

# PRETREATMENT APPLICATION OF MIXED SEWAGE SLUDGE ON SELF-FERMENTATION FOR BIOHYDROGEN PRODUCTION

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The influence of different types of pretreatments had been evaluated to establish their effect on the suitability for hydrogen production from mixed sewage sludge (combination of primary and activated sludge).

Four different pretreatments (thermal shock, freezing–thawing, base and 1-iodopropane) were chosen to compare their impact and effectiveness in the anaerobic self-fermentation production of hydrogen. The major release of biohydrogen was observed in the treatment carried out with NaOH, which also achieved the best removal of methanogenics. This is also the most effective in ratio of conversion to VFA from VS. Best results of potential hydrogen production, *P*, indicate that freezing–thawing treatment gains a 725% compared with raw mixed sludge.

Other parameters as variations in pH, soluble chemical oxygen demand (SCOD), the volatile and total solids and composition of biogas generated were measured during 36 hours of test duration.

**Keywords:** Hydrogen, pretreatment, sewage sludge.

## Introduction

Currently, hydrogen is considered one of the main energy of the future, because it is a clean energy carrier, recyclable, efficient and can be used in energy-efficient devices (fuel cells, for example) to generate electricity (Das, 2001; European Commission, 2004) [1, 2]. Biological processes have the advantage of lower energy costs than thermal (Kapdan and Kargi, 2006) [3] and is especially recommended for waste with high moisture content.

Specific production of hydrogen in an anaerobic acidogenic reactor is produced, usually by bacteria of the genera *Enterobacter* and *Clostridium*. These can form spores under adverse conditions such as changes in pH and temperature, chemical inhibitors and oxidizing conditions

This study examines the influence of different pretreatments on self-fermentation of mixed sewage sludge for bio-hydrogen production: a) alkaline, b) thermal shock, c) freezing–thawing, d) 1-iodopropane. The parameters analyzed were: pH, H<sub>2</sub> production, solubilization of organic matter, Total and Volatile solids and VFA releasing.

## Methods

The tests were carried out in serum bottles of 0.5 L, equipped with a cap with an olive connected to a Tedlar bag to collect generated biogas. The experiment temperature was controlled thermostatically in a water bath at mesophilic conditions (35°C). The tests were conducted under discontinuous conditions (batch), no additional supplies were added during the study period. In both batches were included a control sample (“Ca” and “Cb” samples) to incorporate the possible variations associated with the natural sludge degradation.

The alkaline treatment (named “Ba”) was completed with 8 M NaOH establishing a pH near 10. 1-iodopropane (“Io”) were added at a rate of 0.2 g/L, mixed and kept at room temperature for 30 min. Thermic shock (called “Th”) was performed by boiling the sludge for 15 minutes. Freezing and thawing (“Fr”) was carried out using liquid nitrogen to freeze and thawing was carried out at room temperature

The parameters were: soluble chemical oxygen demand (SCOD), total solids (TS), volatile solids (VS), volatile fatty acid composition (VFA), and the volume and composition of gas generated.

## Results and discussion

Figure 1 shows that alkaline with pretreatment showed the highest release of volatile fatty acids compared with control test (Figure 4). The analysis conducted indicated that acetic (427–1.291 mg / L), propionic (310–571 mg / L) and *n*-butyric acid (138–567) were the main constituents of the volatile fatty acids found in the pretreated sludge.

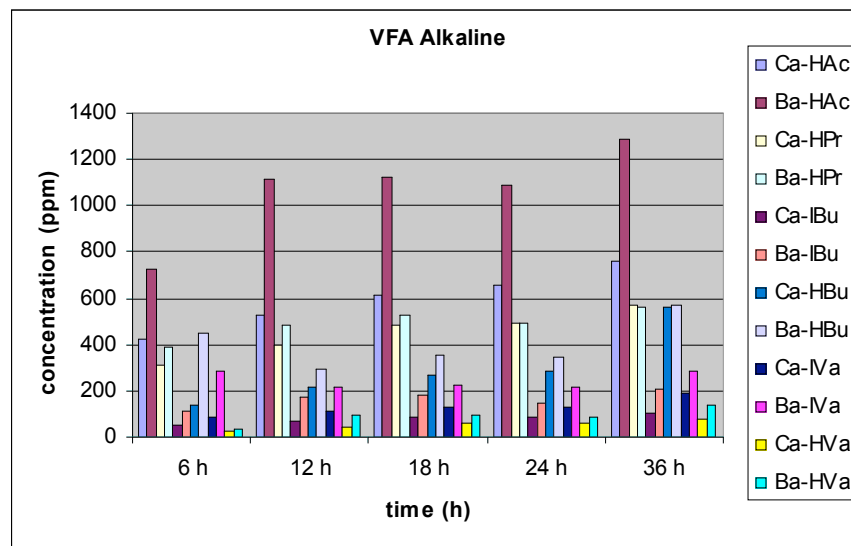


Figure 1. VFA content evolution in the study for alkaline pretreatment.

