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Enhancing Biodegradation of Industrial Wastewater into Methane-Rich Biogas Using an Up-Flow Anaerobic Sludge Blanket Reactor

Lindokuhle Ngema *, Devona Sathiyah , Emmanuel Kweinor Tetteh and Sudesh Rathilal

Green Engineering Research Group, Department of Chemical Engineering, Faculty of Engineering and the Built Environment, Durban University of Technology, Durban 4001, South Africa
* Correspondence: ngemaL673@gmail.com or 21513491@dut4life.ac.za

Abstract: Anaerobic digestion (AD), the oldest technology used for treating waste, converts organic matter into biogas in the absence of oxygen. The current efforts focuses on improving the digestion of a local industrial wastewater to produce biogas and treat water for reuse. A lab-scale up-flow anaerobic sludge blanket (UASB) reactor operated at 37 °C was employed for the biodegradation the industrial wastewater. A one-factor-at-a-time (OFAT) approach was used to study the effects of influent chemical oxygen demand (CODin), hydraulic retention time (HRT), and magnetic nanoparticles (magnetite) on UASB biogas and COD elimination from digestate wastewater. The optimum HRT for the biodegradation of municipal wastewater was found to be 21 days with contaminants' removals of 94%, 90.1%, and 98.9% for COD, color, and turbidity, respectively. The addition of magnetite resulted in 225 mL of cumulative biogas produced with 73% methane content, and treatability efficiency of 85%. The most influential factor was magnetite load, which stimulated the microbial activity via redox catalytic reaction in degrading the high organic wastewater (9590 mg COD/L) into biogas production. The prospects of upgrading lab-scale of this technological concept for bioenergy production is viable to mitigate wastewater management and fossil fuel environmental challenges.

Keywords: anaerobic digestion; biogas; biodegradation; magnetic nanoparticles; wastewater

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1. Introduction

The increase in South Africa's national population has caused an upsurge in household and industrial electricity demand. To meet the current demand, there has been an increase in the utilization of fossil fuels, as over 70% of the country's electricity is produced from coal [1]. As a result, the CO_2 emissions increased significantly, contributing to the issues of climate change. The effects of climate change has become more pressing, and significant measures must be taken to safeguard the Earth from overheating [2]. The world is currently concentrating on reducing primary energy demand in order to minimize CO_2 emissions and mitigate the greenhouse impact. In recent years, there has been a lot of interest in the production of biofuels from organic waste. This approach addresses the issue of waste management while generating biogas. The utilization of wastewater and sewage sludge has become one of the most researched technology in the production of biogas. The resulting biogas can be used directly to generate power, or be upgraded to biomethane and used as a fuel, or fed into the gas network [3]. As a result, the biodegradation of wastewater via anaerobic digestion has gained global interest in the production of biogas. Anaerobic digestion (AD) technology is an attractive way of treating wet organic wastes from energy and nutrient perspectives, where microorganisms break down and convert organic matter into biogas in the absence of oxygen under strictly anaerobic conditions [4]. Biogas produced through AD is the low-carbon green energy carrier resulting from the degradation of organic matter in an oxygen-free environment.

Following the development of the energy crisis, anaerobic digestion technology has advanced at a rapid pace. Even though AD offers many advantages, it faces significant problems that prevent it from being applied in a variety of industries. Low biogas yield has been reported to be caused by a lack of process control and optimization [5]. One of the major technological problems is the formation of toxic intermediate composites, including volatile fatty acids (VFA), due to the presence of acidogenic microorganisms, and the concentration of toxic metals in wastewater [6]. Other difficulties include high financial costs (operation and transportation), insufficient buffer capacity, and process instability [7,8]. These are caused by a pH reduction during the first stage of digestion and the inhibition by ammonia, long-chain fatty acids, and hydrogen sulfide. This proves that anaerobic digestion is very sensitive to toxicants and their presence can inhibit the process and result in process failures [9,10]. Another significant challenge is the lack of appropriate reactor design, where reactor design is still usually created by the rules of thumb. Overall, wastewater characterization, biodegradability, bacterial activity development, accessibility, CH_4 production enhancement, and nutritional balance are regarded as major hurdles to the effective generation of biogas [11].

During digestion using the UASB system, agitation typically improves system performance by providing greater interaction between substrates and microorganisms while reducing the production of scum, which can inhibit gas movement through the surface. By adopting excellent agitation in the anaerobic digester, such as localized build-up of heat, intermediates such as acids and bases from the pH regulating system might also be avoided. Mechanical mixing, biogas recirculation, or slurry recirculation can all be used. Investigations examining the influence of mixing on the overall efficiency of anaerobic digesters suggest that mixing by slurry recirculation outperforms mechanical impeller and biogas recirculation with an increase in COD removals [12,13]. When added into an AD system, all three types of mixing greatly enhance treatment efficiency when compared to unmixed digesters. Furthermore, slow mixing rates have been demonstrated to result in increased methanogenic activities in the operation of anaerobic bioreactors [14].

