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Jesús Rodríguez-Martínez · Silvia Y. Martínez-Amador
Yolanda Garza-García

Comparative anaerobic treatment of wastewater from pharmaceutical, brewery, paper and amino acid producing industries

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Abstract This study concerned the anaerobic treatment of five different industrial wastewaters with a diverse and complex chemical composition. The kinetics of biotransformation of this wastewater at different chemical oxygen demand (COD) were studied in a batch reactor. Wastewater from an amino acid producing industry (Fermex) and from a tank that received several types of wastewaters (collector) contained 0.83 gl^{-1} and 0.085 gl^{-1} sulfate, respectively. During the study period of 20 days, methane formation was observed in all types of wastewaters. Studies on COD biodegradation showed the reaction velocity was higher for Fermex wastewater and lower for collector wastewater, with values of 0.0022 h^{-1} and 0.0011 h^{-1}, respectively. A lower methanogenic activity of 0.163 g CH_4 day^{-1} g^{-1} volatile suspended solids (VSS) and 0.20 g CH_4 day^{-1} g^{-1} VSS, respectively, was observed for paper producing and brewery wastewater. Adapted granular sludge showed the best biodegradation of COD during the 20-day period. The sulfate-reducing activity in pharmaceutical and collector wastewater was studied. A positive effect of sulfate-reducing activity on methanogenic activity was noted for both types of wastewaters, both of which contained sulfate ions. All reactions of methane generation for the tested industrial wastewaters were first-order. The results of this study suggest that the tested wastewaters are amenable to anaerobic treatment.

Keywords Anaerobic treatment · Adapted granular sludge · Non-adapted granular sludge · Industrial effluent

J. Rodríguez-Martínez (✉) · S. Y. Martínez-Amador
Y. Garza-García
Biotechnology Department, Chemistry Faculty,
Autonomous University of Coahuila,
Boulevard V. Carranza, Saltillo, 25000, Coahuila, Mexico
E-mail: jrodrigu@mail.uadec.mx
Tel.: +52-844-4155752
Fax: +52-844-4159534

Introduction

Pharmaceutical industry effluents contain several organic solvents, colorants, acids, bases and a variety of other organic compounds, which are generally treated by costly aerobic processes. Anaerobic decomposition of toxic effluents is attractive due to the lower cost of treatment and biogas generation, which can supplement the energy requirements. There are a few reports on the anaerobic treatment of the pharmaceutical effluent [4, 15]. The anaerobic degradation of different constituents of antibiotic and synthetic drug-based effluents were recently carried out, using methanogenic organisms, sulfate-reducing organisms, nitrate-reducing organisms and iron-reducing organisms [21].

Paper mill effluents are characterized by the presence of color and suspended solids, bad odor, a high concentration of nutrients that cause eutrophication of the receiving waters (carbohydrates, lignin compounds, biocides, surfactants, phenolic compounds, dioxins, furans, resin, wood extractives) and a high overall toxicity [12, 18]. Paper manufacturing generates significant quantities of wastewater, as high as 60 m^3 wastewater t^{-1} paper produced. The raw wastewaters from paper and board mills can be potentially very polluting [23]. Anaerobic treatment has seldom been used for wastewaters from the pulp and paper industry and other branches of the chemical industry [20]. The quality and quantity of brewery effluent can fluctuate significantly, as it depends on various different processes that take place within the brewery (raw material handling, wort preparation, fermentation, filtration, packaging, etc.). Organic compounds in brewery effluent are generally easily biodegradable, as these mainly consist of sugars, soluble starch, ethanol, volatile fatty acids, etc. [5]. The aim of this study was to demonstrate the anaerobic treatment of five different wastewaters with a diverse and complex chemical composition and originating from two Mexican cities. Four wastewaters came from Orizaba (Veracruz, Mexico): amino acid producing industry

(Fermex), paper producing industry (Kimberly Clark), brewery industry (Cuauhtemoc–Moctezuma) and Collector, which receives different types of wastewater and determines which type is more problematic. The pharmaceutical industry wastewater was collected from Ramos Arizpe (Coahuila, Mexico). Two kinds of inoculum were used to study the effect of adapted and non-adapted inoculum with this wastewater.

