4(48h)}$ is calculated. Figs. 4, 5 and 6 show the variation of these initial relative yields (%) as a function of the initial load. The slopes of the curves decrease with increasing load, particularly at 47 °C. The average yield values obtained are lowest in the reference reactor and the one with zeolite support, while the reactors with saponite and esmectite support present the highest values, in particular at 25 °C.

In general, in the mesophilic range about the 50 % of the total methane is produced during the first 48 h, but at 47 °C this yield is less than 45 %.

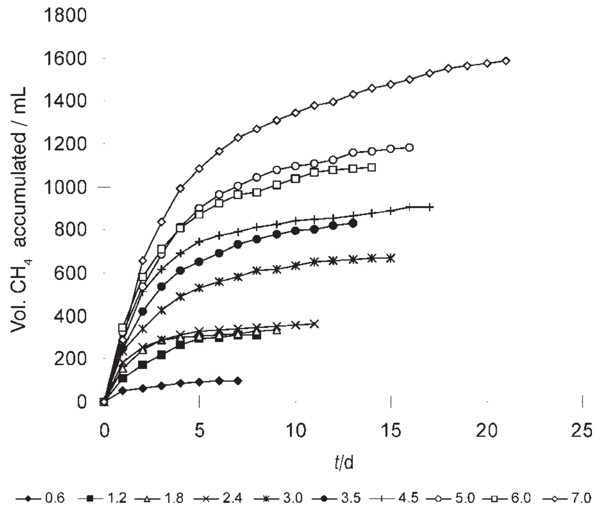


Fig. 1 – *Evolution of the volume of methane accumulated (mL), for the experiments with different initial COD levels (g L^{-1}), in the Esmectite reactor, at 25 °C*

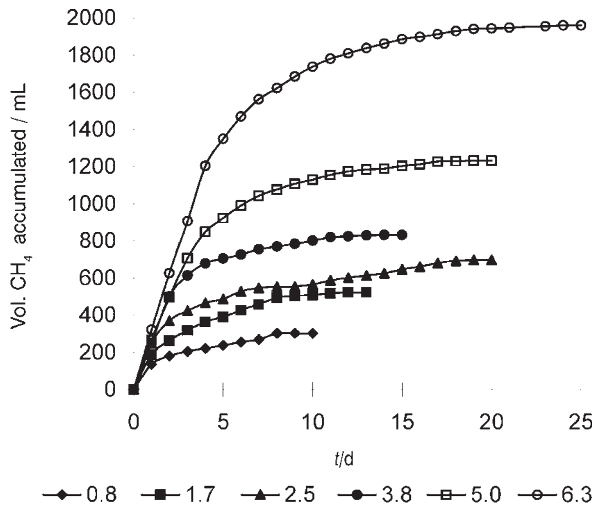


Fig. 2 – *Evolution of the volume of methane accumulated (mL), for the experiments with different initial COD levels (g L^{-1}), in the Esmectite reactor, at 35 °C*

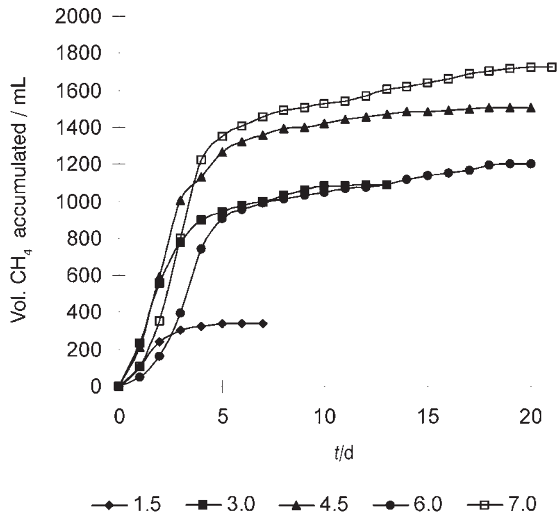
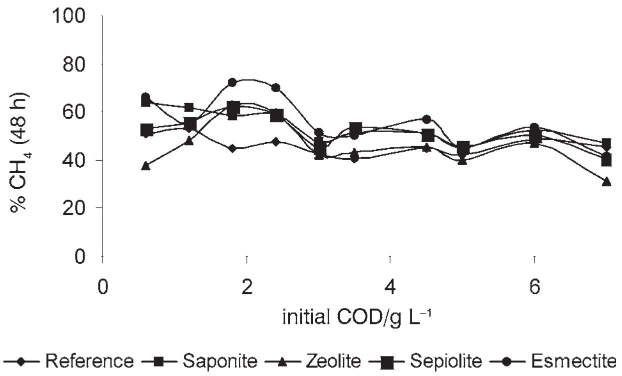
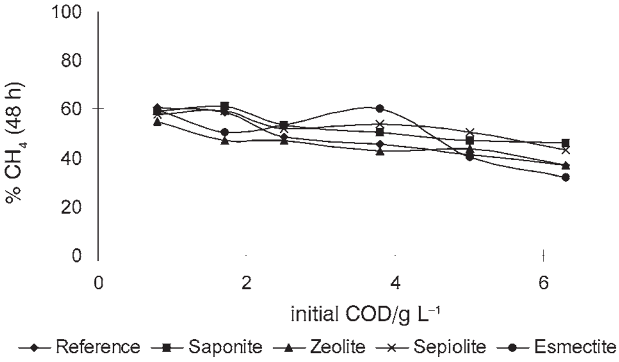