Anaerobic digestion efficiency may be increased by either appropriately changing the existing digester design or adopting appropriate advanced operating procedures. Therefore, low VFA concentrations in the effluent results in excellent sludge retention, and consistent reactor performance, and the up-flow anaerobic sludge blanket (UASB) reactor is destined to be superior to traditional procedures [15]. As the name implies, effluent enters the UASB reactor from the bottom of the tank and travels upward through a layer of sludge blanket before being released from the top of the tank. The setup is intended to improve the interaction between the wastewater and the mixed culture sludge by lowering the up-flow velocity. Similarly, solid retention is improved because the relatively heavier solid part settles to the bottom, far from the effluent outflow at the top. This, in turn, adds to the easier granular solid formation, which is frequently associated with improved treatment efficiency. As a result, the UASB system is preferred because it promotes good settleability, can handle large biomass concentrations, provides excellent solids/liquid separation, and can operate at high loading rates [14].

To improve AD performance and enhance biogas production, many researchers suggest the introduction of trace elements in the form of nanoparticles to the AD feedstock. In anaerobic digesters, nanoparticles (NPs) enhance direct interspecies electron transfer, serving as excellent immobilization matrices and preventing the selection of resistant bacteria and genes, as well as dominating metabolic pathways of microbial communities [16]. Amongst many metallic NPs, iron NPs are excellent additives to the AD process due to their ability to lose or gain electrons, creating oxides/hydroxides on the metal surface [17–19]. The iron oxide NPs with unique properties slowly dissolve to supply the living microorganisms with the required iron ions without causing toxicity to the bacteria. The authors of [20,21] found that the use of Fe_3O_4 results in a 180% increase in biogas production and a 234% increase in methane production if applied in optimum anaerobic conditions. However, excess iron generates toxic free radicals for the effect of Fe^{2+} ions on the AD of organic matter, which affects the stability and growth of the microbial community, thus, affecting methane production after the first four days.

Several operating variables influence the performance of the anaerobic digestion process. These include substrate-to-inoculum ratio, carbon-to-nitrogen ratio (C:N), temperature, pH, HRT, volatile fatty acids (VFA), organic loading rate, toxicity accommodation, nutrients, volatile solids (VS), total solids (TS), and alkalinity. These operating variables are very significant in assessing the performance of the AD process and give a warning of system disturbances that may arise so that preventive measures can be performed appropriately early in the system [14]. The operating variables affecting the anaerobic process have to be properly controlled and well-designed in order to optimize the efficiency of the process, improve stability, enhance the treatment of biological wastewater, and avoid process inhibition. Hence, the one-factor-at-a-time (OFAT) method is a good choice for investigating the effect of operating variables on the AD process. Most AD studies focused on the optimization of pH, VFA, and temperature, with fewer studies on HRT and organic loading rate.

Currently, the inefficiency of AD technology for the production of biogas from South Africa's wastewater is associated with varying physicochemical properties and lack of process optimization. Furthermore, the presence of biodegradable biomaterials affects performance and the quality of biogas produced from the digester. Therefore, this study investigated the biodegradation of local industrial wastewater into bioenergy using an up-flow anaerobic sludge blanket reactor operated batch-wise. The aim was to study the effect of HRT, magnetite load, and organic loading rate (OLR) on biogas production and chemical oxygen demand (COD) degradation using the OFAT method.

2. Materials and Methods

2.1. Materials

Chemicals used for the synthesis of magnetic nanoparticles included sodium hydroxide pellets—NaOH of 98% purity (CAS, Columbus, OH, USA, No. 1310-73-2), ferrous sulphate heptahydrate—$FeSO_4{\cdot}7H_2O$ of 99% purity (CAS, No. 7782-63-0), oleic acid—surfactant of 90% purity (CAS, No. 112-80-1), and ferrous chloride hexahydrates—$FeCl_3{\cdot}6H_2O$ of 98.9% purity (CAS, No. 10025-77-1), which were all analytical grade obtained from Sigma Aldrich, South Africa.