Materials and methods

Wastewater

Fermex wastewater was generated by an amino acid producing industry (lysine, threonine), Kimberly Clark wastewater was generated by a paper producing industry, Cuauhtemoc–Moctezuma wastewater was generated by a beer producing industry and Collector was a receptor tank for five types of wastewater (Fermex, Kimberly Clark, Cuauhtemoc–Moctezuma, Sabritas wastewater from a potato and corn processing industry, municipal wastewater). These wastewaters originated in Orizaba. The pharmaceutical wastewater was obtained from an industry that produces Penicillin G in Ramos Arizpe. Chemical oxygen demand (COD) for wastewaters from Orizaba were (per liter): Fermex 8.62 g, Kimberly Clark 4.71 g, Cuauhtemoc–Moctezuma brewery 3.05 g, Collector 3.88 g. Wastewaters from Fermex, Collector and the pharmaceutical industry also contained (per liter): 0.83 g, 0.085 g, 1.0 g of sulfate ions, respectively. The pharmaceutical wastewater contained 0.120 gl^{-1} of nitrate.

The studies were carried out with a range of dilutions of the different effluents of industrial wastewaters. Table 1 shows the initial volume (and the concentration of each pollutant: COD, SO_4^{2-}, NO_{3-}) of the Orizaba wastewaters and pharmaceutical wastewater that was diluted to give 40 ml of working volume.

Experimental setup

Anaerobic batch reactors (120 ml vol.), with 40 ml of working volume containing 5 ml of granular sludge, were used for testing the wastewaters collected from Orizaba. About 10 ml of granular sludge were used for the pharmaceutical wastewater. The granular sludge that was used as a kind of inoculum was taken from the anaerobic digester treating brewery wastewater. In the case of pharmaceutical wastewater, two kinds of sludge were used: adapted and non-adapted sludge. Adapted sludge was obtained during 20 days of incubation and had a low concentration of COD. The initial pH for all experiments was 7.0 and the temperature of incubation was 37°C. The methanogenic, sulfate-reducing and nitrate-reducing activities are represented as methane formed [g CH_4 g^{-1} volatile suspended solids (VSS) day^{-1}] and substrates (sulfate, nitrate) consumed (g SO_4^{2-} g^{-1} VSS day^{-1}, g NO_{3-} g^{-1} VSS day^{-1}). Triplicate assays and several controls were used.

Analytical methods

The parameters (sulfate, sulfide, nitrate, COD, VSS) of the wastewaters were determined according to standard methods [1], unless otherwise indicated. Methane, molecular nitrogen and carbon dioxide were determined by gas chromatography (GC) on a Varian GC model 3400, equipped with a thermal conductivity detector and using helium as the carrier gas. Volatile fatty acids (VFA) were analyzed in a Varian GC model 3300, equipped with a flame ionization detector (FID) and using helium as carrier gas. pH was analyzed in a VWR model 8000 potentiometer.

Results and discussion

The batch reactors were evaluated for 670 h (28 days). The series of experiments carried out with wastewaters from Orizaba showed that methane formation varied with the type of wastewater, due to differences in the chemical composition of the wastewaters (Fig. 1). The adapted granular sludge showed a better results. Figures 2, 3 show the velocity of methane formation as a function of COD concentration for different industrial wastewaters. The adapted granular sludge effected a higher biodegradation of COD (in the range 5.5–8.0 gl^{-1} for pharmaceutical wastewater; Fig. 2). The maximum velocity of methane formation was observed at COD concentrations of 4.0 gl^{-1} and 2.5 gl^{-1}, respectively, for paper and brewery wastewaters (Fig. 3, crosses, filled triangles). It also demonstrated that this kind of waste-

