APPLICATION OF ULTRAVIOLET LIGHT EMITTING DIODES FOR THE ADVANCED OXIDATION OF GUAR GUM

THESIS

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THESIS

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Abstract

Guar Gum (GG) is one of the problematic water pollutants connected to hydraulic fracturing. There is a pressing need to investigate appropriate unit operations that can be employed to protect the aquatic environment. This study investigated the use of light-emitting diodes (LEDs) in the advanced oxidation process (AOP) of GG. Chemical oxygen demand (COD) removal provided mixed results, depending on the concentration of hydrogen peroxide (H_2O_2) in solution, and was between (0-95%) for H_2O_2-to-GG ratios between 7.0 and 176.3 g H_2O_2/g GG. COD removal was greatest at the lowest H_2O_2-to-GG ratio of 7.0 g H_2O_2/g GG. Additionally, the COD removal was near 0% at the higher H_2O_2-to-GG ratio of 176.3 g H_2O_2/g GG. These results were partially explained by the measured relative absorbance of GG and H_2O_2, which showed that H_2O_2 absorbed 8 times more UV light than GG. This means that the hydroxyl radicals were not inhibited by the absorbance of the GG. The AOP effluent was not chemically identical to the influent and a small pool of transformation byproducts were likely present in the effluent. UV LED/H_2O_2 AOP treatment of GG had no statistically significant effect on microbial respiration.

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Andrew W. Davenport

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List of Acronyms/Abbreviations

AOP = advanced oxidation process

BOD = biological oxygen demand

COD = chemical oxygen demand

CWT = centralized waste treatment

DI = deionized

EPA = Environmental Protection Agency

FPW = flowback and produced water

FrM = first moment of area

Fe = iron

GG = guar gum

HF = hydraulic fracturing

H_2O_2 = hydrogen peroxide

LED = light emitting diodes

mA = milliamps

mg = milligrams

mL = milliliters

O_2 = oxygen

OH = oxygen-hydrogen bond (hydroxyl radical)

POTW = publicly owned treatment works

SDWA = Safe Drinking Water Act

TiO_2 = titanium dioxide

UIC = Underground Injection Control

UV = ultraviolet

UV-Vis = ultraviolet-visible

VOC= volatile organic compounds

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I. INTRODUCTION

1.1 Background

1.1.1 Purpose

The purpose of this thesis was to determine the effectiveness of advanced oxidation processes (AOP) on the degradation of guar gum (GG). The focus of the thesis was to utilize an AOP that combined ultraviolet (UV) light emitting diodes (LED) with hydrogen peroxide (H_2O_2).

1.1.2 Hydraulic Fracturing Process and History

Hydraulic fracturing (HF) is a method to extract oil and natural gas from the ground [4]. The process involves fracturing rock formations that contain oil and natural deposits via injection of high-pressure liquids, which consist of base fluids (water or nitrogen gas), proppants (sand-like material), and additives (chemicals to ease the flow of the fluid throughout the piping). Once the fluid is mixed, it is pumped through thousands of feet of piping embedded into the ground [4].

Next, the proppant in the mixed fluid penetrates the rock fracture and keeps the fracture open. Then, the pressure in the piping is released to pump the natural gas and oil from the rock back up to the surface for extraction and collection [4]. Once the fluid returns to the surface, the oil and natural gas are separated from the flowback and produced water (FPW), which contains hydraulic fracturing fluids as well as salts,

chemicals, and radioactive material from the fracture site. Finally, the FPW is shipped either to an injection site for disposition, to a treatment plant for cleaning, or to a HF site for recycle and reuse [4].

The HF process has been around since the 1960s [4]. However, there has been a recent surge in the US in the use of the process. This is due to the advent of new technologies, which has rendered the process more cost-effective. According to the Department of Energy, from 2000 to 2015, HF has accounted for 50% of US crude oil production [1]. However, HF has potential environmental impacts that could be severe if not addressed.

1.1.3 HF Regulations

There are limited federal regulations posed on HF. For example, according to the Energy Act of 2005, HF is exempt from the Safe Drinking Water Act's (SDWA) policy on Underground Injection Control (UIC) program, which is used to regulate the siting, construction, and operation of chemical injection wells [2][4]. As result of this legislation, the chemicals used in the process are not regulated as potential contaminants unless the HF mixture includes diesel fuel [2][4].

The Environmental Protection Agency (EPA) collaborated with industry stakeholders and developed a revised guidance for deep injection practices that was tailored to oil and natural gas HF activities for diesel fuel. Furthermore, many HF sites utilize this practice for HF fluids that do not contain diesel fuels. Additionally, the EPA revised regulation 40 CFR Part 435 on June 28, 2016 that has prohibited FPW from utilizing publicly-owned treatment works (POTW) [3]. This limits the disposition

options for HF sites. Currently, a study is underway to determine the treatment effectiveness of FPW through private wastewater treatment facilities [3]. Without the necessary federal regulations in place to oversee HF, possible environmental impacts can occur.

1.1.4 HF Impacts.

The EPA released a 2016 report on the possible impacts of HF on drinking water [5][8]. In the report, they stated five conditions that could potentially affect drinking water availability and use. They include water withdrawal during times of low water availability, spills due to mishandling of FPW, injecting HF fluids into wells that are not structurally sound, discharging inadequately-treated FPW to surface water, and disposal or storage of FPW into unlined pits which can contaminate the groundwater [6][9].

Currently, the disposal methods for FPW include reuse of the FPW at HF sites, treatment in centralized waste treatment (CWT) plants for industrial wastes, and disposal through deep injection (Class II Wells). A 2015 study by Veil Environmental, LLC estimated that 93% of FPW from the oil and gas industry, which includes HF, were disposed of via deep injection into Class II Wells [5-6][8]. Additionally, there are concerns about earthquakes being caused by deep chemical injection. This has the potential to reduce the availability of deep injection as an option for disposal in the future [6][9]. With the potential environmental impacts due to HF activities as well as the limited options for disposition, treatment options must be discovered for the contaminants to return water back into surface and ground water.

1.1.5 Advanced Oxidation Process

AOPs are treatment options used to remove organic materials from water. There are many forms of AOPs, but the focus for this thesis is AOP via UV LED and hydrogen peroxide (H_2O_2) because this process was prevalently utilized in treatment facilities and has the potential to efficiently and sustainably provide clean water. The process depends on the production of hydroxyl radicals, highly reactive chemical species that are capable of oxidizing a wide range of chemicals.

1.1.6 Guar Gum

GG is a substance processed from guar beans. It is utilized as an additive in an assortment of products such as food, pharmaceuticals, explosives, oil drilling, and well drilling. For oil and well drilling operations, GG thickens the HF fluids to carry the proppant into the fractured rocks, which forces the rock to stay open and create a pathway for the oil and natural gas to pump through the piping [7]. According to the EPA's 2016 "Report on Hydraulic Fracturing Fluids", additives make up the smallest portion of the overall composition of hydraulic fracturing fluids. However, they have great potential to impact drinking water quality [5][8]. Furthermore, out of the disclosed chemicals on HF sites, GG was disclosed on 37% of well sites between January 1, 2011 and February 28, 2013 [5][8]. The need to treat hydraulic fracturing fluids and produced water is vital since the contaminants have the potential to directly and indirectly impact the military.

1.2 Research Justification

Currently, HF is performed in the following states: California, Colorado, Kansas, Louisiana, Montana, New Mexico, North Dakota, Ohio, Oklahoma, Pennsylvania, West Virginia, Wyoming, and Utah. Many of those states have multiple Air Force bases located within proximity, which include bases such as, but not limited to, Wright Patterson AFB, OH; Minot AB and Grand Forks AFB, ND; and Joint Base San Antonio, TX. As the options for disposition diminish, treatment practices will be necessary to clean the water before returning to surface and ground water. Accidental or improper discharge of chemicals used in HF can cause severe damage to public health and the environment. According to the Executive Summary of the 2016 EPA Report, between January 2006 and April 2012, 151 spills of HF fluids or additives were discovered near well sites in 11 states [5][8]. Also, spills of HF fluids could cause potential natural disaster scenarios for the areas impacted, which can result in the use of the National Guard to mitigate the situation. By analyzing components of HF fluids, treatment could be utilized to limit the amount of environmental impacts in the future.

1.3 Scope

1.3.1 Objective

The experiment tests whether the GG component of HF water can be degraded by AOP via UV/H_2O_2 by utilizing a small reactor in the lab with two sets of UV LEDs with a maximum current of 200 milliamp (mA). The reactor will only pump 2 milliliters (mL) of fluid per minute from a thoroughly mixed 250 mL sample.

1.3.2 Assumptions

One of assumptions during the experiment is that the solution will be thoroughly mixed. Second, the sample of GG tested will be filtered prior to use to remove any suspended particles (large particles in the sample that are floating that did not mix thoroughly) in the solution. This is to ensure that the data collection devices in the experiment can accurately measure the sample from the start of the experiment to the end of the experiment.

1.3.3 Limitations

One of the limitations of the experiment is that not all of the 1,800 reported chemicals that are in FPW are being analyzed due to the limitation in time as well as complexity[5][8]. The 1,800 chemicals include radioactive and toxic material, which would be difficult to experiment in the laboratory due to the dangers of the substances. Further, many of the additives in HF fluids are proprietary blends, so retrieving the chemicals will be difficult to achieve. Instead, the thesis is focused on one component of the HF process to create a profile for how to treat the fluids and will recommend future research to create a large profile for the rest of the substances. Also, the testing will be utilizing a small reactor with a flow rate of 2 mL/minute. A typical treatment plant will have millions of gallons of fluids moving per day, which is not feasible to reproduce in the lab.

1.4 Objective

1.4.1 Research Questions/Hypotheses

The first question the AOP experiment addressed was the relative absorbance of GG and H_2O_2. Next, the experiment was to determine the effect of H_2O_2-to-GG ratio on GG removal in the UV LED/H_2O_2 AOP. Finally, the experiment was to determine the effect of UV LED/H_2O_2 AOP on microbial respiration.

The hypothesis of this thesis was that the relationship between the H_2O_2-to-GG ratio and GG removal would be governed by the relative absorbance of GG and H_2O_2. If the absorbance of the GG was higher than the H_2O_2, then the rationale was that the light from the UV LED would not penetrate the GG solution to react with the H_2O_2 compounds. As a result, the AOP would provide a miniscule pool of hydroxyl radicals to react with the organic pollutant. However, if H_2O_2 absorbed at a higher value than GG, then the pool of hydroxyl radicals should be abundant. As a result, the COD removal should generally be significant, and an increased H_2O_2-to-GG ratio should result in improvements to AOP performance.

1.4.2 Materials and Equipment.

The experiment for AOP treatment included a digital power supply to regulate the amount of voltage and current pumped into the UV LEDs utilized in the experiment. Next, UV LEDs were used as a light source to react with the H_2O_2 at a drive current of 200 milliamps (mA). H_2O_2 was used to produce hydroxyl radicals, which were neutral

compounds that are highly reactive, in the GG solution. The hydroxyl radicals are used to target the organic pollutant in the solution. A reactor was utilized react the GG solution with the UV LED light source. A pump was attached to the reactor to move the fluid throughout the AOP treatment. Finally, a Agilent Technologies Cary 60 Ultra-violet-visible (UV-Vis) spectrophotometer was used to measure the amount of absorbance of the GG solution as it left the reactor. Absorbance was an indication of the concentration of the GG solution. The sample is compared to the absorbance of deionized (DI) water from the 200 to 400 nanometer (nm) wavelength. The goal in the experiment was to determine whether the initial absorbance range decreased during the AOP treatment.

Additionally, the AOP treatment used a COD kit to determine the concentration of GG in the solution. To perform this experiment, samples were taken throughout the AOP treatment and mixed with a dichromate reagent. Finally, influent and effluent samples were taken to perform a respirometry experiment. A respirometer was used to measure the rate of respiration of the microorganism. As the organism consumed O_2, it will produce carbon dioxide. The respirometer will measure the contaminant at the beginning and end of the AOP treatment to determine the differences in the samples to control samples.

II. Literature Review

2.1 Introduction

2.1.1 Key Terms

There are several common terms relevant to this thesis topic. First, AOP is a type of chemical process used for the treatment of organic and some inorganic chemicals. This is accomplished by creating hydroxyl radicals, which are bonds of one hydrogen and one oxygen that are highly reactive with other chemicals. The goal of the treatment was to either bond with the contaminant to form water or degrade the original contaminant to create smaller byproducts.

Another term is UV AOP, which is a form of AOP that utilizes an ultraviolet light source, such as mercury lamps, the sun, or newer technologies such as light-emitting diodes (LEDs) to react with a chemical (such as hydrogen peroxide or ozone) to form hydroxyl radicals. Finally, H_2O_2 scavenging occurs when hydroxyl radicals react with H_2O_2. This often occurs when excess H_2O_2 is present in solution. This will prevent the hydroxyl radicals from reacting with the chemical that needs to be degraded, thus inhibiting the AOP.

2.1.2 Scope of Review

The scope of the literature will first discuss conventional processes for degrading chemicals and the limitations of the conventional processes in regards to hydraulic fracturing fluids. Second, the literature review explains AOPs as well provide a body of research on the degradation of multiple chemicals with the processes, in particular

through UV lights. Next, the scope will focus to chemicals degraded or inactivated by UV LED-driven AOP. Then, the research discusses GG, one of the components of hydraulic fracturing fluid, and what other processes have been utilized to degrade the organic material. Finally, the literature review discusses the gaps in the research of GG's degradation through UV-LED/ H_2O_2 AOP.

