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KINETICS OF THE BIODEGRADATION
OF WINE DISTILLERY WASTEWATERS
BY ANAEROBIC DIGESTION

The anaerobic purification of wine distillery wastewaters (WDW) was investigated in a batch reactor containing immobilized microorganisms. Several experiments were conducted by varying the initial substrate concentration (measured as COD). The removal of the COD is determined and a value of 206 cm^3 of CH_4 produced/g of COD removed is obtained for the methane yield coefficient. By use of the Monod model, a kinetic study for the substrate utilization rate was conducted and the kinetic constant of the process was determined.

1. INTRODUCTION

Wine distilleries produce large volumes of wastewaters (WDW), commonly named "vinasses", whose main characteristics are as follows: a low pH (3–5) and a high content of organic matter, usually measured as chemical oxygen demand (20–60 g/dm^3 of COD). Usually these effluents are disposed on into evaporation ponds or eliminated through public sewerages. Therefore they represent a large-scale environmental problem, mainly owing to the bad smell caused by fermentation processes and the possibility of the pollution of surface waters and underground aquifers.

Anaerobic processes have been recognized in recent years as a viable means for industrial wastewater treatment in general, and specifically for WDW. It is accepted that these processes present several advantages over aerobic treatments [1]: low costs, little energy demands and very small amounts of nutrient. In addition, the low growth rates of anaerobic microorganisms require the development of a variety of methods to retain them within the bioreactors and avoid their loss with the effluent

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which would result in a slowing of the process. Those anaerobic bacteria are capable of transforming most of the organic substances present in the waste into methane.

In this work, the anaerobic fermentation of WDW is studied with the bacteria being immobilized on sepiolite. The aim of the paper is to provide results of the removal of the COD obtained and the methane produced by determining the yield coefficient $Y_{P/S}$. Besides that, a kinetic study is also conducted in order to report several kinetic parameters of practical interest in the design of treatment plants for this type of wastes.

2. MATERIALS AND METHODS

2.1. WINE DISTILLERY WASTEWATERS

The original wastewaters used as substrate were "vinasses" collected from an industrial distillery ("Vinicolas del Oeste" located at Villafranca de los Barros, Extremadura Community, south-west of Spain), which uses "lees" (a by-product of wine fermentation) as raw material. The "vinasses" were analysed according to the procedures described in the *Standard Methods* [2], and the main characteristics and compositions obtained were: pH = 5.4; COD = 13900–15450 mg/dm^3; total phenolic compounds = 114 mg of caffeic acid/dm^3 (determined by the Folin–Ciocalteau method); total volatile solids = 7.46 g/dm^3, and the volatile suspended solids VSS = 176 mg/dm^3.

2.2. INOCULUM

As "vinasses" do not contain microorganisms capable of carrying out anaerobic digestion, each digester was inoculated with biomass taken from an anaerobic reactor of a municipal wastewater treatment plant. During a 15 weeks period, a previous stage was necessary to acclimatize that bacterial flora to this substrate by incrementing the volume of wastewater loaded to the reactor through successive additions, which provide increasing initial substrate concentrations in the digester, measured as COD. During this period, every new fresh feed was added each time when the COD concentration remained almost constant and the methane production had stopped. The biomass acclimatization was finally achieved when, after three experiments conducted with the higher COD initial concentration, a similar removal of COD was obtained.

2.3. FERMENTATION SYSTEM

The experiments were conducted in a magnetically stirred batch anaerobic digestion unit. It consisted of a 1000 cm^3 cylindrical Pyrex glass vessel, provided with a cover containing inlets for loading feedstocks and bubbling the inert gas (required for unloading) and outlets for removing effluents and venting biogas. The reactor is submerged in a thermostatic bath at a constant temperature of 35 °C within ±0.2 °C. The microorganisms effecting the process were supported on sepiolite, a micronized fibrous silicate $(Mg_4Si_6O_{15}(OH)_2·6H_2O)$ that retains methanogenic bacteria preferentially. The methane produced was measured using 1 dm^3 Boyle–Mariotte reservoirs: it was passed through a NaOH solution to retain CO_2 and the volume of methane yielded was determined from the amount of water displaced by the gas.

