Enhancing Smart City Sustainability: Anaerobic Treatment of Semiconductor Industry Wastewater for Improved Efficiency and Environmental Impact

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Abstract- As **cities transition into smart urban environments, managing industrial waste, especially from semiconductor manufacturing essential for smart technologies, becomes paramount. This study assesses the anaerobic treatment of semiconductor industry wastewater, which is laden with heavy metals and organic solvents. Our research focuses on the acclimation of anaerobic biomass and its effectiveness in treating these complex wastewaters over a 132-day period using semi-continuous reactors. We employed a phased approach starting with an initial stimulation using sucrose to boost microbial activity, followed by gradual increases in effluent concentration. The process culminated in stabilization phases where effluent mixtures were managed to evaluate adaptation and efficiency. Throughout these phases, we monitored methanization and Chemical Oxygen Demand (COD) removal, achieving average efficiencies of 61% and 79% respectively. Our findings underscore the complex dynamics between microbial communities and the unique constituents of semiconductor wastewater. While the presence of inhibitory substances challenged methanogenic activity, particularly in the latter stages with higher contaminant loads, the treatment system demonstrated significant resilience. This suggests that while the core anaerobic processes are effective, supplementary pre- and post-treatments could be necessary to handle the high concentrations of contaminants typical in semiconductor wastewater. The study confirms the feasibility of using anaerobic processes to manage the demanding effluents of semiconductor manufacturing, a critical component in smart cities. By enhancing wastewater treatment strategies, this research contributes to the sustainability of smart urban environments, reducing environmental impacts and supporting the continued development of essential smart technologies.**

Keywords- smart cities; Sustainable urban development; Semiconductor wastewater; Anaerobic digestion; Biomass acclimation; Methane production; Chemical oxygen demand.

I. INTRODUCTION

In today's urban landscapes, where the concept of smart cities is becoming increasingly integral to sustainable development, semiconductors play a pivotal role. With a robust market value of $543 billion [1], semiconductors are fundamental to the evolution and functionality of smart city technologies. These materials, known for their specific conductivity properties that can be tailored through doping processes [2], are crucial in determining the performance of electronic circuits and systems.

Silicon, the predominant material used in semiconductor manufacturing, along with other metalloids, forms the backbone of countless smart city applications. From traffic management systems that rely on sensors to public safety solutions empowered by smart surveillance technologies, semiconductors are at the heart of these innovations. They enable the development and efficient operation of LED lighting systems, advanced public transport networks, and integrated communication systems—all essential components of the smart city infrastructure. The production of semiconductors thus underpins not only traditional electronics like smartphones and LED TVs but also the sophisticated microelectronics that drive the smart cities of the future. This interconnection highlights the indispensable role of semiconductor technology in building urban environments that are more connected, sustainable, and responsive to the needs of their inhabitants.

In the evolving landscape of smart cities, the semiconductor manufacturing process plays a pivotal role, requiring high levels of purity to ensure the optimal performance of smart technologies. The complex manufacturing process involves multiple stages including wafer fabrication, oxidation, photolithography, etching, ion deposition and implantation, metallization, and electrical matrix sorting and packaging [3]. These processes use a broad spectrum of chemicals such as metals, solvents, and acids, necessitating extensive cleaning with ultrapure water. In 2022, the consumption of ultrapure water by the semiconductor industries globally was estimated at approximately 5.51×10^8 m³ [4].

The usage of such significant amounts of ultrapure water results in the production of complex WasteWater (WW), characterized by various pollutants like TetraMethylAmmonium Hydroxide (TMAH), phosphoric acid, ammonia, surfactants, organic solvents, and heavy metals [5]. These contaminants, often recalcitrant and environmentally harmful, predominantly exhibit organic characteristics, offering opportunities for biological treatment processes. Anaerobic digestion emerges as a promising method for treating semiconductor WW. Previous researchs validated the effectiveness of anaerobic processes in breaking down chemicals like DiMethyl SulfOxide (DMSO) and TMAH commonly found in these effluents [6][7].

For smart cities, the advantages of anaerobic treatment, such as minimal sludge production, energy recovery via methane production, and the feasibility of compact design, align well with the sustainability goals of reducing operational costs and enhancing energy efficiency [8]. However, the efficiency of anaerobic digestion is contingent upon the concentration of pollutants, as there is a threshold to the degradation capabilities of anaerobic microorganisms.