2.2 Literature Review

2.2.1 Conventional Methods for Treatment and its Limitations

Water is treated with several processes. Typically, a POTW includes three treatment stages: primary, secondary, and tertiary [10]. Primary treatment is used to remove material that is easy to separate from water. This includes processes such as chemical usage to clump the materials together (coagulation and flocculation), followed by a basin for gravity to settle out the larger particles from the water (sedimentation), or through the use of semi-permeable membranes to separate out the material from the water (filtration) [10]. Secondary treatment utilizes biological processes (e.g. microorganisms or activated sludge) to consume the contaminants in the water.

Finally, some treatment plants utilize tertiary treatment to treat specific components in the water that were not removed through the primary and secondary treatment processes. This is the final stage of treatment prior to the water being delivered for consumption or returning to either a surface or ground water source. This includes processes such as filtration (reverse osmosis), transferring the liquid contaminants into airborne contaminants (air stripping), or removal of bacteria and

virus through chlorine, ozone, or UV light (disinfection) [9]. However, the typical methods have difficulty with FPW due to the high-levels of dissolved solids (e.g. salts) in the water as well as the radioactive components from the FPW. Recently, the EPA has prevented the use of POTWs to accept FPW for treatment due to the hazardous chemicals and byproducts in the water [3].

Furthermore, FPW contains substances including radioactive materials and dissolved salts that can affect the efficiency of biological treatment in a POTW due to the resistance of the chemicals to the treatment or toxic components in the substance affecting the microorganisms utilized [3]. As a result, the EPA is conducting studies on the CWTs to determine the efficacy for either a treatment method for the fluids prior to returning back to surface or ground water sources or as an avenue for pretreatment prior to going to a POTW for final treatment [3]. The goal of this research is to determine whether a pretreatment option is available to degrade components of FPW for the chemical safe for further treatment in a POTW. One of those pretreatment options is AOP.

2.2.2 Types of AOPs

AOP is typically utilized in the tertiary stage of a typical wastewater treatment plant due to the high cost of the process in comparison to conventional methods. However, it is gaining traction in use due to the robustness of the method in comparison to conventional chemical or biological processes as the organic compounds are resistant to the methods (e.g. activated sludge, filtration, etc.) [11-15]. Next, AOPs create hydroxyl radicals that oxidize a broad range of chemicals [11-15]. Finally, AOPs

can be used with other processes, such as a treatment after biological methods with compounds that are not biodegradable or used as a pretreatment to convert compounds to biodegradable byproducts before biological processes [15].

The types of AOPs include, but are not limited to: ozone (O_3), O_3 and H_2O_2, UV light, UV light and H_2O_2, UV light and peroxone (O_3 and H_2O_2 mix), fenton reagent (iron (Fe) and H_2O_2), and photocatalysis (UV radiation and a catalyst substrate) [10]. The body of evidence is growing on the effectiveness of AOPs for the degradation of organic compounds in pharmaceuticals [11][13][16-20].

For example, for the degradation of phenol, fenton reagent had the fastest degradation, while UV/H_2O_2 combination showed the highest degradation rate of the UV AOPs [11]. Conversely, VOCs were tested with UV/H_2O_2, fenton reagent, and combination of fenton/UV and it was determined that UV/H_2O_2 degraded VOCs by 80% without any loss to efficiency, while the fenton process was only able to remove 32%, and fenton/UV combination was only able to remove 45% in 120 minutes of reaction [20]. Also, six pharmaceutical chemicals (e.g. clofibric acid, propranolol, etc.) were treated with ozonation (O_3-only), UV/H_2O_2 combination, and UV/titanium dioxide (TiO_2) combination. The results of the experiment stated that ozonation and UV/H_2O_2 were able to reduce the toxicity of the pharmaceuticals after the treatment, while titanium oxidation performed poorly as toxic by-products were created from treatment [17].

However, each of the AOPs have positives and drawbacks. The fenton process utilizes iron catalyst in solution with H_2O_2 to produce hydroxyl radicals without the

need of special equipment such as ultraviolet lighting or chemicals. The drawbacks of fenton process is that a low pH is required to keep the iron in the solution [15]. Additionally, sludge is created due to the formation of iron hydroxide ($Fe(OH)_2$) [15].

Ozonation generates hydroxyl radicals when O_3 is added into water. It is useful because it can be utilized alone or in combination with hydrogen peroxide, ultraviolet light, or both to produce the radicals. Drawbacks of the process include the higher pH needed for the reaction of the ozone as well as potential formation of bromate, which is a potential carcinogen for humans [15][21]. Finally, the presence of carbon dioxide in the forms of bicarbonate or carbonate, which depends on the pH of the solution, may pose a scavenger effect on the hydroxyl radicals in the solution. This has the potential to inhibit ozone from reacting with the contaminants [15].

H_2O_2 is utilized with ultraviolet light to produce hydroxyl radicals. It is beneficial because it has high reaction rates. However, the drawbacks of the method include: the pH of the solution changes the reaction production of hydroxyl radicals, the turbidity of the solution can change the efficiency of the oxidation process, and excess H_2O_2 can react with other chemicals producing oxidizable material as well as inhibit the degradation of the contaminant [15][18].

2.2.3 Ultraviolet/Hydrogen Peroxide (UV/H_2O_2) AOP.

UV/H_2O_2 AOPs typically utilized either a low-pressure mercury or a medium-pressure mercury lamp to create the hydroxyl radicals. H_2O_2 does not absorb light with a wavelength above 300 nm, so sunlight was not typically utilized to produce the reaction [16]. A key feature of this AOP was the regeneration of H_2O_2. For example,

with methanol, the hydroxyl radicals were consumed by the oxidation of methanol. Methanol produced two superoxide radicals (an oxygen to oxygen bond), which could react with two hydrogens in the water to produce H_2O_2 [16].

One example of UV/H_2O_2 process was utilized to degrade N-Nitrosodimenthylamine (NDMA), which was a byproduct of rocket fuel that the EPA has identified as a possible carcinogen [18]. NDMA was able to absorb the UV light at two wavelengths (228 and 332nm) to breakdown the nitrogen to nitrogen bond in the compound. By UV treatment alone, the chemical was degraded by 98%. It was determined that while small amounts of added H_2O_2 did not enhance degradation of NDMA, it oxidized the byproducts from NDMA and resulted in less reformation of NDMA after chlorination [18]. However, larger amounts of H_2O_2 inhibited the degradation of NDMA.

In a second example, cyclophosphamide (CP) and 5-fluorouracil (5FU), two drugs used in chemotherapy, were degraded through UV and UV/H_2O_2 processes. It was determined that while degradation could not occur through UV alone, degradation was significantly increased by low concentrations of H_2O_2, while higher doses of H_2O_2 inhibited the degradation of both drugs [22]. Furthermore, (Zhang et. al, 2014) tested the inactivation of Bacillus subtilis, a bacterium found in soil that caused food contamination, with UV/H_2O_2 utilized in sequence as well as in combination. It was determined that in combination, the disinfection was increased in comparison to sequence of UV to H_2O_2 and H_2O_2 followed by UV [23].

2.2.4 UV LED-driven AOP.

The body of evidence continues to grow on the effectiveness of UV LED-driven AOPs for the degradation of a range of pollutants. Traditionally, mercury lamps are utilized for UV AOP. LEDs are beneficial over mercury lamps due to their durability over the lamps. LEDs have the capability to turn on or turn off instantly. Mercury lamps, on the other hand, necessitate a warm up period prior to use [24]. Another benefit of LEDs is due to the toxic waste generated from mercury lamps. Finally, the light weight and compact design of the LEDs can have multiple configurations, depending on the type of contaminant being inactivated, degraded, or destroyed [24].

In a study utilizing UV LED/H_2O_2 AOP, methylene blue, a blue food dye, was in both continuously-lighted and pulsed-lighted experiments. It was determined that both methods produced degradation of the substance, but as the duty cycle (fraction of time the light is on) was increased, generation of hydroxyl radicals increased [24][25].

In another study utilizing UV LED/H_2O_2 AOP, UV LEDs were used in collaboration with H_2O_2 to degrade two chemicals, brilliant blue FCF (blue food dye) and tartrazine (yellow food dye). It was determined that while brilliant blue was degraded at 83%, the tartrazine was only able to degrade by 17% in the same conditions [26].

Finally, Bacillus subtilis was inactivated utilizing UV LED and H_2O_2 with both continuous- lighting and pulsed-lighting. It was determined that while inactivation achieved more degradation of the bacteria in comparison to the pulsed-lighting, the pulsed-lighting was more effective at causing cellular damage to the bacteria [27]. This

is consistent with Zhang's inactivation of Bacillus subtilis using UV/H_2O_2 combination [44]. The effectiveness of the UV-LED/H_2O_2 AOP depends on the type of contaminant being degraded, the frequency of light being emitted (pulsed or continuous), and the configuration of the reactor being utilized. Furthermore, the need for improved reactor design characteristics to impact the efficiency of the AOP is warranted [26][27].

2.2.5 GG

FPW contain approximately 1,800 different chemicals [3][5][8]. Due to the limited regulations on HF, the chemicals utilized are not equivalent for each location. GG is a prevalent compound utilized in approximately 30% of the chemical injection wells in the US for HF operations. GG is a polysaccharide composed of galactose and mannose, which are two forms of D-aldose sugars where the carbonyl carbon is at the end of the carbon chain [7][28][31]. Additionally, Jain characterized GG as "a natural non-ionic polysaccharide consisting of a polymannose chain of (1→ 4) linked β-D-mannopyranose [six-membered ring] units and α-D-galactopyranose units connected through (1→ 6) glycosidic [sugar to molecule bond through a nitrogen or oxygen] linkages to the mannose backbone chain" [31:299-320][32:146]. Due to GG's nature as a polysaccharide, it is a polymer of high molecular weight. Additionally, as a polymer it does not have a definite molecular weight as the subunits of GG have repeating sequences.

Furthermore, GG was insoluble in hydrocarbons, fats, alcohols, esters, and ketones and needs water as a solvent [33]. Once in cold or hot water, it forms a viscous colloidal solution even at a low concentration and achieved full viscosity in cold water, which differentiated GG from other types of gums [33]. GG has a stable form while in

solution over a vast range of pH. As a result, GG needed extreme pH (<4 or >10.5) to mitigate the polymer from becoming viscous. As a result of GG's viscosity, the substance gelled as it interacted with the water molecules. Additionally, GG's viscosity was reduced as temperature or salinity increased in the solution.

The large structure of GG has made it difficult to treat in membrane separation treatment processes such as filtration or reverse osmosis as the substance may clog up the filters [29]. (Lester et. al 2014) utilized conventional biological processes to treatment guar gum with three total dissolved solid levels of 1,500 mg/L, 22,000 mg/L, and 45,000 mg/L. At lower concentrations (1500 mg/L), 90% of the substance's COD was degraded after 10 hours. However, as the GG concentration was increased to 45,000 mg/L, it inhibited the COD degradation to 60% removal after 31 hours [29]. (Lester et. al 2014) explained that as the TDS concentration is above 10,000 mg/L, the performance of biological treatments decreased due to plasmolysis (loss of water in a cell) and loss of cell activity [29].

2.2.6 UV LED-driven AOP for degradation of GG

Currently, no published information is available on utilizing UV/H_2O_2 AOP to oxidize GG, and it is not clear that this is possible because the UV energy may be absorbed by GG, instead of by H_2O_2. Furthermore, GG may decrease the efficiency of the output of the LED due to its adhesive nature. Higher levels of LED power output may be needed to degrade GG, as the current level in the previous tests were approximately 20 mA. It is also not clear how much H_2O_2 is necessary to degrade GG since excess H_2O_2 inhibits the degradation of the contaminant.

III. Methodology

3.1 Procedures and Process

3.1.1 GG Solution

GG solution was prepared by adding 1 g of Fisher Science Education Reagent Grade (Lot no. 6GJ15051307A) GG powder into a liter of deionized (DI) water. Next, the GG solution was mixed for 12 hours to thoroughly mix. Third, the solution was filtered through Millipore's type GPWP 0.22 micrometer filter paper to remove any suspended particles in the solution (as GG does not completely dissolve into solution). Finally, GG stock solution was put stored into a brown bottle to mitigate the impact of outside light on the solution.

3.1.2 LEDs

First, two LED bulbs provided by Sensor Electronic Technology, Incorporated (SeTi) were tested in the Lezynes Integrating Sphere, which is a machine to test a light under different conditions (voltage and amperage). The lights were tested under 50 mA, 100 mA, 150 mA, and 200 mA input drive currents to determine the peak wavelength of the light as well as the amount of power the light outputs. After the LED output was measured, the LEDs were attached to the reactor for the AOP experiment.

3.1.3 LED Configuration and Reactor Set Up

First, the circuit board for the reactor was created. This circuit board is used to regulate the amount of voltage and current going into the LEDs as well as prevent negative amperage from occurring in the system, which can degrade and destroy the lights. Next, LED lights were embedded into the ends of the Teflon reactor. The Teflon

reactor was made of 2 mm thick polytetrafluoroethylene (PTFE). The central cylinder had an internal diameter of approximately 22 mm with a length of approximately 80 mm. Total interior volume of the assembled reactor was approximately 37 mL.