Table 1 Initial concentrations (per liter) of nitrate, sulfate and COD of the industrial wastewaters

Initial volume of wastewater (ml)	Fermex		Collector		Kimberly Clark	Cuauhtemoc–Moctezuma	Pharmaceutical		
	SO_4^{2-} (g)	COD (g)	SO_4^{2-} (g)	COD (g)	COD (g)	COD (g)	NO_3^- (g)	SO_4^{2-} (g)	COD (g)
5	–	–	–	–	–	–	0.031	0.20	1.95
10	–	–	–	–	–	–	0.052	0.29	3.41
15	0.389	4.24	0.037	2.37	2.91	1.87	0.070	0.40	4.85
20	0.501	5.91	0.047	2.69	3.27	2.07	0.105	0.55	6.29
25	0.595	7.31	0.063	3.0	3.67	2.24	0.112	0.72	7.93
30	0.741	8.62	0.071	3.6	4.44	2.51	0.126	0.99	9.23
35	0.827	9.74	0.077	3.87	4.71	3.05	–	–	–

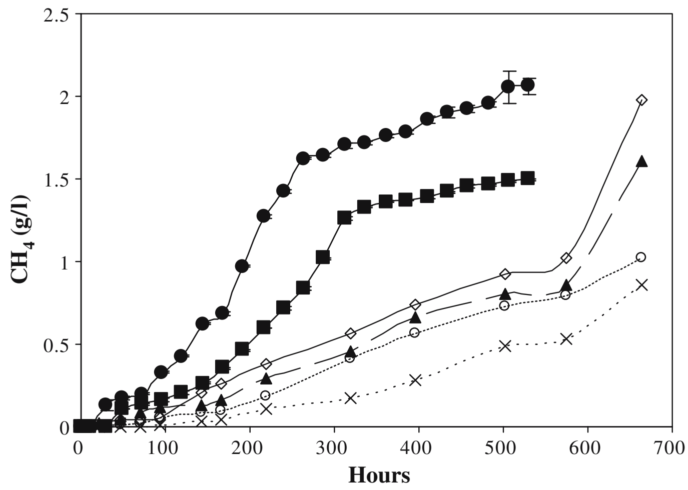

Fig. 1 Kinetic methane formation, in the process of biodegradation of COD from pharmaceutical wastewater for (*filled circles*) adapted and (*filles squares*) non-adapted consortia. *Open diamonds* Fermex, *filled triangles* brewery industry, *open circles* Collector, *crosses* Kimberly Clark

water had an inhibitory effect but this effect was diluted when these wastewaters were discharged into the collector (Fig. 3, open circles). In the case of the amino acid industry wastewater, no negative effect was observed up to 10 g COD l^{-1}, because this kind of wastewater could be easily biodegraded (Fig. 3, open diamonds). Figures 4, 5 represent the kinetics of methane formation at different COD concentrations. Results showed that the formation of methane is a first-order reaction for all wastewaters. The observed results are in agreement with the results for slaughterhouse wastewater discussed earlier [19]. Adapted sludge showed a higher velocity constant of methane formation and methanogenic activity than non-adapted sludge (Table 2). The velocity of methane formation increased with increasing concentrations of COD and was a first-order reaction for the combined wastewater from the collector and for the other wastewaters individually (Fig. 5). It was observed that the amino acid producing industry showed the highest velocity of methane formation and methanogenic activity; and the paper industry showed the lowest activity for both parameters (Table 2). The results further showed that combining wastewaters neutralized the inhibitory effect of paper industry wastewater (Table 2; Fig. 5, crosses). Adapted sludge showed a higher yield coefficient of methane formation than non-adapted sludge from pharmaceutical wastewater (Table 2). Wastewater from the amino acid producing industry showed the highest yield coefficient of methane, followed by brewery, combined/collector and paper industry wastewater (Table 2). A higher COD removal efficiency was observed with higher COD for those wastewaters that contained sulfate (Fermex, Collector, pharmaceutical wastewater). Sulfate reduction is a process that accelerates the conversion of organic compounds [14]. Kim et al. [11] observed that the beneficial effect of sulfate on the degradation of food waste was 76.6% higher than the control, although a delay in methane formation during the treatment of wastewaters

