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Enhancing Anaerobic Digestion and Micropollutant degradation in Wastewater Treatment with Zero Valent Iron

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ABSTRACT

Recent studies have highlighted the incomplete removal of pollutants by biological treatment processes in effluents, especially emerging contaminants, indicating significant environmental risk due to their continuous discharge and degradation products. Among these pollutants, anticancer medications, increasingly detected in surface waters and effluents, represent a particular concern due to their high toxicity. Despite the advantages of anaerobic reactors in wastewater treatment, they do not exhibit high removal efficiencies for emerging pollutants. However, recent research suggests that the addition of zero valent iron nanoparticles (nZVI) can enhance anaerobic digestion and assist in micropollutant removal, making it a promising strategy for sustainable wastewater treatment. To assess the impact of different nZVI concentrations on anaerobic digestion and degradation of anticancer medications, batch assays were conducted in the presence or absence of drugs and nZVI. The results indicated that the ideal concentration was 2 $g.L^{-1}$ of nZVI, showing promising results for biogas production and the quality of the anaerobic digestion process.

Keywords: Anaerobic digestion. zero valent iron. Antineoplastic drugs. Wastewater. Biogas.

1 INTRODUCTION

Antineoplastic drugs, used in cancer treatment, are emerging pollutants present in wastewater, challenging biological treatments by affecting the microbiota and reducing anaerobic digestion efficiency. Additionally, these compounds impact the environment, causing genetic mutations. Mitigating these risks requires improvements in wastewater treatment systems and awareness of proper medication disposal [1]. Further research is crucial to understand and address the environmental and health impacts associated with antineoplastic drugs in wastewater.

Anaerobic digestion (AD) is widely used for organic waste treatment and biogas production. Recently, AD has been applied as a decentralized option for treating hospital wastewater, where micropollutants, particularly pharmaceuticals, pose a significant challenge due to their difficult degradation and potential toxicity [2].

The addition of zero-valent iron (ZVI) has shown promise in enhancing AD performance. ZVI can accelerate organic matter degradation, thereby increasing biogas production. Moreover, ZVI can enhance the degradation of pharmaceuticals in hospital wastewater, facilitating micropollutant removal [3]. Thus, this study aims to investigate the influence of zero-valent iron on the efficiency of anaerobic digestion of synthetic hospital wastewater, focusing on biogas production and pharmaceutical degradation.

2 MATERIAL & METHODS

To evaluate the impact of zero-valent iron nanoparticles on biogas production and quality, without and with pharmaceutical compounds, which were added to the reactors at a concentration of 200 $\mu g \cdot L^{-1}$, considered environmentally relevant [4]. Batch assays were conducted using different concentrations of nZVI (0.2, 0.5, 1, 2, and 4 $g \cdot L^{-1}$). The reactors, with a working volume of 80 mL, were inoculated with anaerobic sludge and maintained at a temperature of 35°C ± 2°C, with constant agitation until biogas production stabilized. The synthesis of nZVI was performed by reducing a 0.27 $mol \cdot L^{-1}$ ferrous sulfate solution with 1.1 $mol.L^{-1}$ sodium borohydride [5, 6].

Table 1. Experimental Reactors

Experiment	Abbreviation	Concentration of inoculum ($gVS \cdot L^{-1}$)	Drug presence*	Zero-valent iron presence**	Substrate
Negative control	NC	10	-	-	-
Positive control 1	PC1		-	-	+
Positive control 2	PC2		-	+	
Positive control 3	PC3		+	-	
Reactors	R		+	+	

* Anticancer drugs at a final concentration of 200 $\mu g \cdot L^{-1}$ each;
** Concentrations of zero-valent iron of 0.2, 0.5, 1, 2, and 4 $g \cdot L^{-1}$.

The pharmaceuticals selected for the study were fluorouracil, cyclophosphamide, etoposide, cytarabine, and methotrexate, commonly used in oncology treatments. Biogas production was monitored daily using a glass syringe to measure the volume of

gas produced. The composition of the biogas was determined by gas chromatography, allowing for the quantification of methane and carbon dioxide.

In addition to biogas production, physicochemical parameters such as pH, total solids (TS), volatile solids (VS), and chemical oxygen demand (COD) were evaluate [7]. These parameters are essential for understanding the efficiency of the anaerobic digestion process and the influence of nZVI on the degradation of organic matter.

3 RESULTS & DISCUSSION

The data from the biogas accumulation reveal varying outcomes with the addition of nZVI (Table 2). Higher concentrations of nZVI, such as 2 $g \cdot L^{-1}$ and 4 $g \cdot L^{-1}$, led to increased biogas production. However, when combined with medications, divergent responses emerged, indicating intricate interactions.