Then, the wires were soldered to the reactor ends to create a closed loop connection between the reactor and the power supply. Then, heat paste was added to the back of the LED to dissipate the heat from the light. This extends the life of the LED and prevent the reactor from overheating. Afterwards, heat shrink was added to the connection points of the wire and LED to insulate the wires. Then, the connectors were added to the ends of the positive and negative wires to create a closed loop between the reactor, the circuit board, and the power supply. Finally, the devices were connected together. Next, the reactor, LEDs, and power supply were connected to perform the AOP experiment. Figure 1 shows the LED inside the Teflon reactor, while Figure 2 shows the set-up of the LED.

Figure 1: LED

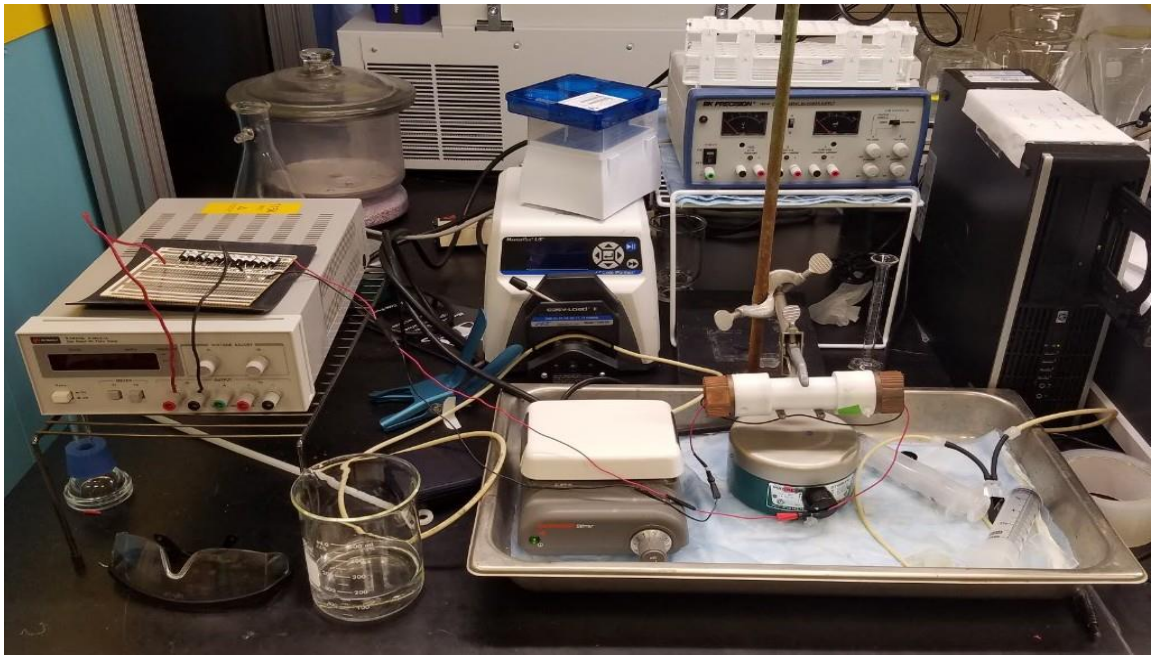

Figure 2: LED Set-Up

3.1.4 AOP

3.1.4.1 Experiment

There were five H_2O_2 concentration tested for this experiment: 0.34 g/L H_2O_2, 0.85 g/L H_2O_2, 1.70 g/L H_2O_2, 3.38 g/L H_2O_2, and 8.46 g/L H_2O_2 solutions from the 500 mL Hydrogen Peroxide 30% in water (Lot 155754). Additionally, each 250 mL solution mixture contained 48 mg/L of GG. The concentrations were reported as H_2O_2 to-GG ratios. The following were used for the treatment: 7.0 g H_2O_2/g GG, 17.6 g H_2O_2/g GG, 35.3 g H_2O_2/g GG, 70.5 g H_2O_2/g GG, and 176.3 g H_2O_2/g GG.

First, a pipette was used to mix 12 mL of GG solution with an assortment of different H_2O_2 solutions, and DI water in a 250 mL volumetric flask. Once the flask was half full, the solution was mixed for 20 minutes in a shaker (a device to shake the solution violently for a thorough mixture). Afterwards, the flask was brought to 250 mL and shaken again for

20 minutes. Next, a stir bar was added to the reactor and the two ends of the reactor were combined with the center tube. Afterwards, the reactor was placed on the stand and the negative and positive leads were connected to the power supply to power the LED lights.

Then, a stir bar was added to the 250 mL solution to keep the solution evenly mixed throughout the entirety of the 90-minute experiment. The line from the pump was then attached to the flask to hydraulically pump the fluid from the flask, through the reactor, through the Agilent Technologies Cary 60 UV-Vis spectrophotometer, and into the beaker for disposition. Figure 3 shows the set-up of the AOP experiment.

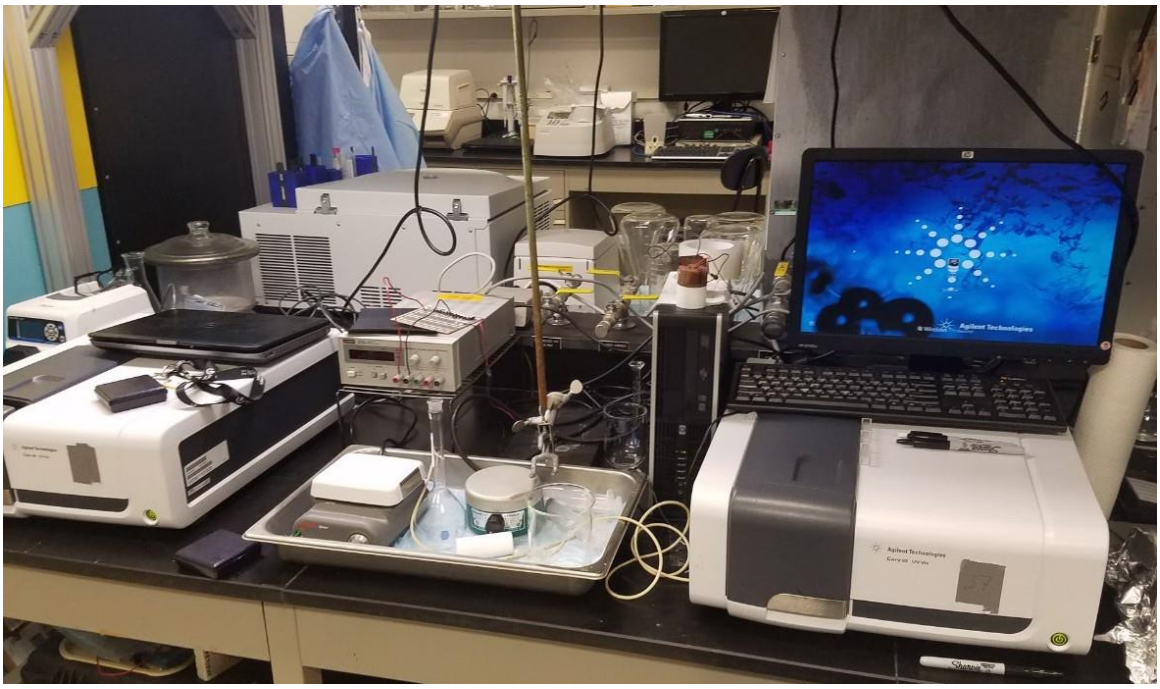

Figure 3: AOP Test Set-Up

Prior to the start of the experiment, DI water was added to the UV-Vis Spectrophotometer to calibrate the machine. After the calibration/zeroing of the UV-Vis spectrophotometer, 60 mL of the initial solution was added to the line with a syringe to fill the line and reactor with the solution. This removes air from the line, thus preventing

interference of the machine by outside air. Once the line was saturated, the pump was closed to prevent any air from coming into the line. Then the hose was inserted back into the flask. Finally, the LED lights were turned on in the reactor by powering up the digital power supply.

3.1.4.2 UV-Vis Spectrophotometer & Computer

The UV-Vis Spectrophotometer program SCAN was used to take the data points observed throughout the experiment. The program was set up to measure the absorbance of the light by the fluid between the wavelengths of 200 to 400 nanometers. Figure 4 shows the Agilent Technologies Cary 60 UV-Vis spectrophotometer.

Figure 4: Agilent Technologies Cary 60 UV-Vis Spectrophotometer

The UV-Vis took readings every minute for 90 minutes. Finally, the results of the data points were graphed in Microsoft Excel to determine the change in absorbance from time 0 to time 90 at the 265 nm wavelength, which was the peak wavelength of the UV LEDs based on the calibration on the Lezynes Integrating Sphere. Additionally, when comparing the influent to the effluent for the AOP experiment, an additional UV-Vis

spectrophotometer was added to the system between the pump and the reactor. This was done to determine what occurred with the absorbance H_2O_2 prior to going into the reactor. Additionally, this was performed to see whether there were changes between the influent and effluent samples.

3.1.4.3 Analysis.

The UV-Vis Spectrophotometer was used to measure the absorbance of the influent and effluent. Samples were collected for COD measurement and for use in respirometry.

3.1.5 COD

3.1.5.1 Experiment

Prior to the start of the AOP experiment, 6 mL of influent sample was collected from the volumetric flask. Furthermore, during the experiment 2 mL samples were collected at time 0, 10, 30, 45, 60, and 90 minutes. Next, each sample point (in triplicate) was mixed with a dichromate reagent (Hach Company Digestion Solution for COD 3-150 mg/L range), which was shown on Figure 5.

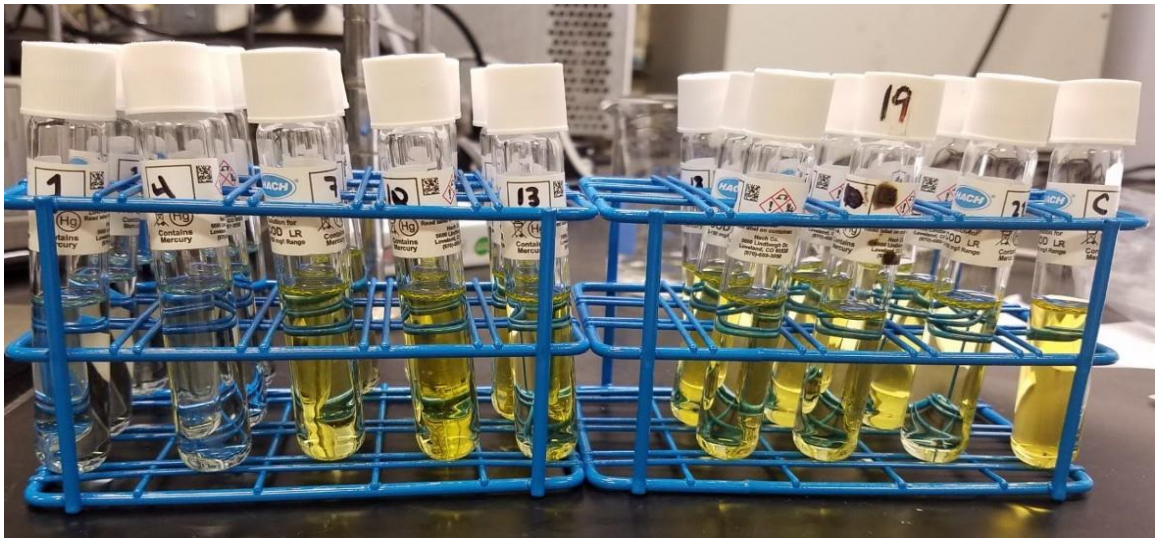

Figure 5: Vials of COD Kit

For the original sample, 2 mL of solution was added to the kit and three sets of samples were created for each sample. Additionally, to ensure the results are within the range of the reagent, the samples were diluted initially with a ratio of 4:1 (1.5 mL DI water to 0.5 mL solution). Additionally, one vial was mixed with 2mL of water as a control. Then, the samples are hand mixed by mixing the sample in the vial 15 times. A thing to note in the process was that as the H_2O_2-to-GG ratio is increased, the dilution must be greater to ensure the data stayed within the range of the reagent. For example, on the 70.5 g H_2O_2/g GG, the dilution was 16:1 (1.875 mL DI water to 0.125 mL solution).

Afterwards, the vials were added into the COD digester to digest the samples for 2 hours. Due to the limitations in the number of vial slots, the 22-25 samples had to be digested in two separate time trials. The first 15 samples were digested for two hours followed by the next 7-10 vials for next two hours. Finally, once all vials were digested, the samples were scanned in the UV-Vis Spectrophotometer through the program SIMPLE READ. The program read the absorbance values of the samples at a wavelength of 420 nm. The control sample was used to calibrate and zero the machine prior to reading the various GG solutions. Each of the samples were analyzed in the UV-Vis Spectrophotometer three times. Once all the samples were read three times, that created one set of data points. Next, the machine was zeroed again with the control vial and each sample was tested in the same configuration as the first set of data points. The method was repeated three times to create three sets of data points. Figure 6 was the COD digester used to digest the COD vials.