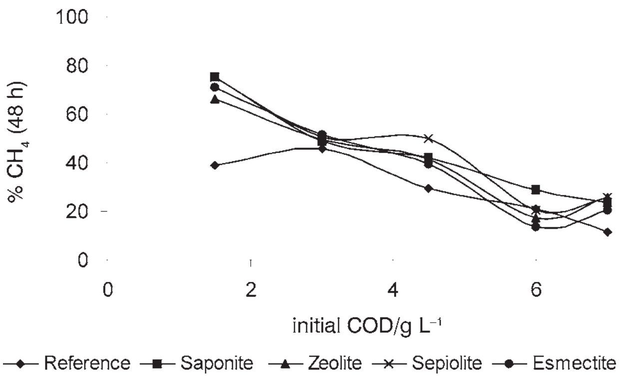
Fig. 3 – *Evolution of the volume of methane accumulated (mL), for the experiments with different initial COD levels (g L^{-1}), in the Esmectite reactor, at 47 °C*



F i g . 4 – *Initial relative yield (% $CH_{4(48h)}$) as a function of the initial COD (g L^{-1}), at 25 °C*



F i g . 5 – *Initial relative yield (% $CH_{4(48h)}$) as a function of the initial COD (g L^{-1}), at 35 °C*



F i g . 6 – *Initial relative yield (% $CH_{4(48h)}$) as a function of the initial COD (g L^{-1}), at 47 °C*

Analytical parameters

The average values of pH, CODs, N–NH_4^+ and CODr of the effluents at each working temperature are shown in Table 4. It can be seen an increase in pH from the mesophilic range at 47 °C, to pH 8.0. The organic matter concentration in the effluents is greater at 47 °C. The reactor with saponite support presents the lowest average CODs values at the three working temperatures. The CODr in the reference reactor is lower than that achieved in the reactors with support. The latter show a similar behaviour at 25 and 35 °C. The average values are about 75 % in the mesophilic range and lower than 70 % at 47 °C.

The lowest levels in NH_4^+–N are obtained at 25 °C. The reactors with support present average values lower than those of the reference reactor.

T a b l e 4 – *Average values of pH, CODs, CODr and NH_4^+–N at the different working temperatures, for each reactor*

		Reference	Saponite	Zeolite	Sepiolite	Esmectite
pH	25 °C	7.64	7.54	7.52	7.63	7.65
	35 °C	7.64	7.64	7.59	7.54	7.53
	47 °C	7.92	7.97	7.98	7.98	7.97
CODs/g L^{-1}	25 °C	1.43	0.75	1.21	0.77	0.66
	35 °C	1.23	0.60	0.88	0.65	0.77
	47 °C	4.10	1.33	2.58	2.41	2.61
% CODr	25 °C	64 %	76 %	65 %	75 %	78 %
	35 °C	62 %	75 %	74 %	73 %	73 %
	47 °C	32 %	69 %	51 %	55 %	52 %
NH_4^+–N/g L^{-1}	25 °C	0.73	0.63	0.34	0.67	0.60
	35 °C	1.07	0.89	0.79	0.95	0.91
	47 °C	1.20	1.10	1.09	1.14	1.09

With increasing temperature, the NH_4^+–N concentrations increase, and at 47 °C are practically double that at 25 °C. The reactor with zeolite support presents the minimum values of NH_4^+–N, followed by those with saponite and esmectite.