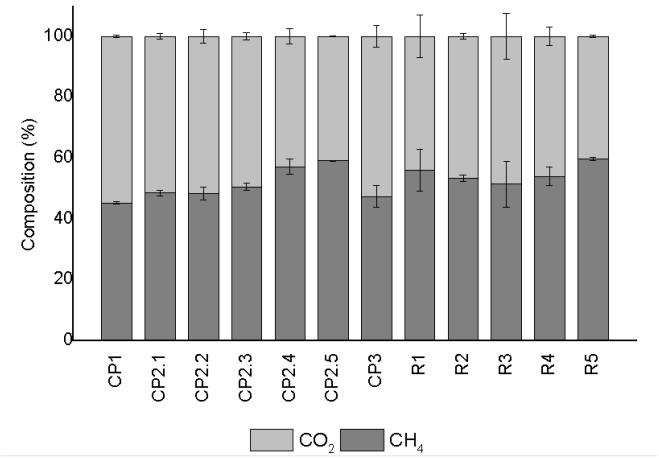
Table 2 - Biogas accumulation.

Experiment	Cumulative Biogas production (mL after 44 days)
CN	16.1
CP1	671.5
CP2.1 (nZVI 0.2 $g \cdot L^{-1}$)	641.2
CP2.2 (nZVI 0.5 $g \cdot L^{-1}$)	720.6
CP2.3 (nZVI 1 $g \cdot L^{-1}$)	665.8
CP2.4 (nZVI 2 $g \cdot L^{-1}$)	695.0
CP2.5 (nZVI 4 $g \cdot L^{-1}$)	681.2
CP3 (Pharmaceuticals 200 $\mu g \cdot L^{-1}$)	652.5
R1 (nZVI 0.2 $g \cdot L^{-1}$ + Pharmaceuticals 200 $\mu g \cdot L^{-1}$)	559.2
R2 (nZVI 0.5 $g \cdot L^{-1}$ + Pharmaceuticals 200 $\mu g \cdot L^{-1}$)	682.2
R3 (nZVI 1 $g \cdot L^{-1}$ + Pharmaceuticals 200 $\mu g \cdot L^{-1}$)	702.8
R4 (nZVI 2 $g \cdot L^{-1}$ + Pharmaceuticals 200 $\mu g \cdot L^{-1}$)	703.2
R5 (nZVI 4 $g \cdot L^{-1}$ + Pharmaceuticals 200 $\mu g \cdot L^{-1}$)	789.2

The reactors with pharmaceuticals showed diverse outcomes in biogas accumulation. While R5, with 4 $g \cdot L^{-1}$ of nZVI and pharmaceuticals, exhibited a notable increase, R1 saw a decrease with both pharmaceuticals and nZVI. Studies showed that adding ZVI (20 $g \cdot L^{-1}$) increased methane production by 11% compared to the control, reducing pharmaceutical intermediates and biotoxicity [8]. Another study with 1.0 $g \cdot L^{-1}$ of nZVI increased methane production by up to 25%, enhancing biogas efficiency and microbial communities [9]. Various nZVI concentrations improved biogas production and micropollutant degradation, indicating complex interactions needing further optimization studies.

The quality of biogas, as measured by methane concentration, significantly improved with nZVI addition. Reactors with 2 $g \cdot L^{-1}$ of nZVI demonstrated a 20% higher methane production than those without. This enhancement stems from nZVI's electron donor capacity, facilitating CO_2 reduction to CH_4 during methanogenesis.

Figure 1 - Methane and carbon dioxide concentration in biogas.



Source: Developed by the author.

The presence of nZVI accelerated biogas and methane production, even in the presence of antineoplastic drugs, through cometabolism. Zero-valent iron acted as an electron donor, easing CO_2 reduction to CH_4 during methanogenesis, while drugs served as additional substrates [10]. This interaction prompted quicker adaptation of anaerobic microbiota and modification of extracellular polymeric substances production, thereby promoting biofilm formation and enhancing anaerobic process stability [11].

4 CONCLUSION

The addition of zero-valent iron nanoparticles in anaerobic digestion has proven to be a promising strategy for improving biogas production and quality. The concentration of 2 $g \cdot L^{-1}$ of nZVI was the most effective, significantly increasing methane production. However, the presence of pharmaceuticals can alter the effectiveness of nZVI, making it necessary to optimize the concentration for each type of substrate used. The results of this study suggest that nZVI can be used as adjuvants in anaerobic digestion, contributing to the sustainability and efficiency of waste treatment systems. Future studies should explore the application of nZVI in larger-scale reactors and evaluate the long-term impacts on anaerobic microbiota and the quality of the biogas produced.

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