Figure 6: COD Digestor

3.1.6 Respirometry

3.1.6.1 Experiment

Prior to the start of AOP experiment, 5 mL of the influent sample was collected for respirometry. Additionally, 5 mL of the effluent sample was retrieved after the AOP experiment passed the 90th minute. Once the samples were retrieved, 500 mL of activated sludge was removed from the stock solution in the laboratory. Next, the respirometry space was set up with nine vials, the first three consisting of the influent sample from the AOP experiment. The next three consisted of the effluent sample. The seventh vial consisted of Allylthiourea (ATU), which was 0.508 g in 500 mL of DI water, that would inhibit the activated sludge during the respirometry experiment, and the final two channels were provided only feed solution. Additionally, channels 1-7 consisted of the feed solution, which was a mix of 200 microliters of feed solution A (1 L DI water and 44.6 g of Sodium Bicarbonate), 425 microliters of feed solution B1 (1 L DI water, 12 g of Casamino Acids, and 2.5 g Sodium Acetate), and 425 microliters of solution B2 (1 L DI

water, 4.52 g Ammonium Chloride, 13.72 g Magnesium Chloride, 3.44 g Calcium Chloride, and 1.335 g Potassium Dihydrogen Phosphate). Afterwards, the Micro-Oxymax program was calibrated the machine for the respirometry experiment.

To calibrate the machine, the two tanks of combined gases were added into the line and calibrated based on restriction, leakage, and volume for each channel. Once each channel was configured properly, the experiment ran for 18 hours. The set-up for the respirometry experiment was shown on Figure 7.

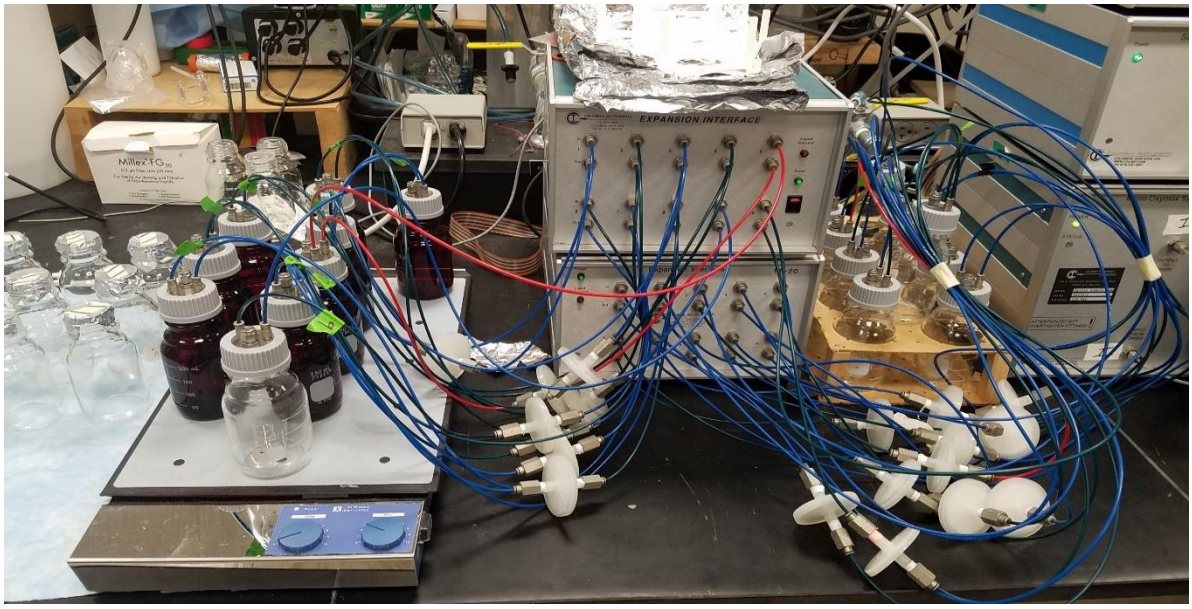

Figure 7: Respirometry Set- Up

3.1.6.2 Analysis.

The effect of GG solutions with different H_2O_2 concentrations as well as different drive currents were analyzed quantitatively by comparing the shape parameters, peak oxygen consumption, and cumulative oxygen consumption of the influent, effluent, and control samples using a Student's t-test with a 95% confidence. Furthermore, the qualitative analysis consisted of visual comparison of the influent, effluent, and control samples of the oxygen consumption profiles, the first moment, and the skewness.

3.1.6.3 Shape Parameters.

Based on previous research, the first moment of area (FrM) was used to determine the centroid of a shape [30]. The graphs for respirometry usually consists of a peak where the microbes consume the feed and as a result produce oxygen. The FrM was calculated using the mid-point approximation for the integral equation, which was shown in Equation 1.

$$Q_y = \int_a^b xf(x)$$

Equation 1: First Moment of Area

The f (x) is the area under the curve, while the x variable is the distance from the vertical axis [29]. The FrM was calculated using the first seven intervals of each influent, effluent, and control samples to utilize the data from under the curve, while also limiting the amount of data utilized once the data stays flat in the experiment. The FrM was used to quantify the shape profiles to compare the influent, effluent, and control samples.

Next, the skewness is a measurement to determine the asymmetry in a statistical distribution, which means whether the curve distorts to the left or to the right. The skewness was determined with Equation 2.

$$g_1 = \frac{n}{(n-1)(n-2)} \sum (\frac{x_i - \bar{x}}{s})^3$$

Equation 2: Skewness

The n represents the number of elements, the s represents the standard deviation, the x_i represents the number of interest, and the $\bar{x}$ is the mean of the data. The skewness was calculated with the first five intervals of each influent, effluent, and control samples. The

skewness was another method to compare the O_2 profiles between the influent, effluent, and control samples and it utilized the Student's t-test [29].

3.1.6.4 Peak oxygen consumption.

The peak oxygen consumption was measured by comparing the greatest measured oxygen uptake rate on each curve regardless of which interval. They are compared using the Student's t-test.

3.1.6.5 Cumulative oxygen consumption.

The cumulative oxygen consumption was selected at the fourth sampling interval to compare the "peaks" of each sampling group. The cumulative oxygen consumed was compared using the Student's t-test.

IV. Results and Discussion

4.1 The relative absorbance of GG and H_2O_2

4.1.1 Relative Absorbance Observation and Interpretation

Figure 8 analyzed the absorbance profiles of GG solution (48 mg/L) against H_2O_2 ($1.11*10^6$ mg/L). The peaks in the absorbance spectrum were related to the amount of light absorbed by the sample at a given wavelength. The H_2O_2 absorbance profiles had several peaks that were greater than 3 absorbance units in magnitude between the 200 and 300 nm wavelength, while the GG solution without H_2O_2 showed peak absorbance of less than 2 throughout the same wavelength range. The H_2O_2 absorbance at 265 nm is 0.931, while that of GG is 0.118, and the comparative absorbance ratio of the two is 7.89. H_2O_2 absorbed approximately 8 times more UV light at 265 nm than the GG solution. This means that hydroxyl radical formation should not be inhibited by GG during the UV/ H_2O_2 AOP treatment of GG. Furthermore, the presence of several peaks in the H_2O_2 spectra shows the possibility of oversaturation of H_2O_2, which can be caused by the H_2O_2 reading above the usual spectrophotometer absorbance of 0 to 3 [34]. The GG absorbance spectra was smooth and continuous, which was the first time seen through the UV-Vis Spectrophotometer to the author's knowledge.

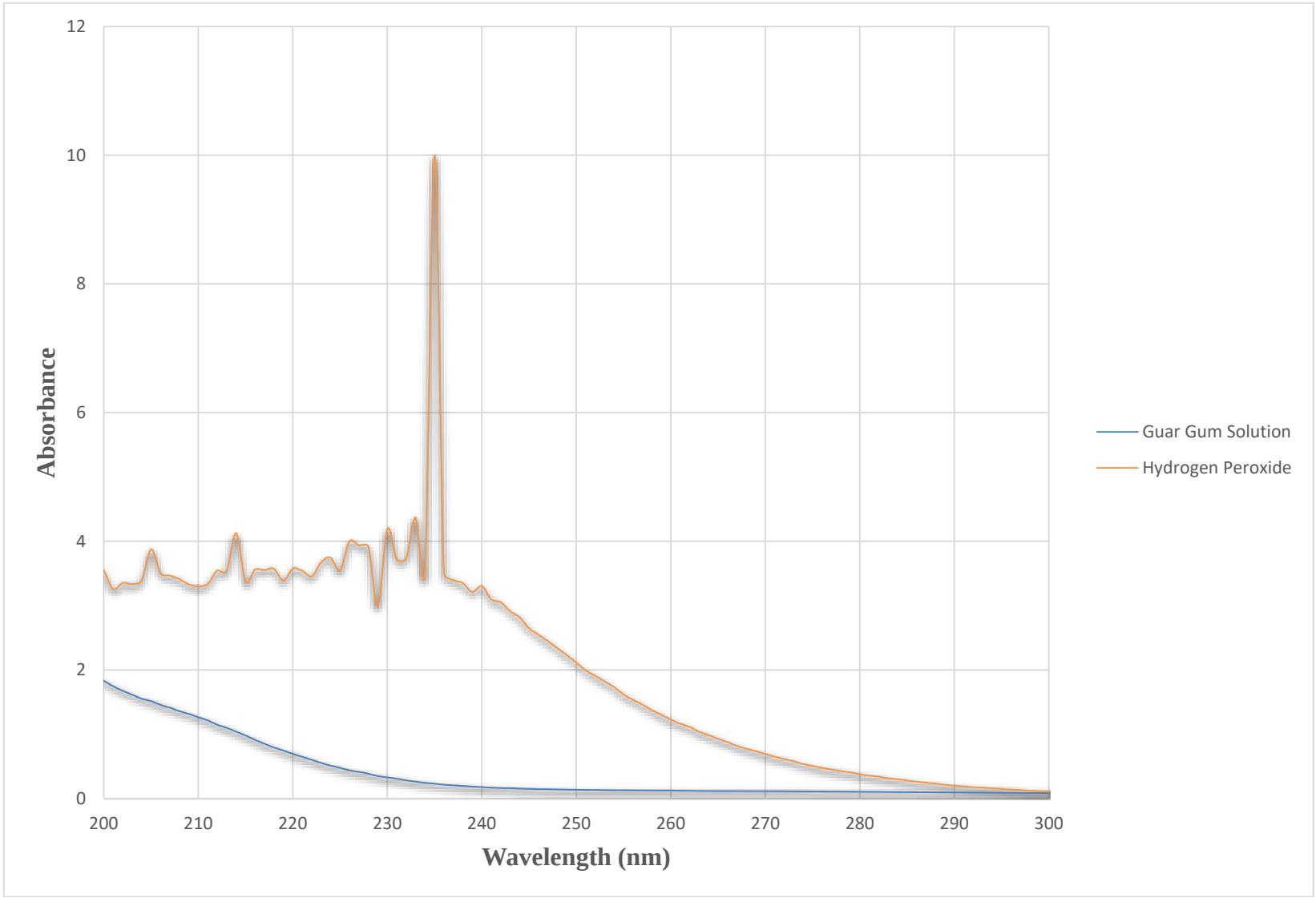

Figure 8: Absorbance Profile of GG and H_2O_2

4.2 The effect of the H_2O_2-to-GG ratio on GG removal in the UV LED/H_2O_2 AOP

4.2.1 COD Observation & Interpretation

Figure 9 shows the effect of the H_2O_2-to-GG ratio on GG removal in the UV LED/ H_2O_2 AOP. The overall COD removal percentage was 95% at the lowest H_2O_2-to-GG ratio of 7.0 g H_2O_2/g GG. The greatest COD removal was observed during the first 10 minutes of the 90-minute experiment, but this was followed by an increase in the COD during the last 60 minutes of the experiment. When the H_2O_2-to-GG ratio was increased to 17.6 g H_2O_2/g GG, the overall COD removal percentage was 45%. The greatest degradation was observed at 60 minutes, which had a COD degradation of 52%. When the H_2O_2-to-GG ratio was increased to 70.5 g H_2O_2/g GG, the overall COD removal percentage was approximately 0%. Overall these results showed that GG removal depended on the H_2O_2-to-GG ratio, which is consistent with previous studies with AOP [15][18][22].

COD is a common method to measure water quality. According to G. Tchobanolglous, COD is a bulk parameter that measures "the oxygen equivalent of the organic material in wastewater that can be oxidized chemically using dichromate in an acid solution" [39]. This method was performed to detect GG and its byproducts. In the current study, the COD method detected GG, as well as H_2O_2 and perhaps a limited mass of GG-related byproduct generated through photolysis or by reaction with the pool of hydroxyl radicals. The data showed that the COD concentration decreased during the first 10 minutes of the AOP test when the H_2O_2-to-GG ratio was 7.0 g H_2O_2/g GG, while it decreased during the first 60 minutes of the AOP test when the AOP test when the H_2O_2-to-GG ratio was 17.6 g H_2O_2/g GG. The data also showed that the COD profile rose after

the first 10 minutes for the 7.0 g H_2O_2/g GG sample, after the first 60 minutes for the 17.6 g H_2O_2/g GG sample, and for the first 80 minutes of the 70.5 g H_2O_2/g GG sample. This is because the COD removal rate is eventually balanced by the flow of water through the reactor. Additionally, H_2O_2 was known to interfere with the chemical oxygen demand analysis by consuming oxidation agents such as the potassium dichromate, which may overestimate the COD measurements [40].

It was worth noting that the hydroxyl radicals that were created from AOP may not have reacted with the GG. Instead, the hydroxyl radicals potentially reacted with other radicals, water, bicarbonate, and the reactor material [41]. A large pool of hydroxyl radicals were probably required to significantly oxidize GG, as the molecules are large and possess numerous hydroxyl groups and mannose and galactose subunits. Furthermore, at higher H_2O_2 levels, the AOP treatment may be inhibited due to the hydroxyl radicals reacting with themselves or with H_2O_2 molecules instead of GG, thus leaving the GG substance intact. This was consistent with results from previous experiments that higher levels of H_2O_2 inhibited the performance of the AOP experiment [15][18][22]. Future research should study the role of GG photolysis more carefully, with special attention on identifying GG byproducts and the production of carbon dioxide.