2.4. EXPERIMENTAL PROCEDURE

Once the acclimatization period was finished, the experiments were carried out by loading different volumes of the original WDW leading to different initial concentrations of substrate to be degraded, which was modified between 1.1 and 4.83 g of COD/dm^3 (see the table). Prior to each new volume of material, which will be degraded by being introduced to the reactors, an equal volume is removed from them after a settlement period of 12 hours in order to avoid biomass losses. Each experiment lasted until the methane production and the COD removal ceased. At regular intervals through an experiment, the COD concentration and the methane released were determined.

Table

COD degraded, volume of methane produced and kinetic constant obtained

Expt.	COD_{al}	COD_0	COD_f	X_{COD}	k_0	V_F	Y_{PS}
	mg/dm^3	mg/dm^3	mg/dm^3		h^{-1}	cm^3	cm^3/g
1	768	1100	355	97	0.102	179	240
2	960	1364	427	97	0.086	179	191
3	1684	1947	295	98	0.096	380	230
4	2529	2835	355	98	0.087	534	215
5	2849	3155	303	100	0.086	606	212
6	3364	3625	380	96	0.086	572	176
7	4538	4830	565	94	0.071	758	177

3. RESULTS AND DISCUSSION

3.1. COD REMOVAL: KINETIC STUDY

As it is observed in figure 1, the COD concentration decreases continuously with degradation time in all experiments, as can be expected.
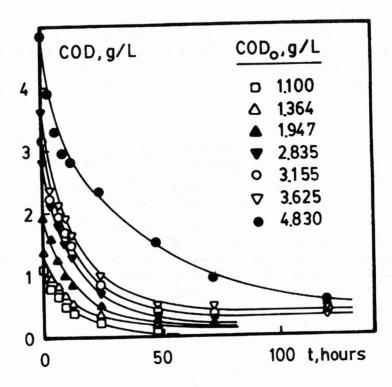

Fig. 1. Evolution of COD degraded with digestion time

The COD removal yield is defined in the form:

$$X_{COD} = \frac{COD_0 - COD_f}{COD_{al}} \cdot 100 \tag{1}$$

where COD_0 and COD_f are, respectively, the initial and final COD; and COD_{al} is the COD contained in the initial volume of WDW introduced to the reactor prior to each experiment. The values obtained for X_{COD} are shown in the table: as it is observed, this removal yield is around 100% in all cases, indicating that most of the substrate

fed to the reactor is degraded, and hardly non-biodegradable substrate is present in this case.

An anaerobic digester can be considered as a bioreactor where the substrate S reacts with a microbial sludge of the concentration X. Both parameters are related by the cellular yield coefficient $Y_{X/S}$ (g of cell mass/g of COD):

$$Y_{X/S} = -\frac{dX}{dS}. \tag{2}$$

In such a process, the rate of production of biomass is well described by a first order kinetic equation:

$$\frac{dX}{dt} = \mu X \tag{3}$$

where μ is the specific growth rate. The introduction of eq. (2) into eq. (3) leads to an expression for the rate of substrate decomposition:

$$-\frac{dS}{dt} = \frac{\mu X}{Y_{X/S}}. \tag{4}$$

For the determination of this rate, the Monod equation [3] can be used:

$$\mu = \frac{\mu_m S}{K_S + S}. \tag{5}$$

At low substrate concentration, where $K_S >>> S$ [4], the denominator in eq. (5) can be simplified, and its introduction into (4) leads to:

$$-\frac{dS}{dt} = \frac{\mu_m X}{Y_{X/S} K_s} S = KXS = k_0 S. \tag{6}$$

It has been assumed that in this equation X remains almost constant because of the low cellular yield coefficient $Y_{X/S}$ in an anaerobic system (0.02–0.06 g of cells/g of COD [5]) and taking into account the small amounts of the COD consumed through these experiments (between 0.8 and 4.5 g, see the table). It was also confirmed by the experimental results: the measured biomass concentration at the end was very similar in all the experiments, and ranged between 9.9 and 10.2 g of VSS/dm^3.

According to eq. (5), the removal of organic matter follows a first order kinetics, this aspect being previously pointed out by several authors (e.g. [6]). Therefore, its integration with the condition $S = S_0$ for $t = 0$ leads to:

$$\ln\frac{S_0}{S} = k_0 t .\tag{7}$$

It must be noted that S represents the biodegradable substrate concentration, which is usually determined by subtracting the non-biodegradable COD from the COD concentration at any time. As it was pointed out above, in this process there is hardly non-biodegradable substrate: therefore, S_0 is equal to the COD_{al} in every experiment, and S is calculated by means of the COD concentration at any time minus the final concentration COD_f.