This study aims to conduct a preliminary analysis to assess the potential of anaerobic biomass for treating recalcitrant effluents produced in the semiconductor industry, underscoring its relevance in supporting sustainable urban development within smart cities. The Materials and Methods (Section II) details the origin and characteristics of the anaerobic inoculum and semiconductor WW (A. Materials), followed by the B. Experimental Setup and Operation, which outlines system configuration, operational parameters, maintenance, and assay duration. The Analytical Methods subsection C, specifies the primary analyses and methodologies employed. In the Results and Discussion (Section III), the complexity and variability of semiconductor WW are examined, highlighting its treatment potential through anaerobic digestion. Tables summarize WW characteristics before and after treatment, with comparative analysis against existing studies. Future research directions and treatment optimizations are also proposed. The Conclusion (Section VI) synthesizes key findings, emphasizing anaerobic digestion's effectiveness and prospects for further study. The paper concludes with Acknowledgments recognizing key contributors and a References section listing all cited sources.

II. MATERIALS AND METHODS

This section describes the materials used and the methods employed in this study.

A. Materials

Two types of effluent were obtained from a semiconductor industry located in northern Portugal, one with chemicals and diluted acid mixture (E1) and the other with a mixture of E1 and strong acids (E2). More specifically, it was also confirmed through the processes carried out by the industry that TMAH, isopropanol, a non-ionic surfactant, sodium persulfate, copper sulfate, citric acid, acetic acid, sulfuric acid, hydrofluoric acid and phosphoric acid were utilized in varying concentrations depending on the needs of production. The tanks from where the effluent was collected contained a mixture resulting from different processes, mainly lithography, packaging, plating, dicing, grinding and laser grooving and the many steps of washing and cleaning. To avoid any setbacks with the strong acidic content in the effluent E2, it was collected after the pH control step. Anaerobic inoculum was obtained from a local MWTP treating both domestic and industrial WW.

B. Experimental setup and operatiom

The experiments were performed on a laboratory scale, in four separate phases, lasting for a total of 132 days, as follows. In the Stimulation phase (36 days) the biomass was only fed with sucrose to enhance the metabolic activity and establish a baseline. The Acclimation phase (30 days) the biomass was fed with a continuous step-increase (10%) in effluent concentration, summing up 10 moments (10%, 13.3%, 17.7%, 23.6%, 31.4%, 41.8%, 55.6%, 74%, 98.5% and 100%). Stabilization 1 phase (15 days) consisted in feeding on 100% effluent. Finally, in Stabilization 2 (51 days) the biomass was fed with a mixture of effluents collected from different periods of the industrial operation, to evaluate a broader and more complex effluent. This phase was also incremented with a Simulated Wastewater (SW) solution made with sodium acetate (representing dissolved acetic acid, a common acid heavily used by this industry) and TMAH with a COD of 145 g L -1.

The anaerobic assays were carried out in four glass reactors, two with a working volume of 5 L and two with working volume of 2 L. A fifth 2 L reactor was used as a control for growing inoculum fed only with sucrose. All assays started with a biomass concentration of 7 g VSS L -1. Neutralized effluent was fed, and samples were collected every three days, with reactors maintained at 35°C. At each phase, nutrients and sodium bicarbonate were added to support digestion [9]. Biomass sludge samples were taken every six days to assess biomass concentration.

C. Analytical methods

Effluent characterization before and after anaerobic treatment followed Standard Methods [10], assessing COD, Biochemical Oxygen Demand (BOD, 5 days, Oxitop®), pH, Electrical Conductivity (EC), Alkalinity, and Total Volatile Acids (TVA). Anaerobic biomass concentration and activity were evaluated via Volatile Suspended Solids (VSS) and Specific Methanogenic Activity (SMA). Methane was purified by NaOH (20% w/w) gas washing [11] and quantified using a syringe [12].

III. RESULTS AND DISCUSSION

The management of wastewater from semiconductor manufacturing is a significant challenge, directly impacting urban sustainability and smart infrastructure. The complexity and variability of semiconductor WW are attributed to the diverse production techniques employed, the mixing of effluents from various processes, and particularly the dilution effects from cleaning operations, as previously highlighted [13]. These factors contribute to the broad range of characteristics observed in semiconductor WW, making it difficult to standardize treatment approaches. The WW samples used in this study are not different, and although they are from the same tank, the difference on collection day is enough to demonstrate high variability in all parameters, as can be observed in Table I. Despite the variations, the characteristics are still within the WW profile of this type of industry [13].