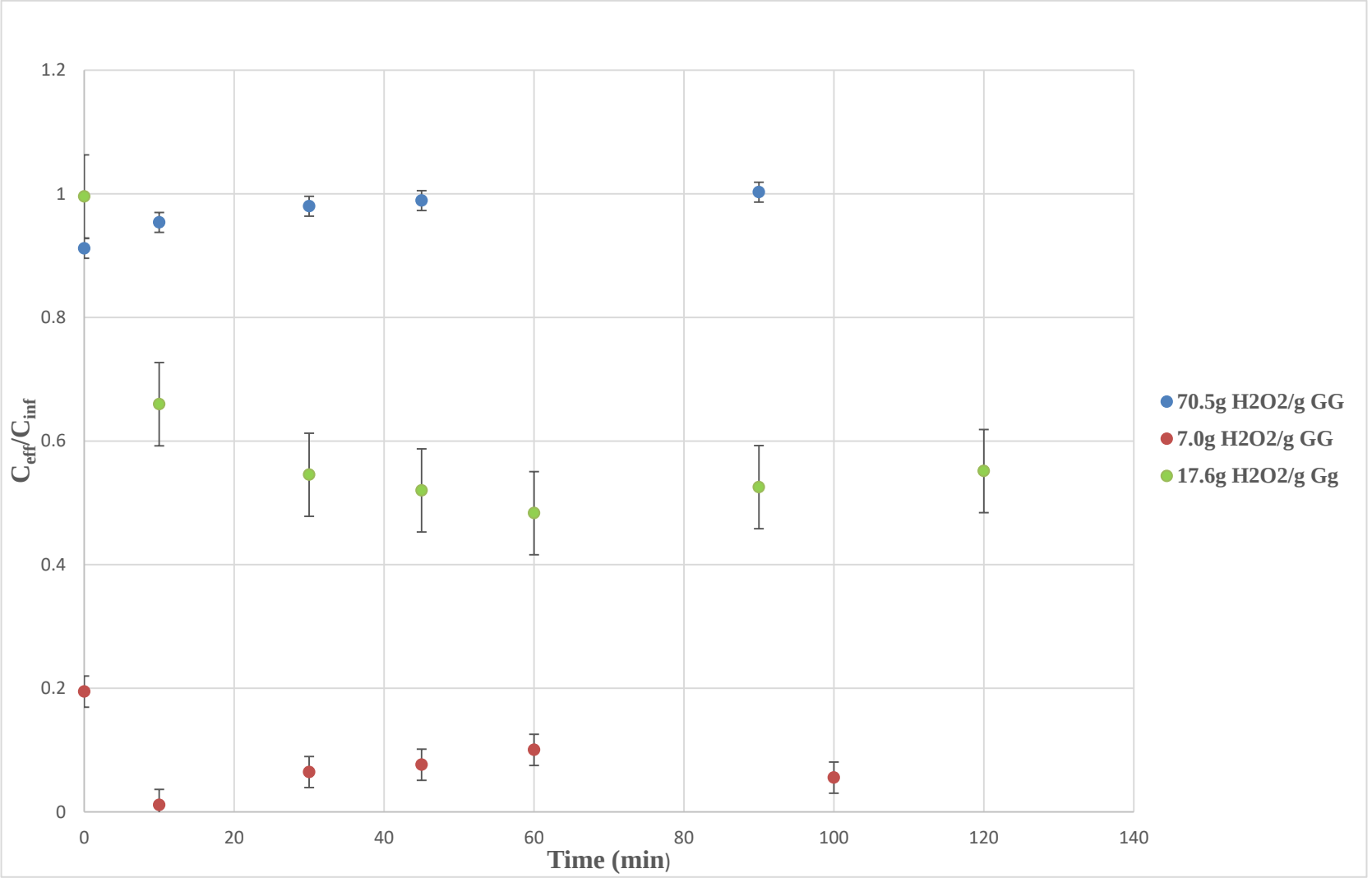

Figure 9: COD Concentration ratios of different H_2O_2-to-GG ratios.

4.2.2 Influent vs Effluent Absorbance Observation & Interpretation

Figure 10 and Appendix G showed the effects of the H_2O_2-to-GG ratio on GG removal in the UV LED/H_2O_2 AOP. The greatest difference between the influent and effluent were shown in the 17.6 g H_2O_2/g GG ratio solution and the effluent absorbance decreased by 7% over the first 10 minutes and then stabilized. The same occurred for the solution when the drive current was decreased to 100 mA. However, when the ratio was increased in the 70.5 g H_2O_2/g GG solution, the influent and effluent had negligible differences between the two absorbance profiles and overlapped during the 90-minute experiment. Additionally, when the H_2O_2-to-GG ratio was increased to 176.3 g H_2O_2/g GG, the influent and effluent had negligible differences between the two profiles and overlapped during the 90-minute experiment. Finally, the profiles showed that as the H_2O_2 was increased in the solution, the absorbance values increased. This was consistent with Figure 8, which showed that the H_2O_2 absorbance was greater than GG and as the H_2O_2 concentration increased in the solution, the total absorbance of the solution increased.

A possible reason for the difference between the influent and effluent readings for the lower H_2O_2-to-GG ratio solutions could be due to minor chemical transformations that occurred during the AOP treatment via photolysis and reaction with hydroxyl radicals. D-Galactose and D-Mannose both possess six carbons in the molecule with a carbonyl group on one end of the chain, with the other carbon elements attached to hydroxyl groups (OH) as well as singular hydrogen atoms. Photolysis could break the individual hydrogen atoms or the hydroxyl group (OH) from GG. One likely event was the atoms were reacting with the hydroxyl radicals to form either H_2O or proliferate new

H_2O_2. In the lower concentration, the GG reacted with the hydroxyl radicals and decreased the concentration of H_2O_2, while at the higher concentrations, the hydroxyl radicals were reacting with other hydroxyl radicals, H_2O_2, or bicarbonate in the system instead of the GG [15][18][22][31].

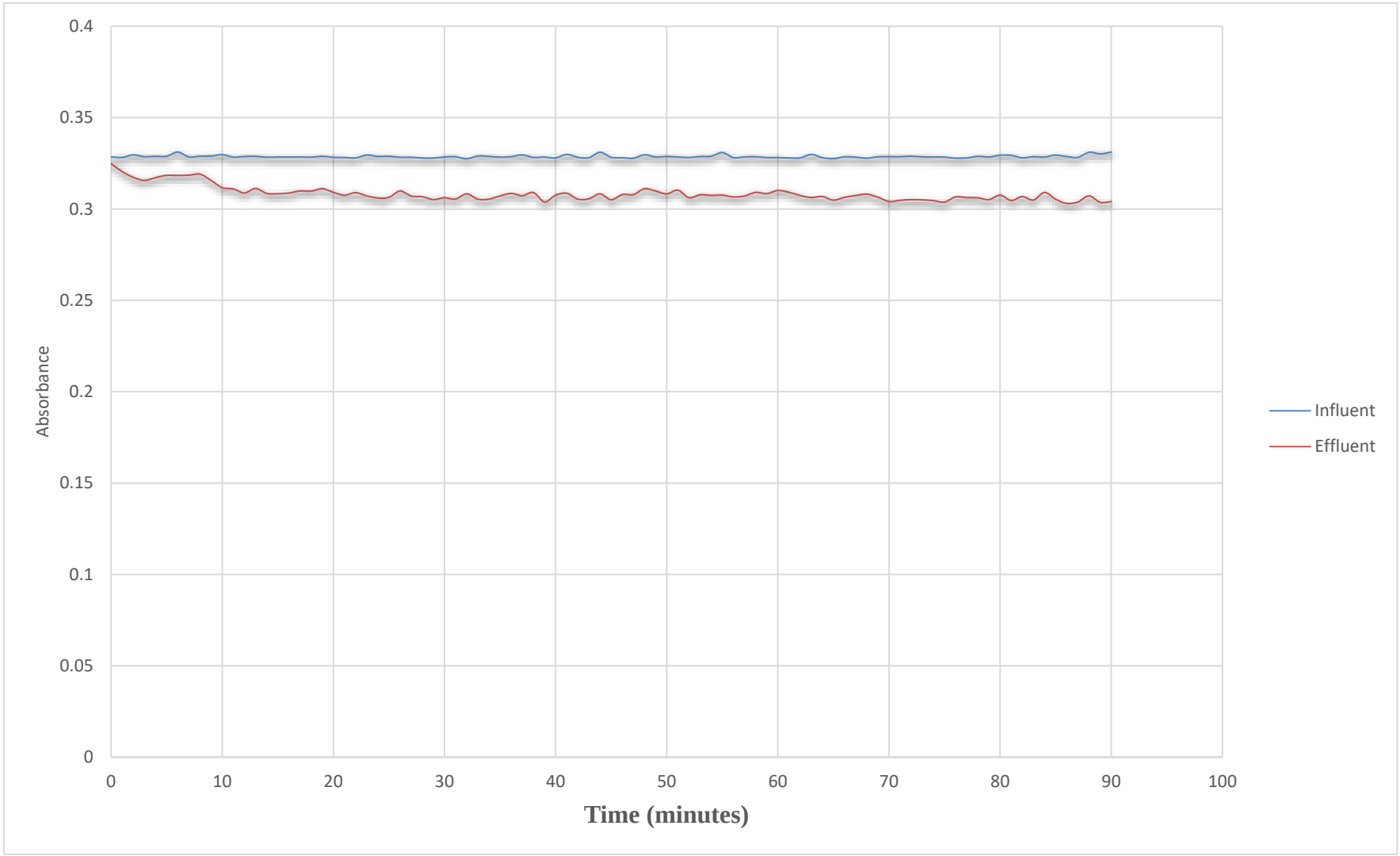

Figure 10: Influent vs Effluent Absorbance Profiles at 265 nm. Treatment condition: 17.6 g H_2O_2/g GG, 200 mA.

4.3 The effect of UV LED/H_2O_2 AOP treatment on microbial respiration

The respirograms exhibited a typical O_2 consumption profile. Upon the start of the experiment, a sharp increase in respiration occurred, as seen in Figure 11. The peak respiration rates were approximately 18 µg/min for the AOP influent, 19 µg/min for the AOP effluent, and 18 µg/min for the average negative control. In the third hour of the experiment, the respiration rates sharply declined to an endogenous respiration rate that was between 3 and 10 µg/min. In this trial, channel 8 of the control group had the highest peak of any channel, while channel 9 of the control group had the lowest peak of any channel. Every channel, except the ATU channel, experienced a peak and immediately decreased to the tail of the experiment. Channel 9 (ATU channel) experienced a sharp increase at the initial portion of the experiment and then stabilized to an endogenous respiration rate without a peak.

Table 1: Student's T-Test values for all microbial respiration parameters.

H_2O_2-to-GG ratios (g H_2O_2/g GG)	DCL (mA)	Exp. (ivc = inf-vs-ctrl, evc = eff-vs-ctrl, ive = inf-vs-eff)	Peak Rate	Cumulative O_2 Consumption	FrM	Skewness
0	200	ive	.538	.451	.28	.158
0	200	ivc	.0495	.643	.139	.0006
0	200	evc	.031	.851	.857	.0016
17.6	200	ive	.815	.49	.557	.184
17.6	200	ivc	.985	.57	.908	.173
17.6	200	evc	.734	.66	.777	.331
17.6	100	ive	.601	.73	.416	.0655
17.6	100	ivc	.0777	.245	.766	.012
17.6	100	evc	.839	.329	.419	.0018
17.6	50	ive	.15	.51	.0848	.144
17.6	50	ivc	.0842	.26	.928	.023

17.6	**50**	**evc**	**.141**	**.63**	**.923**	**.008**
70.5	**200**	**ive**	**.167**	**.006**	**.656**	**.129**
70.5	**200**	**ivc**	**.099**	**.012**	**.336**	**.01**
70.5	**200**	**evc**	**.029**	**.699**	**.106**	**.003**
176.3	**200**	**ive**	**.107**	**.0464**	**.152**	**.024**
176.3	**200**	**ivc**	**.261**	**.232**	**.084**	**.0000084**
176.3	**200**	**evc**	**.212**	**.483**	**.158**	**.005**
Note: values appearing in red are less than 0.05 (alpha value), the 95% confidence threshold.						

Furthermore, statistical tests were performed on the peak oxygen uptake rate (OUR), cumulative O_2 uptake, and the shape of the oxygen profile. Table 1 showed the Student's t-test values for the different H_2O_2-to-GG ratios and drive current levels (DCL) for the GG solutions. For the tests that involved OUR, cumulative O_2 uptake, and the shape of oxygen profile with respect to FrM, the results revealed that AOP treatment did not significantly affect microbial respiration for 18 of 21 conditions between the influent, effluent, and negative control (see Appendix A through F). However, the results of the shape of the oxygen profile with respect to skewness revealed that there were statistical differences between the influent, effluent, and negative control for 11 of the 21 conditions. A possibility of the skewness change could be due to "automatic refreshes" that occurred in the sample bottles. The refresh occurred when the gas in the bottle is replaced with fresh air if the oxygen consumption in the sample is high enough that the oxygen in the bottle becomes depleted [35].