HAc = acetic acids, HPr = propionic acids, IBu = *iso*-butyric acids, HBu = *n*-butyric acids, IVa = *iso*-valeric acids, HVa = *n*-valeric acids

Khanal et al. (2004) [4, 5, 6, 7] reported that this increasing is suggestive of the presence of *Clostridium butyricum* and other propionate producing species of the genus *Clostridium*, as *Clostridium arcticum*, *Clostridium novyi* and *Clostridium propionicum* in the microbial consortium.

The analysis indicated that some of the pretreatments made are valid in themselves for the self-fermentation of mixed sewage sludge without further addition. The basic pretreatment without subsequent adjustment of pH has been shown effective in the elimination of methanogenic bacteria. Cai et al. (2004) [8] had reported an increase in hydrogen production from alkali-tolerant bacteria. The increased potential for hydrogen production rose to 228%.

Treatment with 1-iodopropane showed how the generation of methane decreases while increasing the hydrogen, but the study time is insufficient to completely elimination of the methanogenic. The reason may be due to the nature of the sludge, which prevents to obtain the desired effects. In the treatment carried out by thermic shock was observed that for the first 30 h of study remained inactive methanogenic population. Due to the conditions of this type of treatment, the physical characteristics of sludge were altered, changing texture and colour, also observed a small clumping of solids, as reflected in the analysis made, although the low releasing of volatile fatty acids, the individual percentages of acetic acid and *iso*-butyric acids detected were similar to those found in the most effective treatment, so it is presumed that this treatment has an effect on the population of producing hydrogen bacteria, reducing their number and slowing the production of H<sub>2</sub>.

Interestingly, no production of methane were found in these samples in the last treatment applied, the freezing and thawing at room temperature, the results obtained in the potential production of hydrogen had been the best, with an approximate increase of 725% compared to the control sample. As for the removal of solids recorded, the TS decreased by 69.59% and 57.20% in VS.

## Conclusions

As a result there was a small amount of hydrogen in control samples (untreated). The highest yields were observed for the samples treated by freezing and thawing (0.0975 mL H<sub>2</sub>/g VS), much higher than values recorded in the corresponding control sample (0.0133 mL H<sub>2</sub>/g VS), representing an increase of more than 725%. The treatment that have proven most effective in the elimination of methane production have been treated with alkali, in which no methane was detected in any collected samples. Treatments carried out by heat shock and freezing-thawing have also proved effective, although the latter is observed that the rate of methane produced low to 0% at the end of this study.

The reasons of the hydrogen consumption in this study are several, among them is the presence of homoacetogenic bacteria capable of hydrogen consuming and spore forming and resist many treatments. Another reason is that the increase of VFA, specially acetic acid, who can inhibit the growth of hydrogen

producing bacteria and therefore the ratio of production. The last reason is that in protein degradation occurs not only H<sub>2</sub> production but also consuming this molecule.

Studies have shown the possibility of using mixed sewage sludge as substrate for the production of H<sub>2</sub> and opens the door to further experiments. Pretreatments to individually and their combination are presented as the basis for the development of techniques for extracting a resource from a waste, giving it added value.

## References

1. Das D., Veziroglu T.N., (2001). Hydrogen production by biological processes: a survey of literature. *International Journal of Hydrogen Energy*, 26: 13–28
2. European Commission (2004) Sustainable energy: the fairy hydrogen. RTD info Magazine on European Research 42
3. Kapdan I.K., Kargi, F., (2006). Bio-hydrogen production from waste materials. *Enzyme and Microbial Technology*, 38: 569–582
4. Khanal, S.K., Chen, W.H., Li, L., Sung, S., (2004). Biological hydrogen production: effects of pH and intermediate products. *International Journal of Hydrogen Energy* 29 (11): 1123–1131
5. Jordan, D.C., McNicoll, P.J., (1979). A new nitrogen-fixing *Clostridium* species from a high arctic ecosystem. *Canadian Journal of Microbiology* 25: 947–948
6. Holdemann, L.V., Cato, E.P., Moore, W.E.C., (1977). *Anaerobe laboratory manual*, 4<sup>th</sup> ed. Blacksburg: Anaerobe Laboratory, Virginia Polytechnic Institute and State University: 1–156
7. Cardon, B.P., Barker, H.A., (1947). Amino acid fermentation by *Clostridium propionicum* and *Diplococcus glycinophilus*. *Archives of Biochemistry and Biophysics* 12: 165–180
8. Cai, M.L., Liu, J.X., Wei, Y.S., (2004). Enhance biohydrogen production from sewage sludge with alkaline pre-treatment. *Environmental Science and Technology* 38: 3195–3202