TABLE I. AVERAGE PHYSICAL-CHEMICAL VALUES FOR THE SEMICONDUCTOR WASTEWATER USED IN THIS WORK

Parameters	*Diluted Acids tank (E1)*	*Lowest - Highest values*	*Effluent Mixture tank (E2)*	*Lowest - Highest values*
pH	6.06	4.74 - 9.10	9.47	5.48 - 11.50
EC (mS cm^{-1})	3.93	0.27 - 11.6	4.43	3.49 - 6.20
Alkalinity (mg L^{-1} of $CaCO_3$)	98.18	68.75 - 125	283.33	150 - 425
TVA (mg L^{-1})	245.84	100 - 365.63	233.34	159.38 - 375
Kjeldahl Nitrogen (mg L^{-1})	13.16	11.20 - 14.84	13.72	10.36 - 17.08
Total Phosphorus (mg L^{-1})	1.03	0.27 - 1.64	0.42	0.29 - 0.50
COD (mgO_2 L^{-1})	749.91	270.4 - 1,245.4	757.19	504.1 - 1,114.1
BOD (mg L^{-1})	259.94	162 - 411.1	281.43	184.89 - 353.6
Biodegradable COD fraction (%)	34.66	19.83 - 82.90	37.17	25.39 - 66.3
Total Solids (g L^{-1})	5.63	1.85 - 11.76	3.55	1.93 - 4.39
Dissolved Solids (g L^{-1})	5.35	1.76 - 11.32	3.29	1.63 - 4.32
Suspended Solids (g L^{-1})	0.21	0.03 - 0.54	0.26	0.06 - 0.34
Volatile Solids (g L^{-1})	0.11	0.01 - 0.18	0.13	0.05 - 0.18

The overarching goal of this study was to conduct a preliminary analysis and demonstrate the effectiveness of anaerobic processes for treatment of this WW with high variability in its composition, as has been proposed in previous studies [7][14]. By analyzing the characteristics of the WW, it is possible to determine that it has a considerable biodegradable content, with the presence of macronutrients nitrogen and phosphorus which are essential for microbial metabolism. In addition, most of the solids, and the organics, are dissolved. It is important to note that these favorable conditions for anaerobic processes are not always found for this type of WW [8]. Therefore, it is essential to emphasize the advantages of the application of a cost-effective method capable of WW treatment that enables energy and water recovery. Despite the various favorable conditions, it is important to highlight the presence of highly recalcitrant and inhibitory compounds for microorganisms, such as fluoride [15], copper [16], surfactants [17] and TMAH itself [14], potentially leading to metabolism disruption, but adaptation of the anaerobic microbiota is expected. Table II depicts the results of the treated effluent after 132 days of operation.

TABLE II. AVERAGE PHYSICAL-CHEMICAL VALUES OF FEED AND EFFLUENT FROM ANAEROBIC DIGESTION TREATMENT

Parameters	*Diluted Acids tank (E1)*	*Lowest - Highest values*	*Effluent Mixture tank (E2)*	*Lowest - Highest values*
Feed COD (mgO_2 L^{-1})[a]	1,113.9	837.6 - 1,390.7	1,211.7	901.3 - 1,433.2
Final COD (mgO_2 L^{-1})[a]	230.4	130.1 - 393.8	238.4	163.7 - 370.6
COD Removed (%)	79	71 - 84	80	74 - 81
Final pH[a]	8.04	7.45 - 8.54	8.07	7.53 - 8.66
Final Alkalinity[a]	1,262.90	543.75 - 2,262.50	1,356.78	612.50 - 2,337.50
Final EC (mS cm^{-1})[a]	3.97	2.77 - 4.60	4.42	3.24 - 5.36
Final Total Volatile Acids (mg L^{-1})[a]	58.77	27.50 - 140.62	62.53	33.75 - 126.06
CH_4 Produced (mL)[a]	131.68	12 - 412	111.50	2 - 442
Methanisation Efficiency (%)[a]	66	46 - 83	53	27 - 69
SMA (g CH_4-COD g^{-1} VSS d^{-1})[a]	0.009	0.002 - 0.028	0.011	0.003 - 0.038

a. Global average for each feeding run

It is worth mentioning that methane production remained constant despite the different stages. COD removal was on average 79% for both types of WW, and although the values are lower when compared with other investigations, such amount of degradation is in accordance with other studies that reported COD removal ranging 70-90% with a influent COD of 1,800 mg/L, but when the organic load was increased to 8,000 mg/L the microbial culture was inhibited and COD removal dropped to values below 70% [6]. Another investigation reported a COD removal rate of 50% for a WW containing 1500 mg/L of COD before the acclimation of biomass to TMAH degradation and achieving COD removals of 90% on average after acclimation despite being operated in psychrophilic temperatures [18]. Following studies in such conditions, reported a removal of 96% of COD [7]. It is important to emphasize that in the studies cited, synthetic or diluted WW were used, thus reducing the impact of other contaminants in a real WW.

The methanisation efficiency obtained values ranged between 66% and 56% based on the input gCOD and produced gCOD.CH_4. However, SMA had low values when compared to other works, resembling SMA from reactors with a notable presence of sulfidogenic microbiota [19]. A low SMA and high conversion of COD to CH_4 may indicate that there is little substrate available for all microorganisms, indicating that there is the possibility of generating even more methane when at higher loads. Even considering the potential presence of sulfidogenic microbiota competing for resources, there was no significant impact on methane production, as a high consumption of TVA confirms that there was no accumulation of volatile acids, demonstrating stability in the system. The constant production of volatile acids from acidogenesis was confirmed through the alkalinity reduction throughout the experiment. It is also possible to verify from Figure 1 that there was no accumulation of organic compounds over the different phases, confirming its degradation even when higher loads were added with different mixtures of WW.