The results in Figure 11, Table 1, and Appendix A through F showed that UV/H_2O_2 AOP treatment did not have a significant impact on the biological degradation of GG. It was reasonable to observe that the influent respirograms were similar to the effluent

respirograms. Additionally, it is notable to observe that the influent and effluent respirograms were more closely aligned with the negative control of the feed stock (i.e. the control in which inhibition was not observed) than the positive control of the ATU channel (i.e. the control in which inhibition was observed), within the observed range of variability. This implied that GG was not inherently toxic, a finding consistent with (Tripathy et.al, 2013), who states that "it is a safe and non-toxic natural polysaccharide" [33]. Additionally, it was consistent with (Lester et. al, 2014), who showed that GG was biodegradable through conventional methods [29].

While the biodegradation of GG was not affected by the UV/H_2O_2 AOP, the change in COD reduction rates in section 4.2 and the differences in O_2 rates between the influent and effluent samples implied that the AOP effluents were not chemically identical to the influents. While the precise nature of the chemical transformation is not known, each mole of GG possesses numerous hydroxyl groups (OH) available to participate in redox reactions. Furthermore, there are numerous glycosidic linkages connecting the mannose and galactose subunits that were subjected to hydrolysis by acids [31]. These potential transformation points could yield a wide range of byproducts, including chemicals that were small enough to be incorporated into the cell and readily biodegraded. However, the extent of such transformations were not significant enough to impact microbial respiration. Additionally, H_2O_2 had the possibility to hinder biological treatment of waste water and the difference in values between the influents, effluents, and controls could be due to the H_2O_2 in the GG solution [41].

Another observation of note was GG's ability to adhere to surfaces and aggregate, which is consistent with previous findings on GG [7][29][33]. According to (Tripathy et.

al, 2013), this was caused as the GG was added to water because the galactose side chains attached to the mannose back bone interacted with water molecules. This led to an inter-molecular chain entanglement in the aqueous phase, causing gelling or thickening of the substance [33]. When the concentration of GG increased, there was also an increase in the entanglement or the inter-molecular chain interaction, which causes increased viscosity and gelling [33]. Furthermore, hydrogen bonding activity of the GG was due to the presence of hydroxyl groups in GG [7]. These forces appeared to be responsible for GG effectiveness in adsorption processes [37-38]. When introduced to activated sludge, GG likely adheres to the bacterial surface, covering the cell wall and key external proteins. Such adhesion did not impact microbial respiration in short term experiments, however the long term impact of GG on microbial respiration could become significant, and proper pretreatment processes may be appropriate.

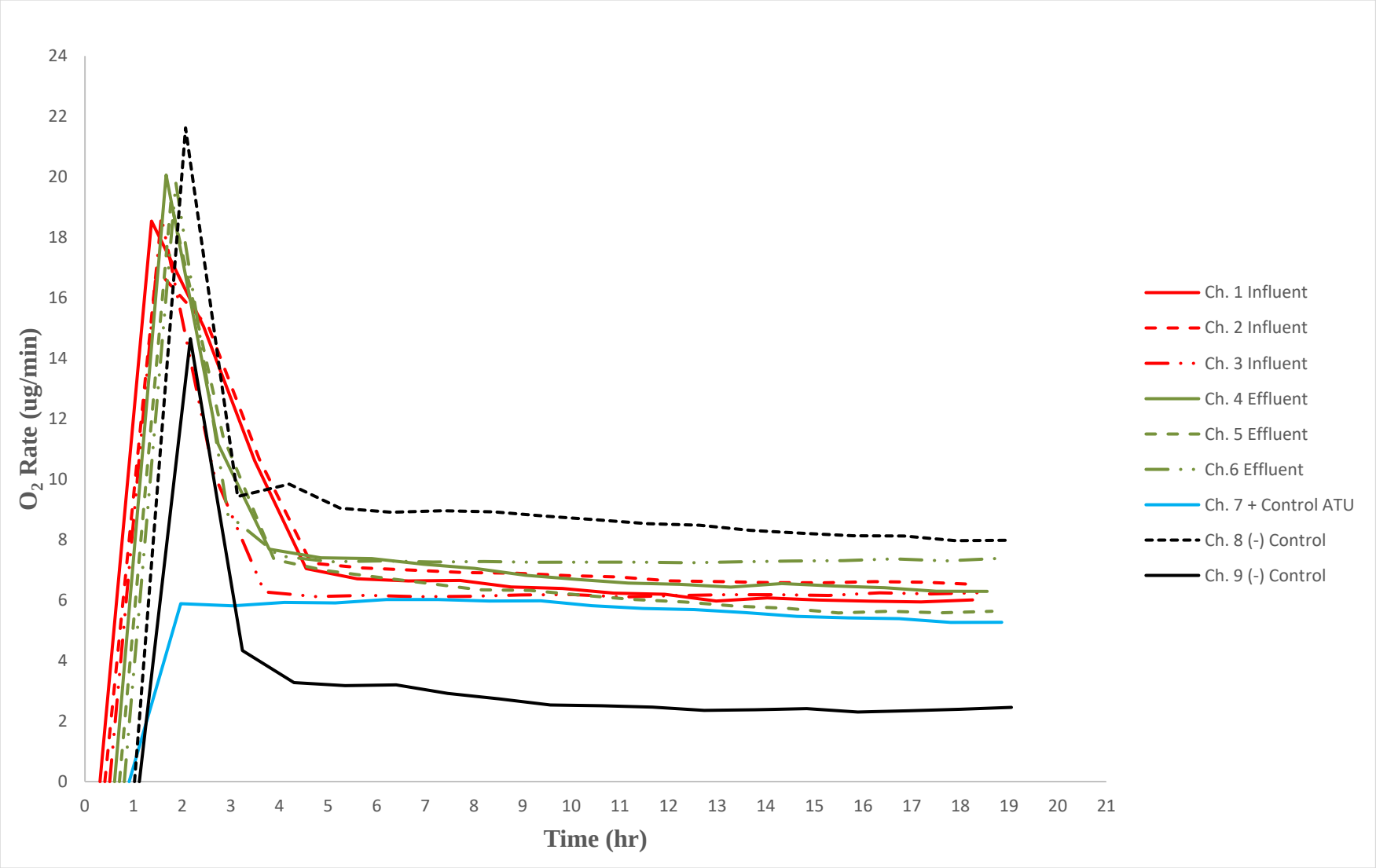

Figure 11: The Effect of AOP Treatment (17.6 g H_2O_2/g GG @ 200 mA) on the O_2 Uptake Rate of Activated Sludge.

V. Conclusion

5.1 Summary

The conclusions of this study are:

i. The GG absorbed 8 times more UV light at 265 nm than H_2O_2. This means that hydroxyl radical formation was not inhibited by the presence of GG during UV/H_2O_2 AOP treatment.

ii. UV/H_2O_2 AOP treatment of GG yielded COD removal percentages between 10 to 95% over a range of H_2O_2-to-GG ratios between 7.0 to 70.5 g H_2O_2/g GG. COD removal was greatest at the lowest H_2O_2-to-GG ratio of 7.0 g H_2O_2/g GG.

iii. The AOP effluent was not chemically identical to the influent; transformation byproducts and residual peroxide were likely present in the effluent.

iv. UV/H_2O_2 AOP treatment of GG had no statistically significant effect on microbial respiration. The peak respiration rates were typically between 12-18 µg/min (with AOP influent), 11-20 µg/min (with AOP effluent), and 15-22 µg/min (negative control, average). The profile shapes were not generally impacted by GG or by the AOP treatment described in this study.

5.2 Implications

The results showed that UV LED/H_2O_2 AOP was able to provide partial degradation of the GG solution depending on the H_2O_2-to-GG ratio. However, an implication of these results is that the treatment should be performed as part of a treatment train option instead of as a standalone method. This is because H_2O_2 provides a potential hazard for human consumption and would need to be removed from the water prior to returning the water to a ground or surface source or delivering water for consumption. Additionally, FPW has

more than GG as a contaminant and will need multiple treatment options to remove a wide range of chemicals.

5.3 Future Research

The following is recommended for future research:

i. Byproducts should be identified during UV/H_2O_2 AOP experiments with GG.

ii. UV/H_2O_2 AOP experiments should be repeated with higher drive current levels (200mA was the maximum drive current used in the current study).

iii. UV/H_2O_2 AOP experiments should be repeated with different reactor configurations, including the sequencing batch reactor (SBR) with and without internal recycle lines.

iv. UV/H_2O_2 AOP experiments should be repeated for the removal of other organic constituents found in FPW, including biocides, oil, and methanol.

v. The long-term effect of GG on activated sludge should be examined.

vi. Future research should study the role of photolysis on the chemical transformation of GG.

Appendix A

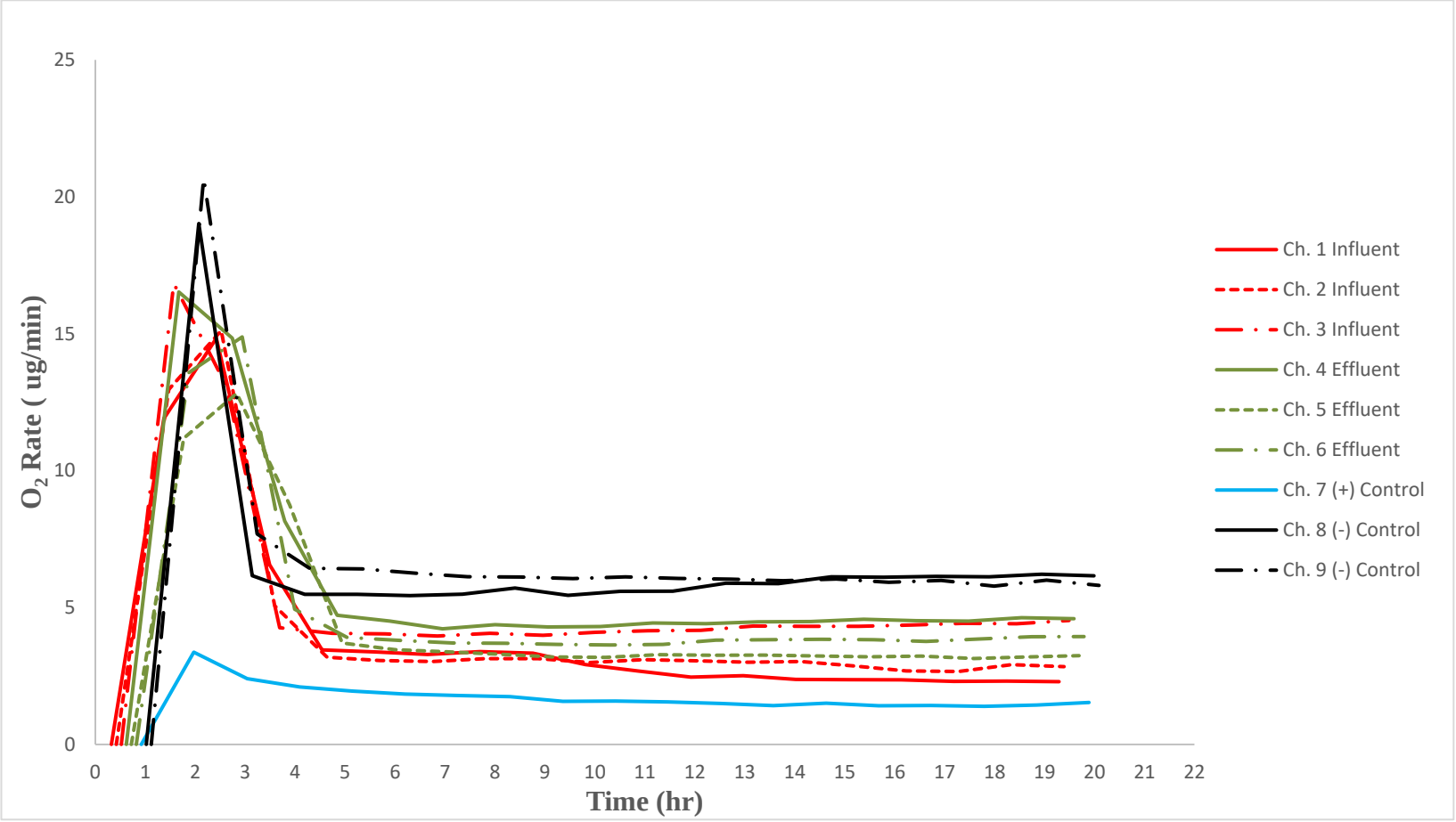

Figure 12: The Effect of AOP Treatment (0 g H_2O_2/g GG @ 200 mA) on the O_2 Uptake Rate of Activated Sludge.