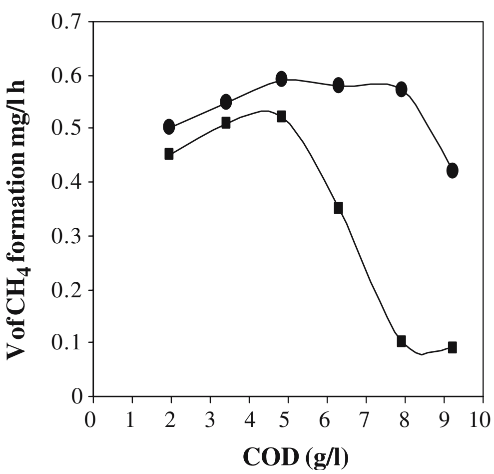

Fig. 2 Reaction velocity of methane formation as a function of different concentrations of COD from pharmaceutical industry wastewater: *squares*) non-adapted sludge, *circles* adapted sludge

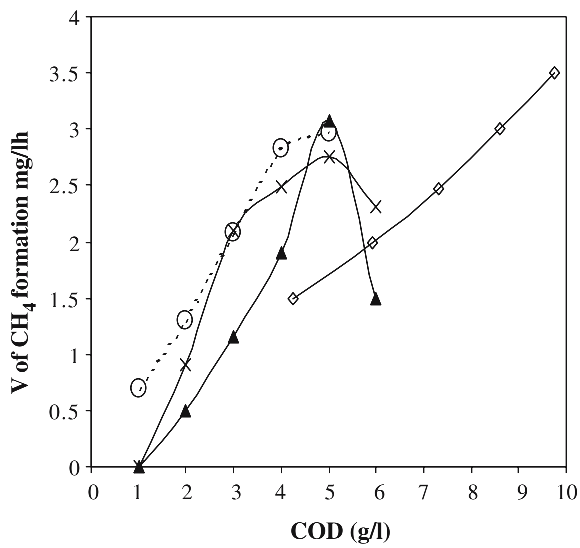

Fig. 3 Reaction velocity of methane formation as a function of different concentrations of COD, from different wastewaters: *crosses* paper industry, *filled triangles* brewery industry, *open diamonds* amino acid producing industry, *open circles* collector

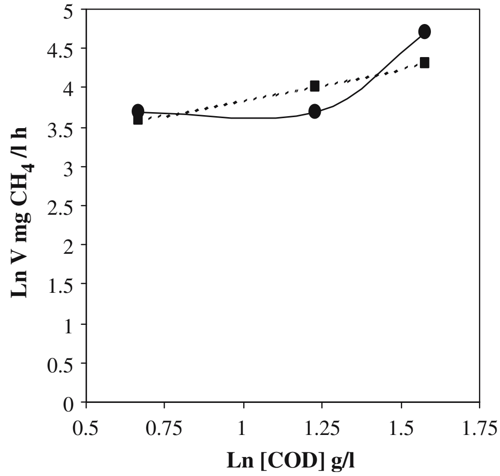

Fig. 4 Reaction velocity of methane formation as a function of different COD concentrations in pharmaceutical wastewater using the equation: LnV= LnK + nLn[COD] for: *squares* non-adapted sludge (y = 0.7635x + 3.0728) and *circles* adapted sludge (y = 0.9975x + 2.8784)