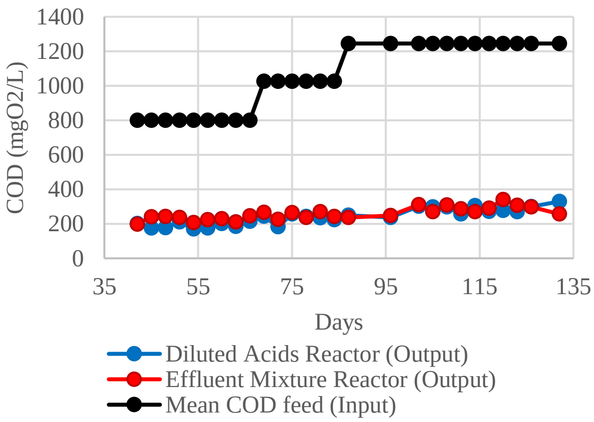

Figure 1. Mean COD concentration for feed and treated effluents, from Acclimation to Stabilization 2 phases.

Stabilization 1 achieved the highest COD removal and methanization, with SMA increasing from 0.0061 to 0.0137, indicating microbial adaptation to the effluent's composition and organic load. In contrast, Stabilization 2, with a mixed effluent containing higher contaminant concentrations, caused system destabilization, confirmed by the SMA decrease to 0.0070, suggesting inhibition. While complex effluents with harmful compounds like heavy metals or TMAH can be treated, their effectiveness is reduced. Other works also experienced a drop in overall treatment efficiency, by presence of heavy metals [20], especially copper [16] and high concentrations of TMAH [13]. Not only the compounds in the effluent can cause inhibitions, but also the degraded products of the digestion can also be inhibitory, such as the case with the degradation of TMAH, where its final product is ammonia which in high concentrations can destabilize the anaerobic system [21].

One study observed that not only the methanogens are responsible for the degradation of TMAH in semiconductor WW, corroborating that a reactor with greater diversity of microorganisms is more capable of degrading complex compounds [22]. Although sulfidogenic microorganisms can destabilize the anaerobic system due to competition for resources with methanogenic, other studies demonstrated that they are capable of mineralizing copper ions, thus being an alternative for reducing this metal in the final effluent and as a form to reduce the impacts generated by toxicity [23]. The presence of sulfidogenic microorganisms can also be effective in degrading other compounds that are not suitable for methanogenic archaea such as surfactants [24].

The experimental design and execution, characterized by semi-continuous feeding, inherently promotes the accumulation of inorganic compounds and other substances that are non-biodegradable by anaerobic microorganisms, such as copper, fluoride, and ammonia, within the reactor. Over time, as these compounds progressively accumulate, the efficiency of the anaerobic treatment is expected to decline, despite the system's adaptation to the WW. This context is possible to occur even in other types of reactors and in continuous systems due to a greater flow of effluent to the reactors, therefore, it is necessary to consider strategies such as pre and post treatments for this type of WW. Numerous studies have already sought the combination of treatments to increase the treatment efficiency of these effluents. Considering the increase of biodegradation to improve the degradation of organics, different authors proposed the use of oxidative systems as a pre-treatment to achieve this, either by using ozone [25], Fenton [26] or anodic oxidation [27] with varying degrees of efficiency. As a post-treatment for the removal of anaerobic degradation products, such as ammonia, authors have studied the use of aerobic and anoxic systems [28] reaching a maximum removal of nitrogen of 63% along with a TMAH reduction between 70 and 100%. One study combined a crystallization reactor filled with quartz salt and a sulfate reducing bioreactor to remove copper, reaching 99% and 70% removal of copper and COD, respectively [23]. Alternatively, electrochemical processes can complement anaerobic treatment by facilitating the removal of solids, including heavy metals by electro flotation, or promoting the degradation of complex compounds by electrooxidation [29].

IV. CONCLUSIONS

This study demonstrated that semicontinuous bioreactors inoculated with anaerobic microorganisms from a MWTP can effectively treat WW from the semiconductor industry. On average, methanization and COD removal efficiency were 61% and 79%, respectively, with methane production of 0.1 mL of CH_4 per mg of COD. The continuous production of methane, TVA consumption, alkaline decline and the absence of COD accumulation confirmed system stability. Low SMA and high methanization suggest limited carbon sources for microorganisms. The potential presence of sulfidogenic biota may help remove inhibitory compounds like copper and surfactants. The increased organic load and effluent complexity reduced treatment efficiency, highlighting the need for pre-treatment to improve biodegradability and post-treatment to remove inhibitory byproducts. Further research at larger scales is needed to validate these findings in industrial settings.

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