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Methane production from secondary paper and pulp sludge: Effect of natural zeolite and modeling

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HIGHLIGHTS

- The effect of zeolite on methane production from paper and pulp sludge was studied.
- Modeling of methane production by three simplified models was evaluated.
- Doses between 0.2 and 1 g/L of zeolite increased the accumulated methane.
- A dose of 20 g/L of zeolite decreased methane production.
- The modified Gompertz and logistic function models fit the experimental data.

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ABSTRACT

The effect of natural zeolite on methane production from secondary paper and pulp sludge and its modeling are evaluated. Five tests with zeolite concentrations of 0, 0.2, 0.5, 1 and 20 g/L were evaluated at 30 °C. The modified Gompertz equation, the logistic function and the transfer function were evaluated. The results show that doses between 0.2 and 1 g/L of zeolite produce a statistically significant increase of accumulated methane, giving values greater than 183 mL for CH_4/g of VS_{added}. On the contrary, the 20 g/L dose of zeolite reduced the methane production. The modified Gompertz and the logistic function models concur with the experimental data, the former having the best fit.

1. Introduction

The paper and cellulose manufacturing industry is one of Chile's main industrial sectors. The country's production of paper and pulp had increased to 4.94 million tons per year by 2008 [1]. The process produces wastewater that is treated by a conventional primary–secondary treatment. The secondary treatment, namely aerobic activated sludge, generates secondary sludge with high moisture content composed of microbial biomass, cellulose, cell decay products, and non-biodegradable lignin precipitates [2].

One way of treating this pulp and paper sludge (PPS) is anaerobic digestion (AD) to generate methane. This treatment helps to reduce sludge volume, degrading potentially toxic compounds, recovering energy and nutrients that can be applied as fertilizers or added to degraded forest and agricultural soil. Recently, several authors have explored the use of anaerobic digestion in order to recover or reuse secondary sewage sludge from paper mills [2–5]. However, the main problem regarding PPS is the low biogas production compared to other sewage sludge. According to Astals et al. [6], methane yield from sewage sludge coming from municipal wastewater plants varied between 324.5 and 379.7 mL CH_4/g volatile solid added (VS_{added}), while methane yields from PPS ranged from a very low 50 mL CH_4/g VS_{added} for bleached Kraft [7] to 199 mL CH_4/g VS_{added} for chemi-thermo mechanical and Kraft pulp [4]. These values are almost 50% lower than the values reported for methane production from municipal wastewater plants. In order to improve this yield, several pretreatments have been studied, including thermal, ultrasound, ozone oxidation, alkaline, enzymatic and mechanical [8]; however, this process may increase the cost and cause operational problems regarding AD.

A cheaper way to increase methane production is by using zeolite as amendment of anaerobic digestion. Zeolites are crystalline minerals that have cavities forming channels in their structure.

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Because of this, some molecules can go into the channels or cavities, filling the available space. Several researchers [9–12] have found that natural zeolite is a good supporting material in the anaerobic digestion process of different substrates, because it has a high capacity for immobilizing microorganisms or trapping organic materials, making their interaction more accessible in the whole reactor. Several reports have shown that the use of zeolite in the anaerobic digestion of different kinds of wastewater (municipal, piggery industry, synthetic) and solid waste (grass silage) improves methane yield [13]. The effect of natural zeolites on the anaerobic degradation of synthetic substrates such as acetate and methanol was evaluated by Milan et al. [14], showing that the addition of zeolites determined an increase in the apparent kinetic constant of the process and achieved values twice as high as those seen in a control reactor. Montalvo et al. [9] studied the influence of particle size in the range of 0.07–1 mm and zeolite doses in the range from 0.05 to 0.40 g zeolite/g of inoculum (volatile suspended solids, VSS) on the anaerobic digestion of synthetic wastewater, showing that the anaerobic process was favored by the addition of zeolite at doses between 0.05 and 0.30 g/g VSS, with an optimum value of 0.10 g/g VSS. The effect of different natural zeolite concentrations on the anaerobic digestion of piggery waste was studied in batch mode by Milan et al. [10], who found that the anaerobic process was favored by the addition of natural zeolite in doses between 2 and 4 g/L and increasingly inhibited in doses beyond 6 g/L. The effect of adding natural zeolite to the batch thermophilic anaerobic decomposition of pig wastes was also studied at zeolite doses of 0, 4, 8 and 12 g of zeolite/L of waste at 55 °C [12]. In this case, methane production was up to 65% higher in treatments with natural zeolite at doses of 8 and 12 g/L of waste, compared to those without zeolite. Furthermore, in treatments with natural zeolite, the reduction of volatile solids and biological oxygen demand (BOD_5) was statistically significant. Even though the use of zeolite as amendment has shown positive results, there are no studies that evaluate the use of zeolite as amendment in the anaerobic digestion of PPS, and this is one of the goals of this work.