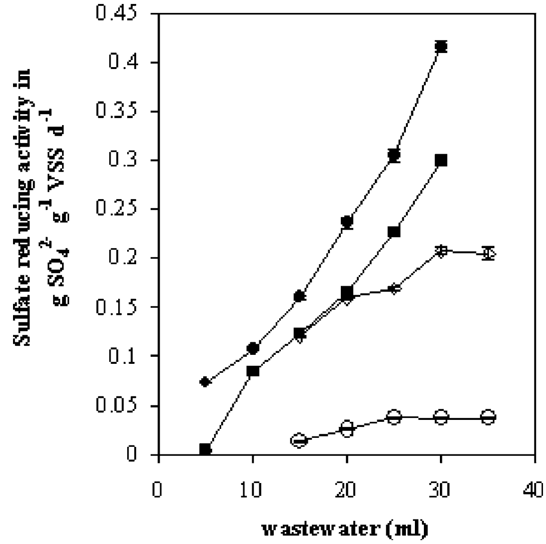

Fig. 6 Sulfate-reducing activity as a function of different sulfate concentrations for: *filled circles* pharmaceutical wastewater using adapted sludge or *filled squares* non-adapted sludge, *open diamonds* Fermex, *open circles* Collector. Temperature 37°C, initial pH 7.0

containing sulfate was observed in many studies [24, 26, 27]. The ratio of COD to SO_4^{2-} is considered to be more important; and several investigations suggest an approximate ratio larger than 10:1 [16, 18]. The COD to SO_4^{2-} ratio of the wastewater of Collector, Fermex and the pharmaceutical industry were 50.0, 11.77 and 9.23, respectively. The sulfate removal efficiency was 100% for these three wastewaters. In the case of pharmaceutical wastewater, the sulfate-reducing velocity increased proportionally with the concentration of sulfate ion (0.99 gl^{-1}). Van Houten et al. [25] demonstrated that concentrations below 450 mgl^{-1} of sulfate did not inhibit sulfate-reducing activity. There is a possibility of that the sulfide from sulfate-reducing microorganisms is utilized by nitrate-reducing microorganisms [6]. In fact, the sulfide in the medium was detected in low concentrations. For example, in the case of pharmaceutical wastewater, the concentration of sulfate was up to 1 gl^{-1} but the amount of sulfide detected was only 3–9 mgl^{-1}, so that the sulfate-reducing microorganisms were not inhibited by this low sulfide [17, 18]. Sulfate-reducing activity increased proportionally with the sulfate concentration. Figure 6 shows the same pattern in dif-

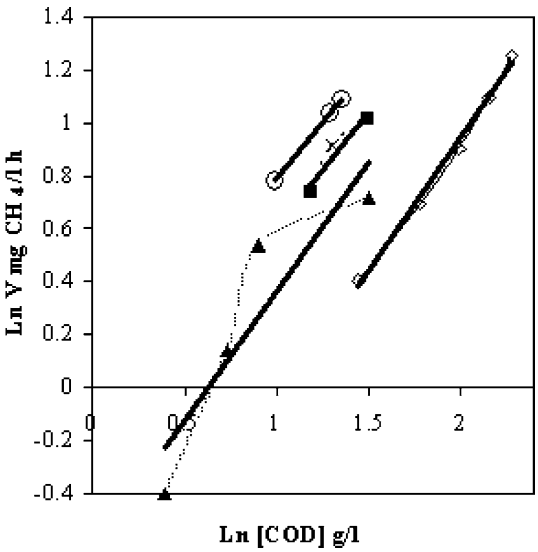

Fig. 5 Reaction velocity of methane formation as a function of different COD concentrations in the function: LnV = LnK + nLn[COD] for: *open diamonds* Fermex (y = 1.031x – 1.0825), *open circles* Collector (y = 0.8509x – 0.0622), *crosses* Kimberly Clark (y = 0.8723x – 0.2678), *filled triangles* Cuauhtemoc–Moctezuma (y = 0.9759x – 0.6082)