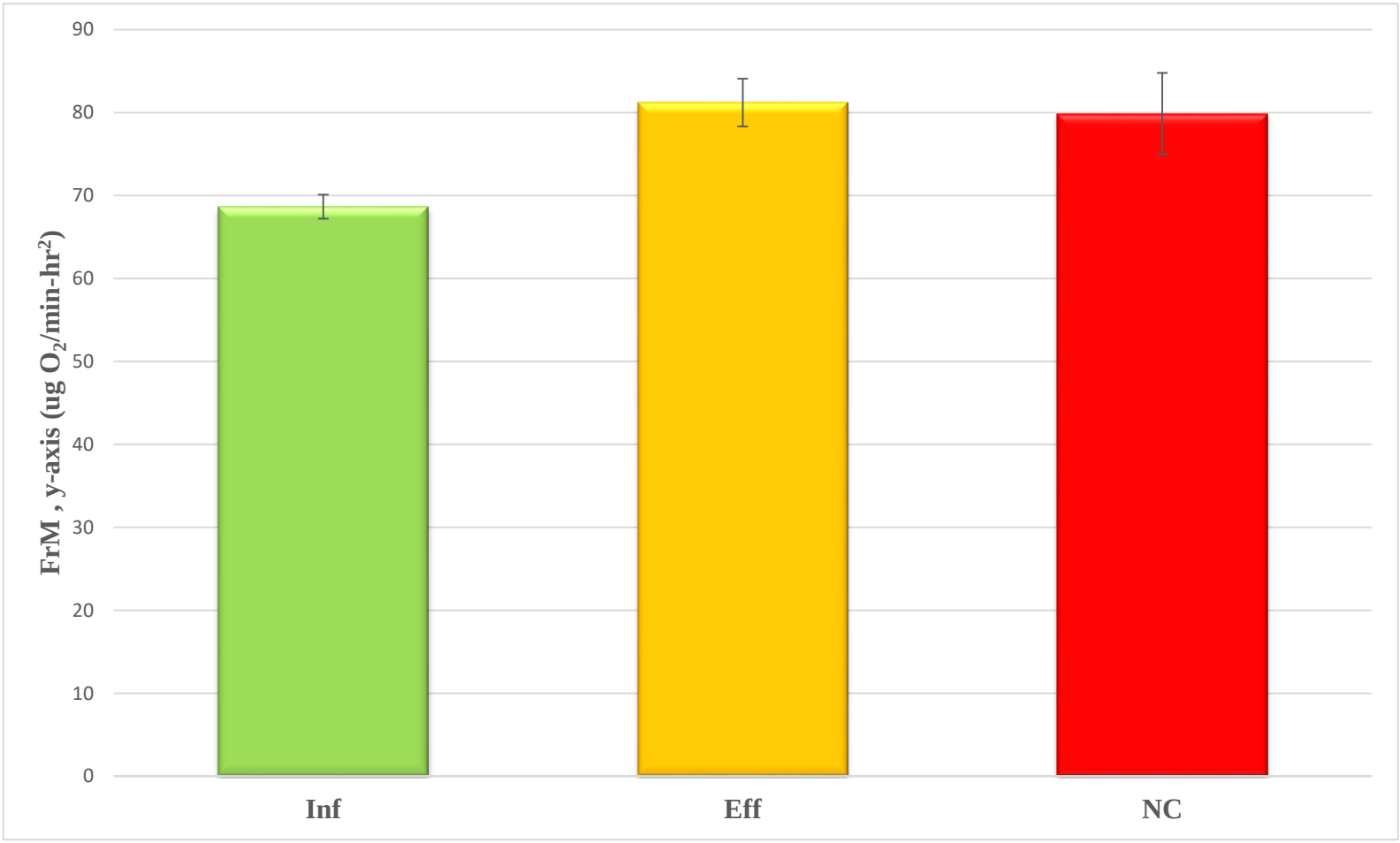

Figure 13: The Effect of AOP treatment (0 g H_2O_2/g GG @ 200 mA) on the FrM of Respirometry Profile.

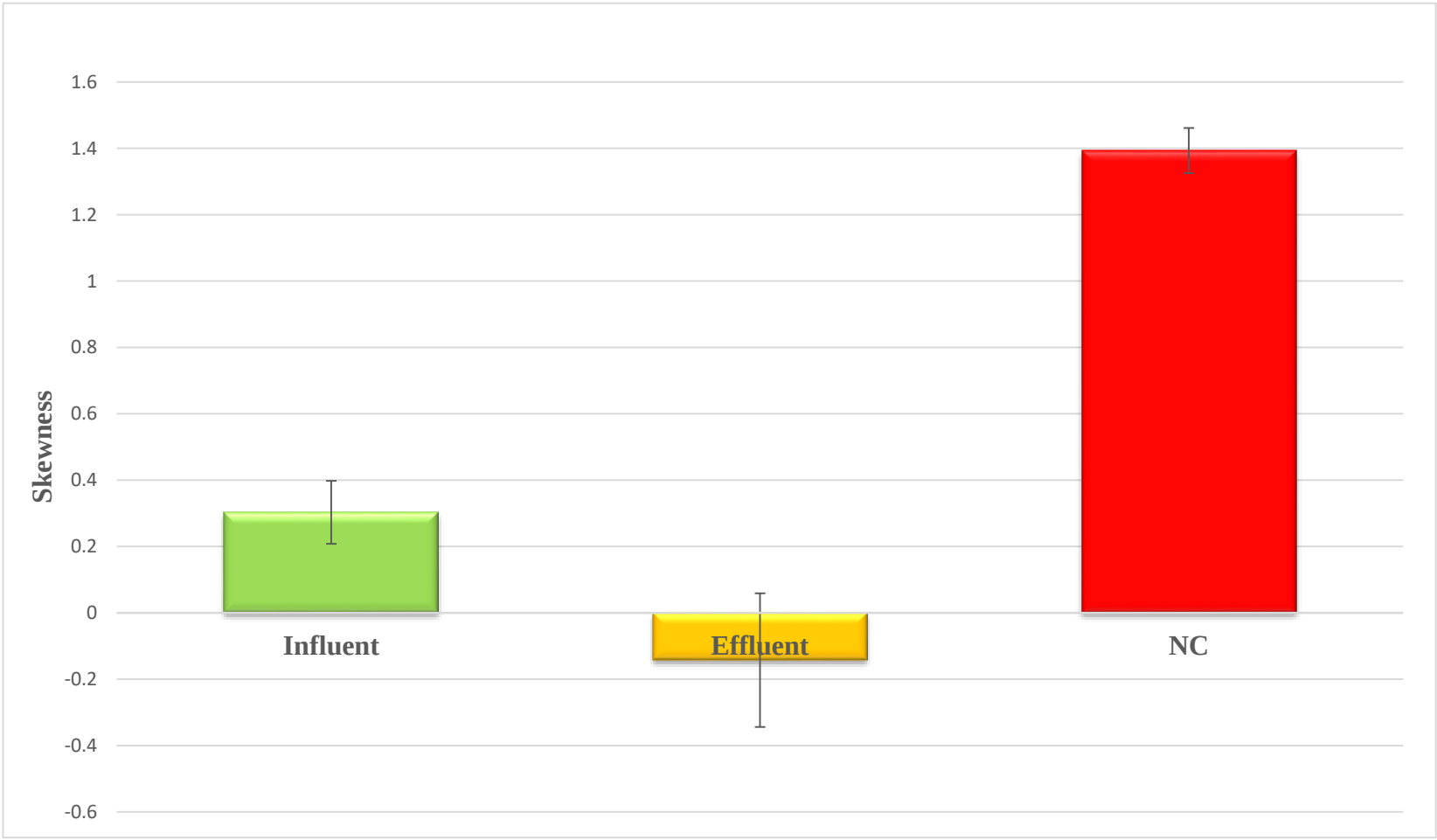

Figure 14: The Effect of AOP treatment (0 g H_2O_2/g GG @ 200 mA) on the Skewness of Respirometry Profile.

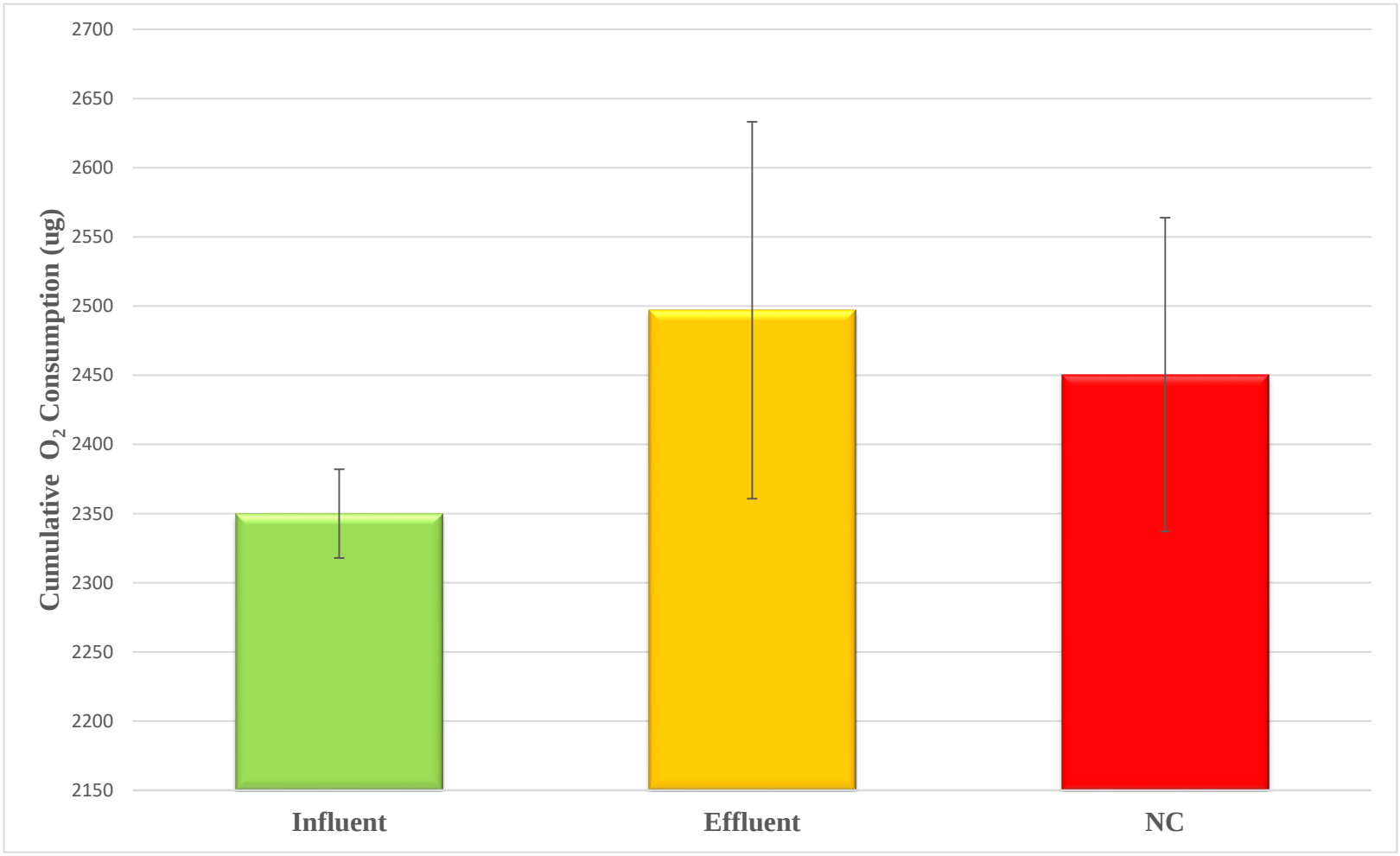

Figure 15: The Effect of AOP treatment (0 g H_2O_2/g GG @ 200 mA) on the Cumulative O_2 Consumption.

Appendix B

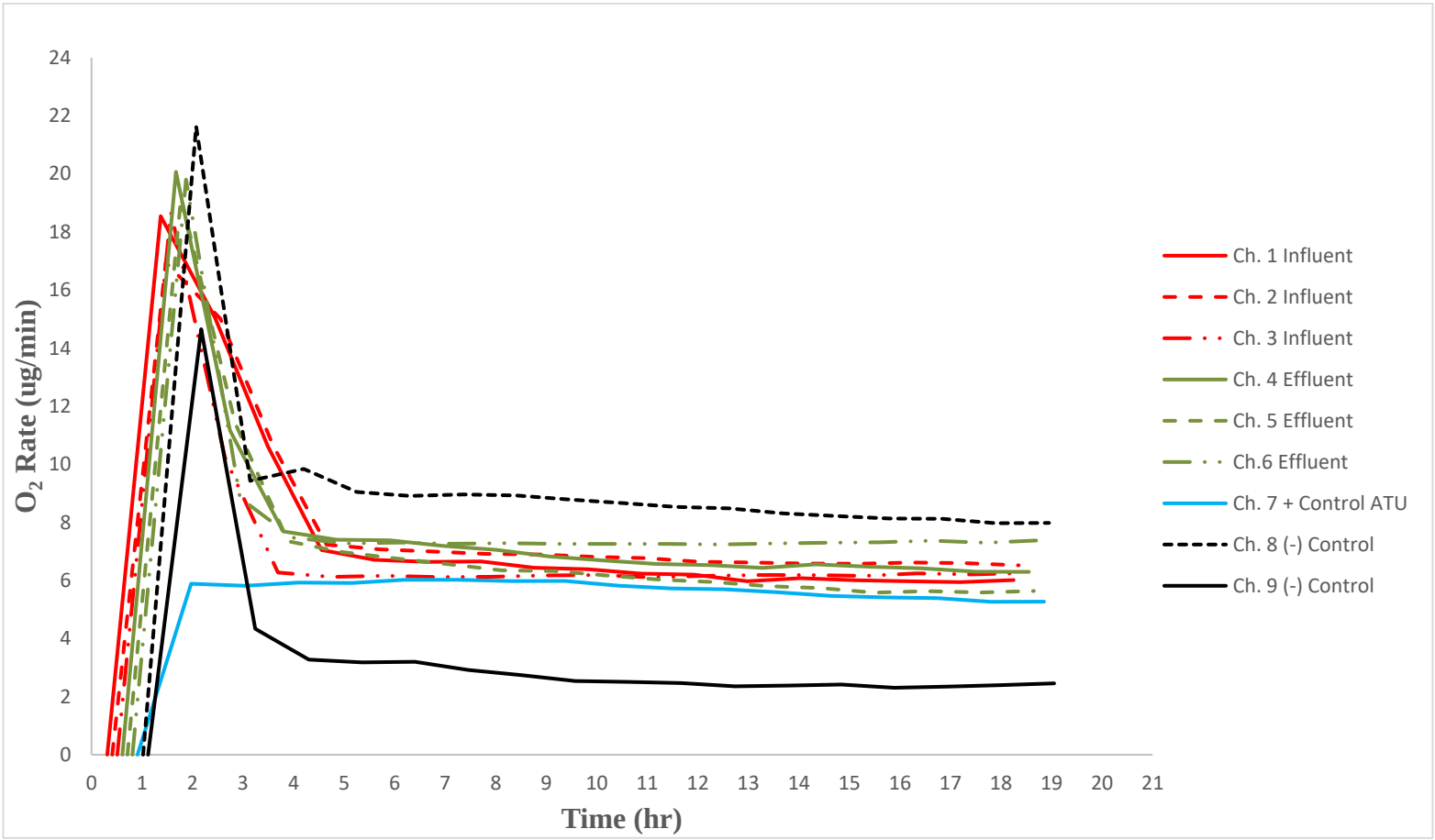

Figure 16: The Effect of AOP Treatment (17.6 g H_2O_2/g GG @ 200 mA) on the O_2 Uptake Rate of Activated Sludge.