2.2. Wastewater and Analyses

Wastewater was collected from two local South African wastewater treatment plants in the KwaZulu-Natal province. It was kept in gas-tight containers to retain industrial properties prior to characterization. A Hach DR 3900 spectrophotometer (Hach, Loveland, CO, USA) was used to measure color, total organic carbon (TOC), total dissolved solids (TDS), phosphorus, nitrates, and chemical oxygen demand (COD) before and after digestion. A Hach 2100N turbidimeter was used to measure turbidity. Table 1 shows the characteristics of the two local wastewater streams. Stream 1 from a local industrial wastewater treatment plant has a relatively low organic content and low concentration of contaminants. The second stream is composed of municipal wastewater and sugar refinery wastewater in equal proportions. It has high organic content, dark yellow color, and is nutrient-rich (nitrates and phosphates), which makes it suitable for biogas production through biological treatment. Compared to other streams in South Africa, brewery wastewater has low organic content with high nutrient strength due to acids used during brewing processes [22].

Table 1. Characteristics of two local wastewater streams.

Containments	Stream 1	Stream 2
COD (mg COD/L)	4320 ± 12	9590 ± 58
TOC (mg TOC/L)	18.2 ± 2	200.6 ± 2
TDS (ppt)	3.07 ± 2	15.69 ± 0.7
Turbidity (NTU)	1480 ± 16	3590 ± 14
Color (Pt-Co)	2725 ± 24	22,100 ± 60
Phosphorus (mg PO_4/L)	3.2 ± 0.2	52.1 ± 0.2
Nitrates (mg NO_3/L)	65 ± 1.1	512 ± 0.18

2.3. Magnetite Nanoparticles Synthesis

The magnetite (Fe_3O_4) NPs used was prepared in-house via the co-precipitation technique with details reported in previous works [19,23]. Of interest, 2.5 L stock solutions of Fe^{2+}/Fe^{3+} were prepared and mixed homogeneously in a 1:1 volume ratio (0.5 L/0.5 L). The pH was then adjusted to 2 by dropwise addition of 2 mL surfactant to the mixture (Fe^{3+}/Fe^{2+}). A microemulsion was then formed by continuously agitating at 15 rpm for 2 h, while adjusting the pH with 250 mL of 3 M NaOH. At a pH of 10–12, a black precipitate was formed and was heated to 70 °C for 2 h (ageing). The precipitate was then washed with distilled water and ethanol, where the supernatant was decanted. Oven drying was performed at 80 °C for 12 h, followed by 1 h calcination at 550 °C. The success of synthesizing Fe_3O_4 as reported was affirmed by analytical techniques such as BET, XRD, and FTIR [24,25]. It was found that the active BET surface area of 27.59 m^2/g, pore volume of 0.008 cm^3/g, and pore size of 1.43 nm of the Fe_3O_4 enhanced the biological activity.

2.4. Biogas Production Up-Flow Anaerobic Sludge Blanket (UASB) Reactor Setup

An up-flow anaerobic sludge blanket (UASB) reactor of 10 L capacity was employed with 8 L working volume and 2 L headspace. To maintain mesophilic anaerobic conditions, water from a water bath with a constant temperature of 37.5 °C was continuously circulated through the water jacket of the reactor. The reactor had several ports, as shown in Figure 1: the two top ports were used for (1) loading and purging the system and (2) gas collection. The side ports were used as sampling points for monitoring the quality of effluent and for desludging the reactor. During operation, wastewater and the activated sludge were fed into the system at a constant ratio of 5:3 with magnetite dose varying for each experiment, purged with nitrogen to create an inert atmosphere, and allowed to stabilize for two days after purging with nitrogen. Thereafter, the production of biogas was monitored using the downward displacement technique and the biogas composition was characterized at the end using gas chromatography (GC). The quality of effluent was examined every three days using the DR 3900 Hach spectrophotometer. The removal percentage for the contaminants was calculated using the equation below, where C_o and C_f represent initial concentrations and final concentrations, respectively.

$$\text{Removal efficiency } (\%) = \frac{C_o - C_f}{C_o} \times 100$$

3. Results and Discussion

3.1. Effect of Hydraulic Retention Time on Biogas Production and COD Removal

The effect of the HRT on the natural anaerobic digestion (AD) of municipal wastewater with low organic content without additives was monitored. During the AD process, microorganisms require time to adapt to a new environment before they can produce methane. In this study, the first five days had no production of biogas and COD degradation, as shown in Figure 2a, and 2b. The microorganisms responsible for the biodegradation process were probably still adapting to the environment. After five days, a gradual increase in biogas production and COD reduction was achieved, with an exponential increase in both biogas and COD reduction between days 9–18. A slow performance towards the end of digestion was achieved between days 19–21 and thereafter, no AD performance was observed between days 22–30. These findings are in agreement with the study by [26], which reported that the best performance in anaerobic digestion of municipal sewage waste was achieved between days 10–20 under mesophilic AD conditions.