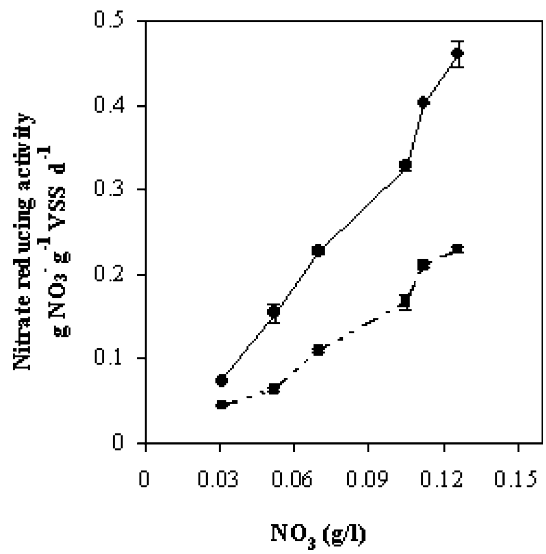

Fig. 7 Nitrate-reducing activity as a function of different nitrate concentrations for pharmaceutical wastewater utilizing: *filled circles* adapted sludge and *filled squares* non-adapted sludge. Temperature 37°C, initial pH 7.0

Table 2 Kinetic data and yield coefficients obtained for anaerobic biodegradation of pharmaceutical industrial wastewater (using both adapted and non-adapted sludge) and industrial wastewaters from Orizaba

Type of wastewater	V_{CH4} (gl^{-1} $h^{-1}$$\times10^{-3}$)	K_v ($\times10^{-3}$ h^{-1})	Methanogenic activity (g CH_4 l^{-1} g^{-1} VSS $day^{-1}$$\times10^{-1}$)	VSS (gl^{-1})	Yield coefficient
Non-adapted	5.2	1.778	3.34	3.0658	0.487
Adapted	5.9	2.16	3.9	3.0083	0.674
Aminoacid producing	3.5	2.1972	5.74	1.22	1.98
Brewery	3.0	1.8371	3.92	1.53	1.60
Collector	2.93	1.046	3.68	1.59	1.024
Paper	2.75	1.370	3.27	1.68	0.858

ferent dilutions of pharmaceutical wastewater that employed an adapted and a non-adapted consortium; and the sulfate-reducing activity had a clear, positive effect due to the adaptation of granular sludge for pharmaceutical wastewater (Fig. 6, filled circles). The efficiency of sulfate and COD removal was improved substantially with the use of adapted sludge. One hundred percent sulfate removal efficiency was obtained in half the time required with the non-adapted sludge [4, 7, 13, 18, 21]. Better nitrate removal efficiency was achieved in less time as a consequence of the increase in nitrate reduction velocity with adapted sludge [2]. The nitrate consumption velocity and nitrate-reducing activity increased with nitrate concentration, due to the increased rate of nitrate utilization [2, 22]. Furthermore, the COD to NO_3 ratio in this pharmaceutical wastewater was optimum at approximately 73:1. Several investigators agree that the increase in nitrate consumption is linear, while some authors propose ratios between 3 and 7, which depends on the type of carbon source [3, 8–10]. Nitrate-reducing activity was superior with adapted sludge for pharmaceutical wastewater (Fig. 7, filled circles) and the tendency was linear when compared to non-adapted sludge, as observed earlier [2]. The pH was maintained stable around pH 7.3–7.8 until the end of the experiment. The accumulation of VFA (acetic, propionic, butyric) was not observed in all cases and the fatty acids formed were consumed totally. The formation of carbon dioxide was proportional to methane formation.

From the results, it can be concluded that the use of adapted sludge for the start-up of wastewater treatment reactors improved the efficiency of COD removal and methane formation. Further, analysis of the kinetics of wastewater treatment for individual wastewaters showed us the possibility of understanding the problems unique to each type of wastewater. This understanding can help us to choose a strategy for combining different types of wastewater to achieve a higher efficiency of treatment and to buffer the inhibitory effects of the wastewater, such as the paper industry wastewater used in this study. It was clearly observed that the kinetics of methane formation was first-order for all the wastewaters tested individually and for the combined wastewater. In addition, it was confirmed that the presence of sulfate ion helped to achieve a higher COD removal and that a COD:SO_4 ratio of 10:1 helped to achieve a higher rate of methane formation.

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