The degree of dissociation of NH_4^+–N calculated as NH_3(g) (toxic to microorganisms) as a function of temperature[9] at 35 °C is twice that at 25 °C and is up to ten times higher at 47 °C with respect to 25 °C. This toxic compound originates the inhibition phenomena observed in the evolution of the accumulated volume of methane in all the reactors at 47 °C.

The average values of MSS and VSS in the effluents, so inoculum and support losses, are present in Figs. 7 and 8. In general, the reference reactor and the one with zeolite support show the highest losses of mineral matter and biomass, whatever the temperature. The reactor with saponite support shows the best clarifying efficiency, above all at 25 °C, that is minimum losses of biomass and support with the effluents.

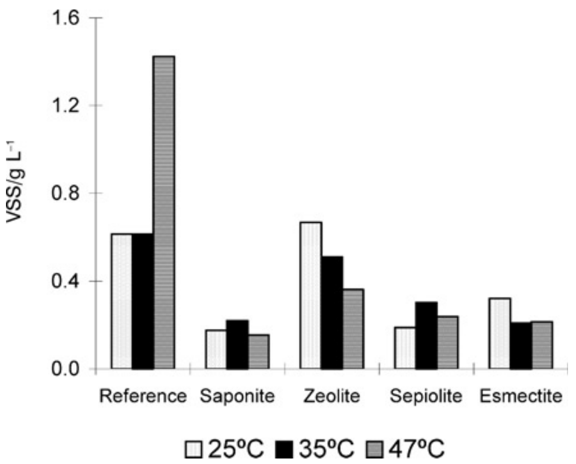


Fig. 7 – *Average values of the volatile suspended solids ($g\ L^{-1}$) in the effluents, for each working temperature*

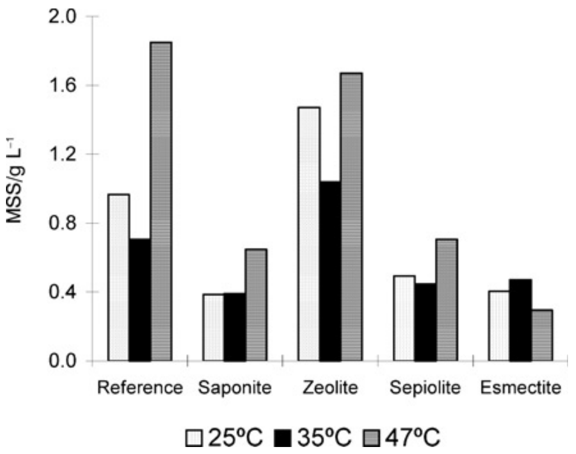


Fig. 8 – *Average values of the mineral suspended solids ($g\ L^{-1}$) in the effluents, for each working temperature*

Biokinetic parameters

The model used to obtain the biokinetic parameters must be appropriate for fermentation in reactors with complete mixed regime, containing a suspension of micronized clay to which the microorganisms responsible for the process are adhered. In the Romero model, special attention is paid not only to the fact that the model correctly fits the experimental results, but it must also have a clear physical interpretation.

The kinetic model used is an empirical one developed by Romero[10] for different processes and operational conditions. They demonstrated that it is a general model that can be applied for the interpretation of the anaerobic digestion of wine distillery wastewater,[11,12] and with dairy wastewater,[13] excellent results being obtained in all cases.

Those authors conclude that the substrate removal rate fits to a polynomial of 2nd degree with respect to the substrate concentration in the reactor according to eq. (1).

$$(-r_S) = k_2\gamma_S^2 + k_1\gamma_S + k_0 \qquad (1)$$

The corresponding expression with respect to the product obtained when $k_2 \approx 0$, in batch regime, is (2):

$$V = V_0 + Y_{P/S}\,(\gamma_{S_T} + k_0/k_1)\,(1 - e^{-k_1 \cdot t}) \qquad (2)$$

V_0 – volume of methane accumulated at initial time, mL
$Y_{P/S}$ – yield of produced methane, mL CH_4 STP g^{-1} CODr
γ_{S_T} – initial substrate concentration, $g\ L^{-1}$
γ_S – substrate concentration, $g\ L^{-1}$
k_0 – constant, $g\ L^{-1}\ d^{-1}$
k_1 – specific rate constant, d^{-1}
k_2 – rate constant, $L\ g^{-1}\ d^{-1}$
r_S – reaction rate, $g\ L^{-1}\ d^{-1}$
t – digestion time, d
$(\gamma_{S_T} + k_0/k_1)$ – biodegraded substrate concentration, $g\ L^{-1}$

V_0 was zero at $t = 0$ and the rate of gas production became zero at $t = \infty$.