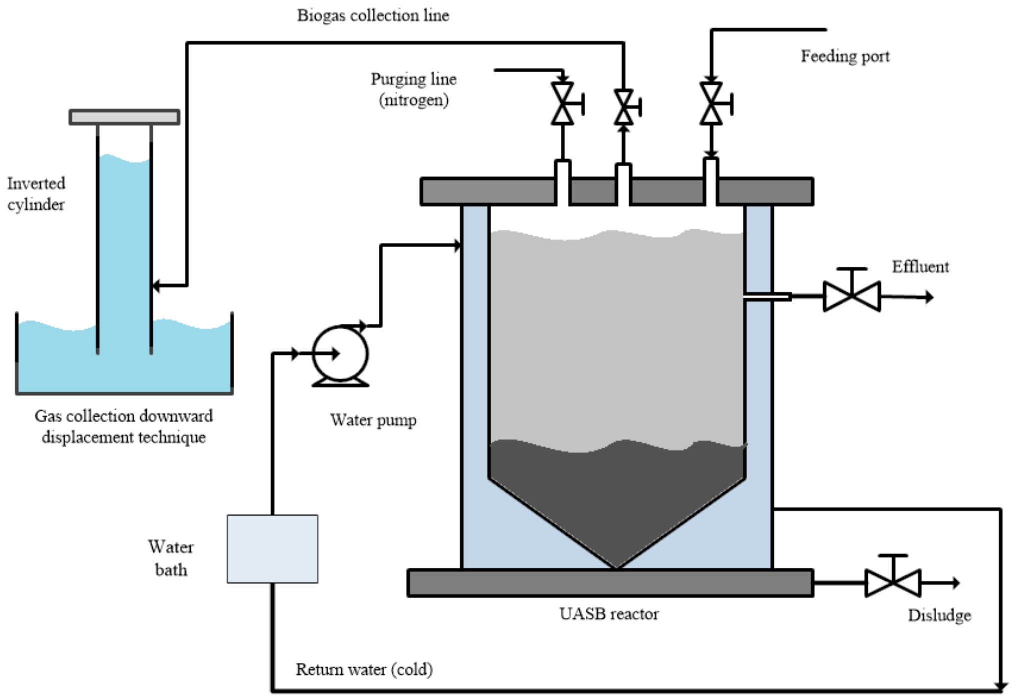
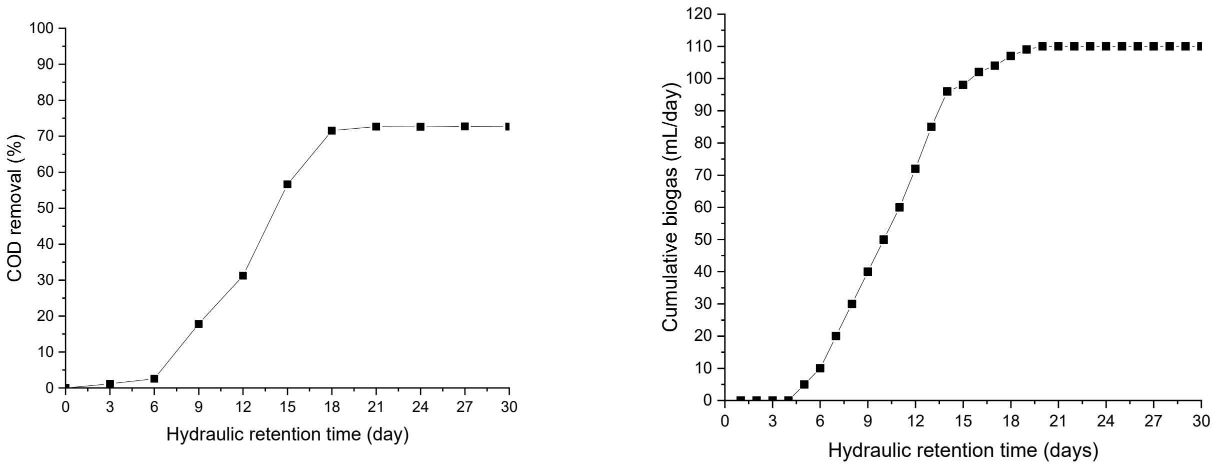


Figure 1. An experimental setup consisting of the UASB reactor and the downward displacement gas collection technique.