According to eq. (7), a plot of $\ln (S_0/S)$ versus time must lead to straight lines. After least square regression analysis, the constants k_0 showed in the table are deduced. A mean value of $0.088 \ h^{-1}$ can finally be proposed for k_0.
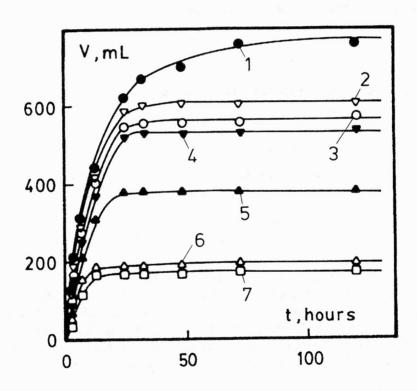
3.2. METHANE FORMATION

Fig. 2. Evolution of methane produced with digestion time
(COD_0, g/dm^3: 1 – 4.830; 2 – 3.625; 3 – 3.155; 4 – 2.835; 5 – 1.947; 6 – 1.364; 7 – 1.100)

The volume of methane produced V is measured several times through each experiment. In figure 2, the values of V versus time are plotted: it can be observed the high production at initial times of reaction, specially in the experiments where the COD_{al} was higher. The values of the maximum volume of methane V_F generated at an infinite digestion time (i.e., the volume of methane accumulated at the end of each experiment) are also depicted in the table.

Similarly to the cellular yield coefficient (eq. (2)), the methane production yield coefficient $Y_{P/S}$ (cm^3 of CH_4/g of COD degraded) is defined in the form:

$$Y_{P/S} = -\frac{dV}{dS} = \frac{V_F}{S_0 - S_F} \tag{8}$$

where S_F is the substrate concentration at the end of the experiment.

Based on the results obtained for this parameter $Y_{P/S}$ (see the table) it can be proposed an average value of 206 cm^3 of CH_4/g of COD. This value is in the range of another values reported by several authors in similar processes: 150 cm^3 of CH_4/g of COD by HAMDI et al. [7] for olive oil mill wastewaters, and 234 cm^3 of CH_4/g of COD by CAIL and BARFORD [8] for palm oil mill wastewaters.

ACKNOWLEDGEMENT

REFERENCES

[1] WHEATLEY A., *Anaerobic Digestion: A Waste Treatment Technology*, published for the SCI by Elsevier Applied Science, London, UK, 1990.
[2] American Public Health Association (APHA), *Standard Methods for the Examination of Water and Wastewater*, Washington D.C., 16th ed., 1985.
[3] BAILEY J.E., OLLIS D.F., *Biochemical Engineering Fundamentals*, McGraw-Hill, New York, 1985.
[4] WINKLER M.A., *Biological treatment of wastewater*, Ellis Horwood Publishers, 1986.
[5] JERIS J., *Industrial wastewater treatment using anaerobic fluidized bed reactors*, Water Sci. Technol., 1983, **15**, 169–176.
[6] MCCARTY P.L., MOSEY F.E., *Modelling of anaerobic digestion processes (a discussion of concepts)*, Water Sci. Technol., 1991, **24**, 17–33.
[7] HAMDI M., FESTINO C., AUBART C., *Anaerobic digestion of olive mill wastewaters in fully mixed reactors and in fixed film reactors*, Process Biochem., 1992, **27**, 37–42.
[8] CAIL R.G., BARFORD J.P., *Mesophilic semi-continuous anaerobic digestion of palm oil mill effluent*, Biomass, 1985, **7**, 287–295.

KINETYKA BIODEGRADACJI ŚCIEKÓW Z DESTYLARNI WINA W PROCESIE FERMENTACJI BEZTLENOWEJ

Zbadano proces beztlenowego oczyszczania ścieków z destylarni wina. Badania prowadzono w reaktorze porcjowym zawierającym immobilizowane mikroorganizmy. Przeprowadzono szereg eksperymentów dla różnego początkowego stężenia substratu (mierzonego jako ChZT). Określono stopień obniżenia ChZT. Efektywność produkcji metanu wynosiła 206 cm^3 CH_4/g usuniętego ChZT. Korzystając z modelu Monoda, określono stałą szybkości rozkładu substratu i stałą kinetyczną procesu.