The parameters $Y_{P/S}$, k_0 and k_1 were calculated by substituting the accumulated methane values (STP) and time using a non-linear regression program. The fit of the theoretical and experimental methane data corresponded to linear regressions with correlation coefficients of 0.99 in the experiment at 25 °C and ranged from 0.98 and 0.99 at 35 and 47 °C, respectively, with a 95 % level of confidence.

Table 5 – *Average values of k_1 and $Y_{P/S}$ obtained for each temperature and reactor*

T/°C	Parameter	Reference	Saponite	Zeolite	Sepiolite	Esmectite
25 °C	k_1/d^{-1}	0.291	0.390	0.299	0.352	0.424
	$Y_{P/S}$ /mL CH_4 g^{-1} COD	216.5	204.6	225.1	220.7	207.7
35 °C	k_1/d^{-1}	0.344	0.352	0.285	0.338	0.327
	$Y_{P/S}$ /mL CH_4 g^{-1} COD	222.7	224.8	224.4	235.2	243.8
47 °C	k_1/d^{-1}	0.226	0.352	0.321	0.358	0.322
	$Y_{P/S}$ /mL CH_4 g^{-1} COD	210.3	225.2	212.1	211.2	208.5

The variation of the k_1 values is similar to that obtained with the % $CH_{4(48h)}$ versus initial COD curves. The average values of k_1 for each reactor and temperature were calculated, showing that esmectite and saponite present the highest constants in the experiment at 25 °C (Table 5).

According to Romero, k_1 is equal to the maximum specific growth rate of the microorganisms, μ_{max}, under these working conditions. Table 6 shows the average values of k_1 at the same temperature in the reference reactor and in the reactors with support. The highest values of μ_{max} correspond at 25 °C with the use of supports.

Table 6 – *Average values of the maximum specific growth rate of the microorganisms, μ_{max}/d^{-1}, of the reference reactor and the ones with supports, for each working temperature*

T/°C	Reference	With supports
25	0.291	0.366
35	0.344	0.325
47	0.226	0.338

Chemical composition of the support and release of nutrients from the minerals and their interaction with the clay surface also may play an important role. Murray and van der Berg[17] found that any clays contained and released nutrients beneficial in stimulating methanogenic activity and that the cation exchange capability of clays provided a slow release of nutrients to attached bacteria. Also, magnesium cation has been seen to play an important role[18] though this study has not found any significant difference between the use of each support.

Though it is known that a higher temperature improves the activity of the microorganisms,[14] the results obtained in this work are due to:

1. The toxicity of high levels of NH_3(g), produced when the temperature increases.

2. A lower temperature avoids losses of mineral and volatile suspended solids with the effluents, that is to say microorganisms and support losses.

The high biomass activity at 25 °C confirms the previously obtained CODr values at this temperature in the reactors with sepiolite and esmectite support.

Such results are in accordance with those reported in the literature with swine wastewater anaerobic processes at ambient temperature (5 to 25 °C), compared with processes developed at higher temperature.[15,16]

Conclusions

– The lowest average values of the initial relative yield (% $CH_{4(48h)}$) are obtained at 47 °C, whatever the reactor.

– Depending on the CODr, we recommend working at 25 °C with the esmectite, saponite and sepiolite support, in this order, to obtain a substrate removal of 80 %.

– The zeolite support provides the lowest levels of NH_4^+–N in the effluents because of its ionic exchange capacity.

– At the working conditions, the microorganisms show an increasing activity with decreasing temperature, as can be observed from the average values of μ_{max} obtained.

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List of symbols

k_0 – constant of reaction rate, g L^{-1} d^{-1}
k_1 – specific rate constant, d^{-1}
k_2 – rate constant, L g^{-1} d^{-1}
r – reaction rate, g L^{-1} d^{-1}
t – time, d
γ – mass concentration, g L^{-1}
η – removal efficiency of COD, %
μ – specific growth rate, d^{-1}

Abbreviations

VSS – volatile suspended solids
MSS – mineral suspended solids

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