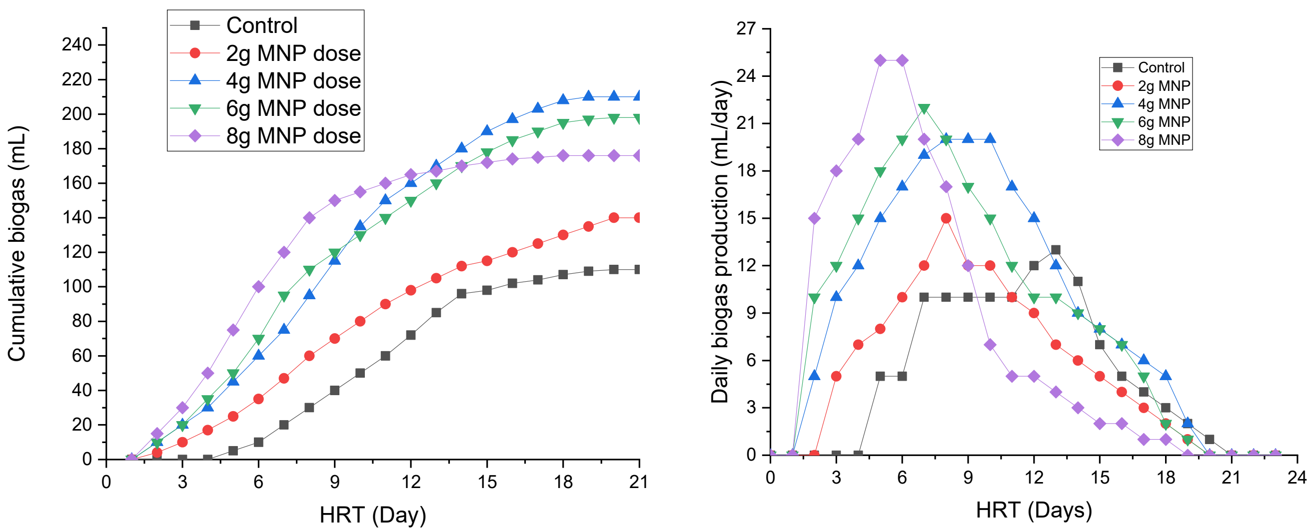


(**a**) (**b**)

Figure 2. Effect of hydraulic retention time on (**a**) cumulative biogas generation; (**b**) degradation of chemical oxygen demand (COD).

3.2. Effect of Magnetite Loading on Biogas Production and COD Removal

The AD system was operated with various magnetite doses in a range of 0.25–1.0 g/L with an increment of 0.25 g/L at a constant HRT of 21 days. The graph of cumulative biogas can be useful in investigating bacterial adaptation and growth during AD. Figure 3a shows the performance of each dose in biogas production and bacterial adaptation.



(**a**) (**b**)

Figure 3. Effect of magnetite load on (**a**) cumulative biogas for the duration of AD; (**b**) daily biogas production.

It is clear that the production of biogas at the start of the period for all the digester systems varies with the amount of magnetite loaded. The amount of time it takes for microorganisms to adjust to their new environment is determined by the first steady rise of biogas accumulation, which is commonly referred to as the lag phase period (acclimatize) [27]. As evident from the graph in Figure 3a, the control has a lag phase of 5–6 days, suggesting that it takes longer for the microorganisms to fully adapt to the traditional AD system. The use of magnetite is found to reduce the lag phase of the AD process. This is because the use of magnetite in anaerobic digestion improves the interspecies electron transfer, which ultimately enhances biogas production [19,25,28]. Due to the high surface area of magnetite at the nanoscale, the reaction is relatively fast [29], making it interact with the sludge cell membrane, causing structural changes in the cells that eventually result in bacteria-permeable membranes. As a result, more bacteria find their way to attack sludge, increasing overall biogas production [16,28].

The best-performing digesters in terms of lag phase are the 4 g, 6 g, and 8 g MNP digesters, which have lower lag phases, fewer than 3 days. Following the lag phase, all digesters reach the exponential stage where the cumulative biogas output grows significantly due to methanogen exponential growth. The 6 g and 8 g MNPs show the highest maximum growth rate between days 4 and 10. However, due to the very high magnetite concentration, the 8 g digester experiences overloading, which results in a rapid decrease in biogas generation after 9 days. The addition of excess Fe ions to the anaerobic microbial community gives rise to toxicity and excess reactivity, thus, hindering the growth and activity of microorganisms [30].