Studying the kinetics of methane production from feedstock(s) is important when designing and evaluating anaerobic digesters. First-order models are common models for describing methane production from solid waste materials compared with soluble substrates [15]. Few studies have applied mathematical models to anaerobic degradation using zeolite as amendment, focusing mainly on the removal of organic matter. Montalvo et al. [9], Milan et al. [10] and Montalvo et al. [11] applied a Contois kinetic model in order to determine the effect of zeolite on the anaerobic digestion of PW, focusing their efforts on reproducing chemical oxygen demand (COD) removal. Recently, Montalvo et al. [16] used the Monod kinetic equation to explain the effect of zeolite on anaerobic digestion of synthetic wastewater. None of these studies applied a model for methane production, so the study of the effect of zeolite on the parameters of three practical mathematical models was another aim of the present work, using natural zeolite in the production of methane from residual sludge derived from the paper industry.

2. Materials and methods

2.1. Experimental setup

Every experimental run considered the installation of twenty 280-mL anaerobic mini-digesters with an effective operating volume of 250 mL. Thirteen of them were meant for measuring parameters in the liquid phase (chemical oxygen demand (COD), volatile solids (VS), pH); five were used to measure methane by liquid displacement using a system shown schematically in Fig. 1; and two were used as controls, one without adding inoculum and one without adding secondary sludge. The mini-digesters operated in discontinuous mode for 33 days, at which time gas accumulation remained constant. Manual stirring was performed once or twice per day before reading the volume displaced by methane.

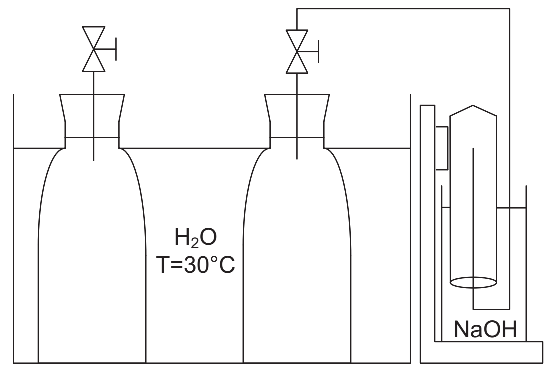

Fig. 1. Schematic of the experimental setup of the anaerobic digestion process.

The volume of the digesters was completed with distilled water, they were stoppered with rubber stoppers and sealed with white silicone to ensure anaerobiosis, and they were covered with aluminum foil to prevent the growth of photosynthetic organisms. All the runs were done in duplicate.

2.2. Inocula, substrate and experimental design

The inoculum was obtained from an anaerobic reactor of the La Farfana Water Treatment Plant of Aguas Andinas in Santiago, Chile. The substrate was secondary sludge from the Liquid Industrial Residues Treatment Plant of Papeles Cordillera, Santiago, Chile. Table 1 shows their characteristics. Zeolite was obtained from a company that commercializes natural zeolite and is located in Quinamávida, Linares, VII Region, Maule, Chile.

In each treatment 25 mL of inoculum and 25 g of sludge were added, completing the reactor's volume with distilled water up to 250 mL. With these quantities, the inoculum-substrate ratio was 0.25 g VS inoculum/g VS substrate in all the assays. The low value of inoculum-substrate ratio (high F/M ratio) was in order to reduce the lag-phase, because of the inoculum coming from an anaerobic digester of municipal wastewater. The zeolite masses were 0, 0.05, 0.125, 0.25 and 5 g for 0, 0.2, 0.5, 1 and 20 g/L concentrations, respectively. For each assay, three weekly measurements were made in duplicate of soluble and total COD, suspended VS, and pH. The temperature in the container was kept at 30 °C using three automatically controlled aquarium heaters.

2.3. Chemical analyses

The following parameters were determined: total COD (t_{COD}), soluble COD (s_{COD}), total and suspended solids, volatile suspended solids, and pH. COD (total and soluble) was measured by colorimetric method according to APHA [17]. Total and suspended solids,

Table 1
Characteristics of pulp and paper sludge and inoculum used in the study ((a) $n = 6$, (b) $n = 8$).

Parameter	Inoculum	Pulp and paper sludge
TSS (mg/L)	10630.667 ± 1307.934$^{(a)}$	–
VSS (mg/L)	16696.667 ± 936.412$^{(a)}$	–
TS (mg/L)	28525 ± 2501.629$^{(a)}$	0.118 ± 0.014 g/g$_{sludge}^{(b)}$
VS (mg/L)	17212 ± 654.413$^{(a)}$	0.107 ± 0.013 g/g$_{sludge}^{(b)}$
pH	7.69	–
%C, dry weight	51.3 ± 1.5	51.1 ± 2.4
%N, dry weight	1.8 ± 0.2	1.5 ± 0.3
C/N ratio	28.5 ± 7.5	34.1 ± 8