The trend of the 6 g digester in Figure 3b suggests that there is a disturbance in biogas generation between days 9–10, which sees the 4 g digester surpassing all other digesters with a steady increase in biogas generation. This could be the effect of excess magnetite, which promotes the formation of toxicants and inhibits the sensitive methanogenic activities during AD, thus, meaning a decrease in biogas production up to day 18. The daily biogas production in Figure 3b confirms that the 8 g MNP digester has the highest biogas production, reaching its peak of 25 mL/day within 6 days, however, after 9 days the biogas production is very low. The 6 g digester also reaches its peak production of 23 mL/day on day 7 and a gradual decrease is seen after day 9, which is due to MNP overload. The 4 g digester is at peak production between days 9–12, with a production rate of 20 mL/day, followed by a gradual decrease after day 12, towards completion of organic degradation within the digester. The 2 g and control digesters reach their peak production of 15 and

12 mL/day on days 8 and 7, respectively, because of low and no magnetite in the reactor to promote the growth and activity of microorganisms. The five digesters generated cumulative biogas in this order; 4 g > 6 g > 8 g > 2 g > control, with values of 210, 190, 175, 140, and 110 mL, respectively. Therefore, the addition of 4 g to the 10 L UASB reactor results in the highest biogas production. This is in agreement with studies by [25] that show there is an optimum quantity for nanoparticles in stimulating biogas production.

In addition to biogas production, the degradation of organic content in the form of chemical oxygen demand (COD) increases exponentially with the addition of magnetite. The trends in Figure 4 confirm that the highest COD removal of >90% is achieved in the digester dosed with 4 g of magnetite. The reduction in organic content corresponds to the generation of biogas with microorganisms degrading and converting it into biogas.

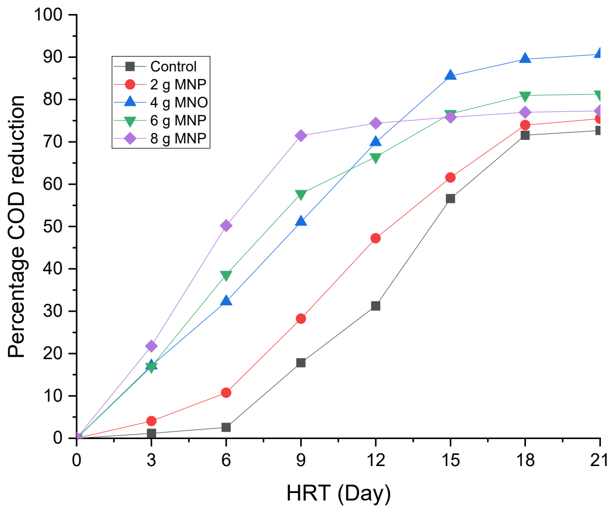


Figure 4. Degradation of chemical oxygen demand (COD) for the five digesters over the optimum AD period.

3.2.1. Biogas Quality

The use of magnetite supports the methane-producing microorganisms during anaerobic digestion. Figure 5 shows that the methane content in biogas generated without the addition of magnetite is low (55%), however, when magnetite is introduced, the grade of biogas improves, with methane content reaching 73%. Previous studies reveal that the methane content in biogas produced during the digestion of municipal wastewater is generally low because of relatively small concentrations of suspended and dissolved organic and inorganic solids. Previous studies by [31] reveal that the utilization of iron in magnetite by the microbial community and the potential mechanism of promoting interspecific iron uptake improves the carbon conversion efficiency of organic matter during anaerobic digestion, thus, an increase in methane content occurs.

3.2.2. Effect of Magnetite on the Overall Treatability Efficiency for the UASB System

The overall treatability efficiency of the digester was monitored in the removal of turbidity and color in the final effluent, as presented in Figure 6a,b. The control digester achieves the lowest removal percentages of 67 and 79% for the removal of color and turbidity, respectively. On the other hand, the 4 g digester outperforms all the digesters in the removal of color (91.2%) and turbidity (98.9%). The removal of color and turbidity corresponds to the degradation of dissolved and suspended solids, which are converted to methane-rich gas by microorganisms. The microbial community in the 4 g digester is well-adapted to the environment, which sees them continuously converting the organics in wastewater throughout the digestion period to produce cleaner effluent. The 6 g digester is the second-best performing, with color and turbidity removals of 89% and 92%, respectively.

The 8 g and 2 g digesters both achieve removals of 70–80% in color and above 80% for the removal of turbidity.

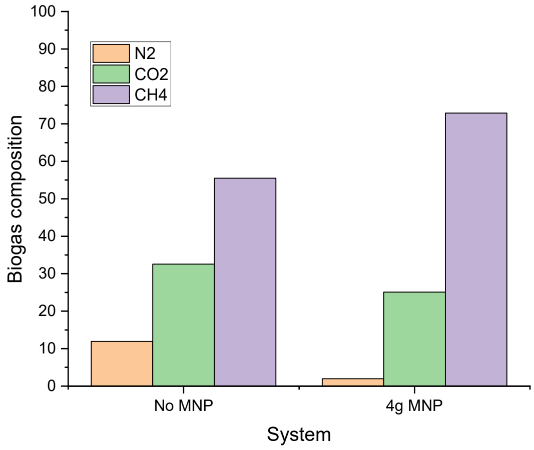


Figure 5. Comparison of the quality of biogas produced with and without magnetite for the same stream of wastewater.

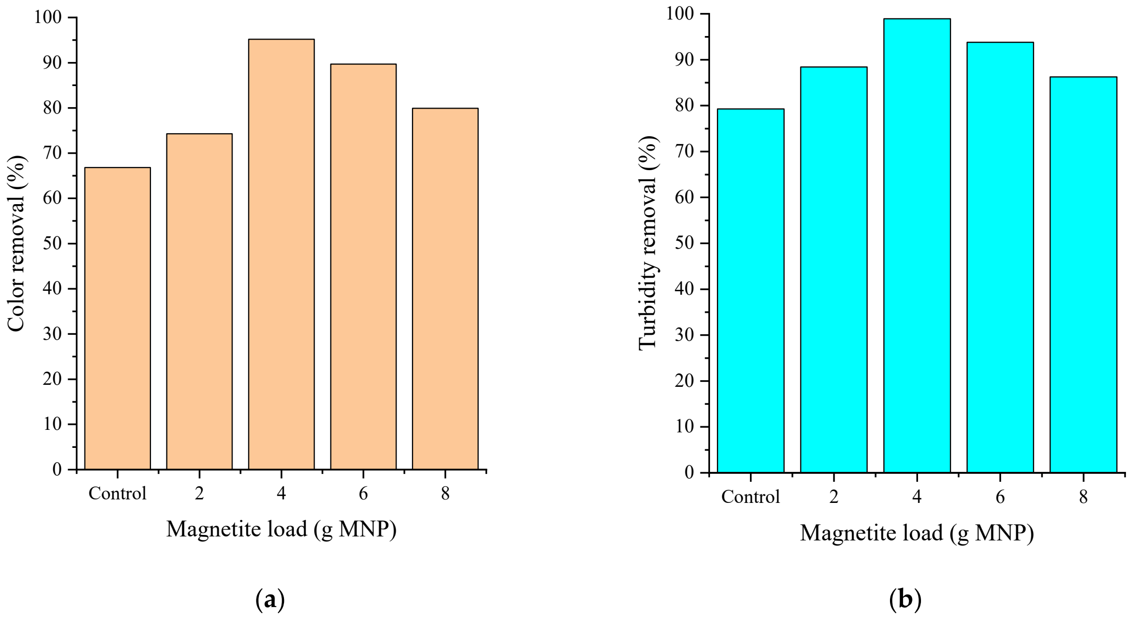
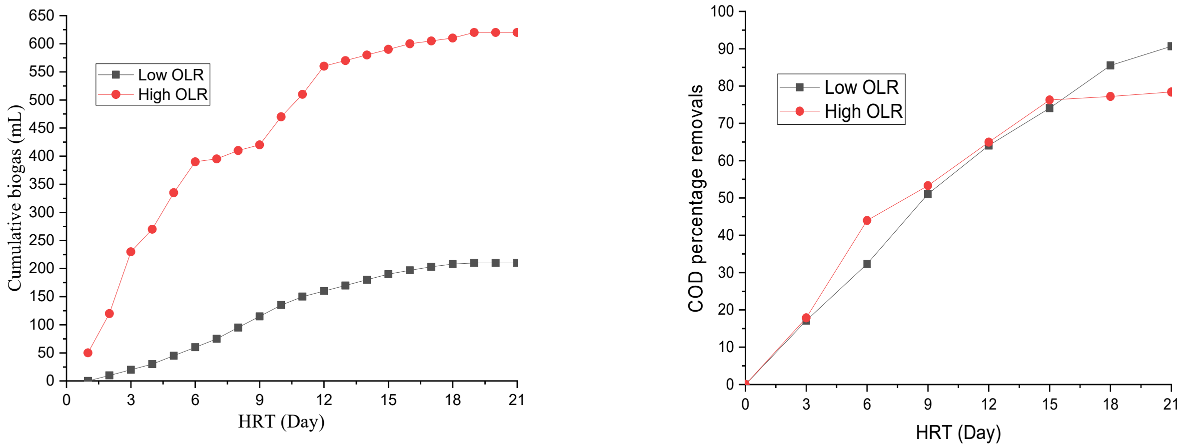


Figure 6. Effect of magnetite load on (**a**) color removal (%); (**b**) turbidity removal (%).

3.3. Effect of Organic Content on Biogas Production and COD Removal

The impact of the organic loading rate was studied on the response of the digester using the HRT for 21 days and a magnetite load of 4 g. The two streams compared were municipal wastewater and a mixture of municipal and sugar refinery streams with high organic content and both being nutrient-rich, as presented in Table 1. Figure 7 shows a 300% increase in cumulative biogas with the increase in organic content from the mixed stream. This is a result of high organic content (CODin of 9590 mg/L) and total dissolved solids exposed to microorganisms for degradation. Compared to municipal wastewater, this stream achieves a low reduction in contaminants even though it has a high biogas production. An increase in organic content results in a decrease in pH due to the accumulation of VFAs and long-chain fatty acids (LCFA) [32]. The study by [33] also reveals that LCFA and the presence of organics that are difficult to degrade are inhibitory to all groups of microorganisms, hence, the AD of high organic content results in 70–80% removal of contaminants.



(a) (b)

Figure 7. The effect of organic loading rate on (**a**) cumulative biogas production; (**b**) degradation of chemical oxygen demand (COD).

Effect of Organic Content in the Treatability Efficiency for the Digester

The effect of organic content in the removal of water contaminants for the digester is presented in Figure 8. The digester with high organic content achieves 65% in the removal of color and 75% in the removal of turbidity. This confirms that this stream has highly dissolved and suspended solids, with dark-yellow color and high viscosity. Although biogas production increases exponentially for this digester, a post-treatment step is necessary for further reduction in contaminants to produce cleaner water and to meet wastewater discharge standards.

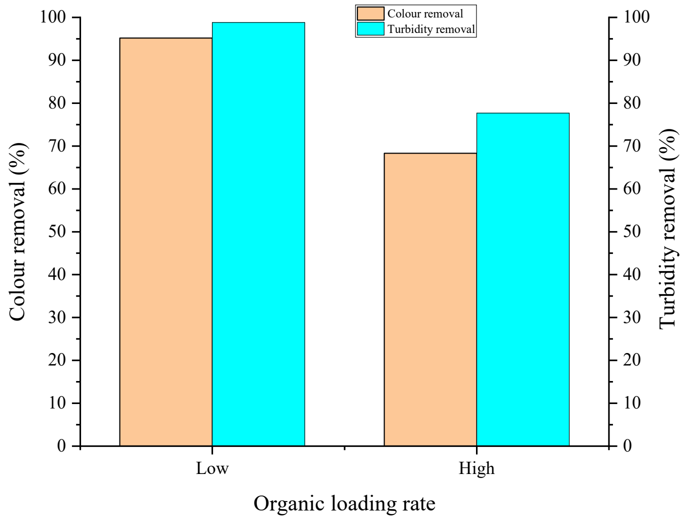


Figure 8. Effect of organic loading rate on the removal of color and turbidity.

4. Conclusions

In this study, the effect of magnetic nanoparticles (magnetite) along with hydraulic retention time and organic loading rate were studied in the degradation of municipal wastewater into bioenergy. This was carried out in the UASB reactor using the OFAT system at constant mesophilic temperature and solid-to-liquid ratio. The conventional AD of the municipal wastewater was monitored over 30 days to allow adaptation and the stimulation of bacterial activity. With such a low concentration of solids and organics in municipal wastewater, the maximum degradation and biogas production was achieved between 18–21 days. This is due to the use of the UASB reactor that allows the settleability of solids and contact between organics and microorganisms. A shorter HRT would be economically favorable, since it reduces the cost of operation in terms of labor and energy consumption. To further enhance the performance, the effect of magnetite addition was studied by varying magnetite load from 0.25–1 g/L and compared to the control system. The addition of magnetite reduces the lag phase by stimulating early bacterial activity and increases methane content in biogas by 40%. Furthermore, a significant increase in the removal of contaminants is achieved with the addition of 0.25 g/L (4 g) magnetite with COD reduction, color, and turbidity removals reaching 91%, 95%, and 98.9%, respectively. It is evident that the iron ions in magnetite play a significant role in the activity of microorganisms. The 4 g dose (0.5 g/L load) and 21 days HRT were further investigated in the digestion of highly concentrated wastewater effluent for biogas production. The production of biogas increases by over 300% with the increase in organic loading rate, however, there is a decrease in the removal of color, turbidity, and COD reduction compared to the other digesters, which, therefore, warrants a post-treatment step for this stream for the production of cleaner and reusable effluent. Conclusively, the addition of magnetite has the potential to improve the anaerobic digestion of municipal wastewater and increase the production of biogas. These findings form the baseline of upscaling a lab-scale UASB setup into a pilot plant.

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