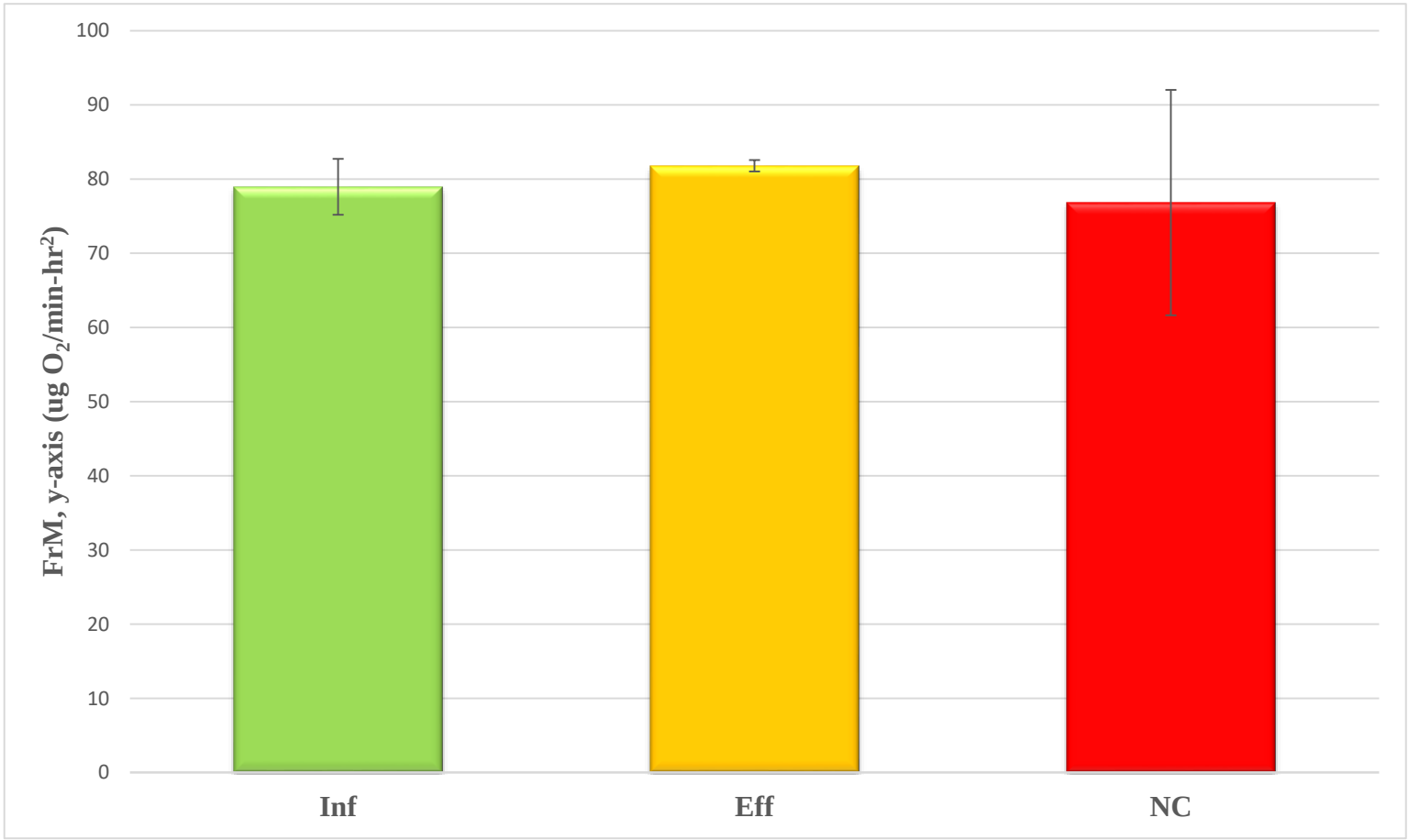

Figure 17: The Effect of AOP treatment (17.6 g H_2O_2/g GG @ 200 mA) on the FrM of Respirometry Profile.

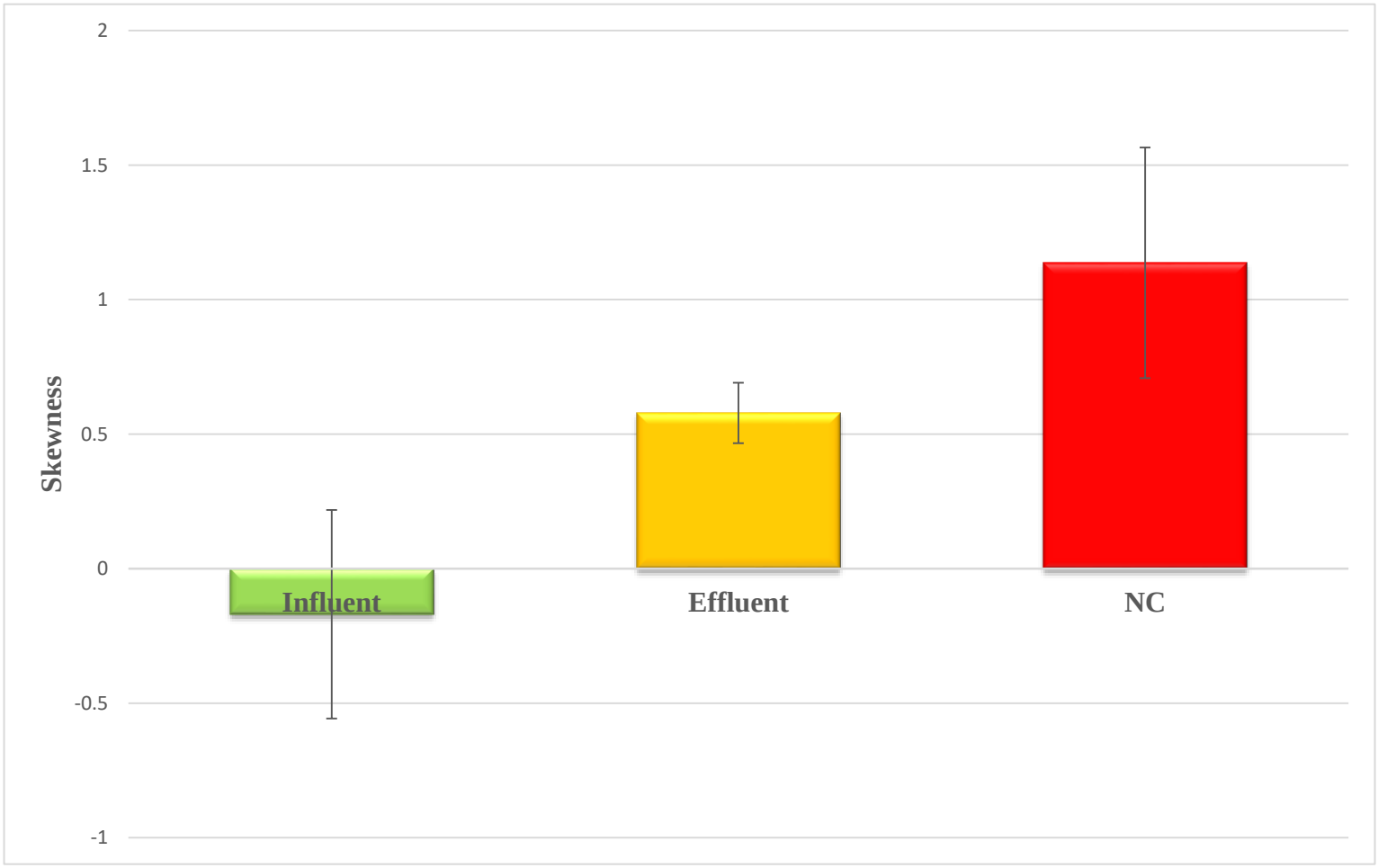

Figure 18: The Effect of AOP treatment (17.6 g H_2O_2/g GG @ 200 mA) on the Skewness of Respirometry Profile.

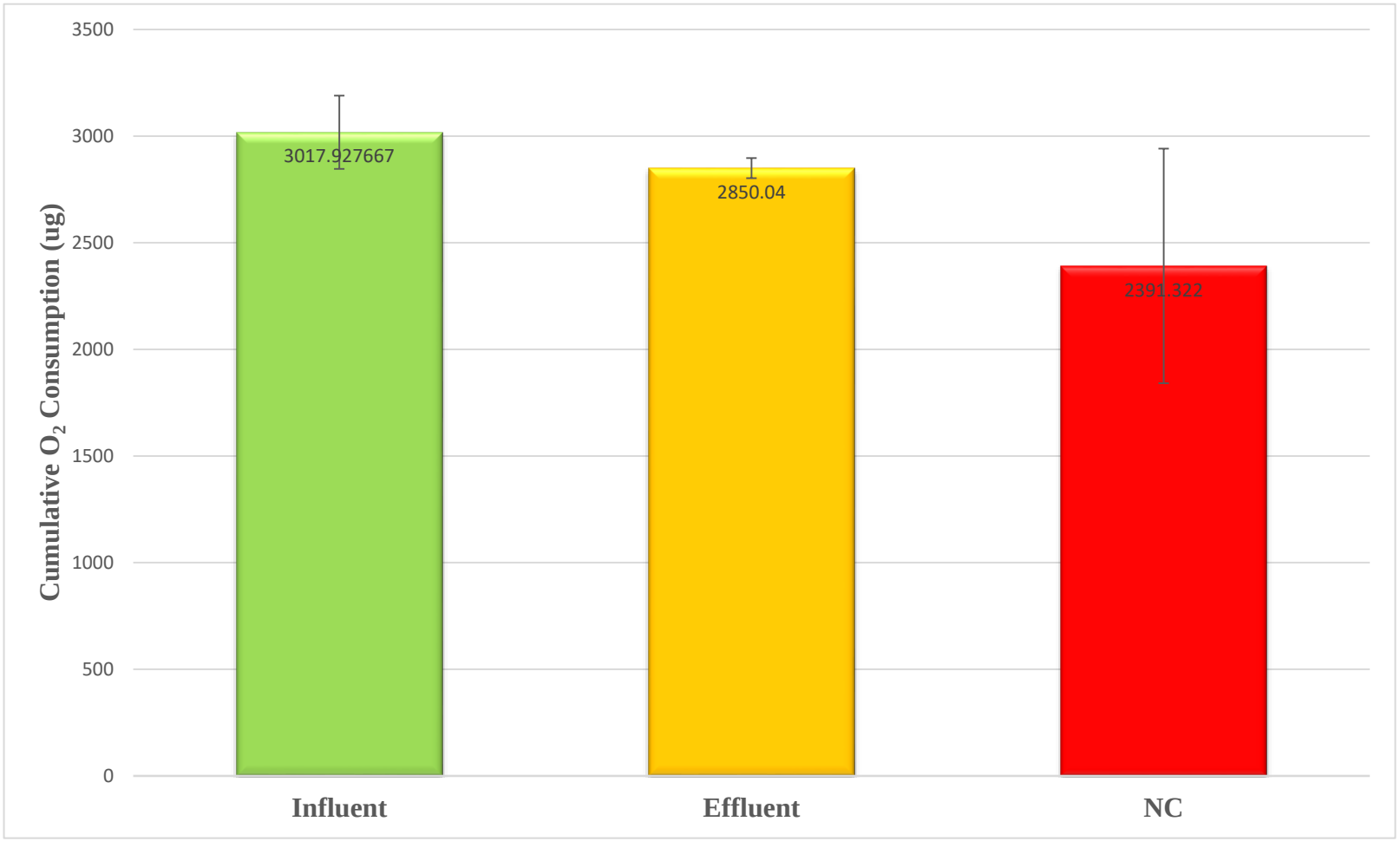

Figure 19: The Effect of AOP treatment (17.6 g H_2O_2/g GG @ 200 mA) on the Cumulative O_2 Consumption.

Appendix C

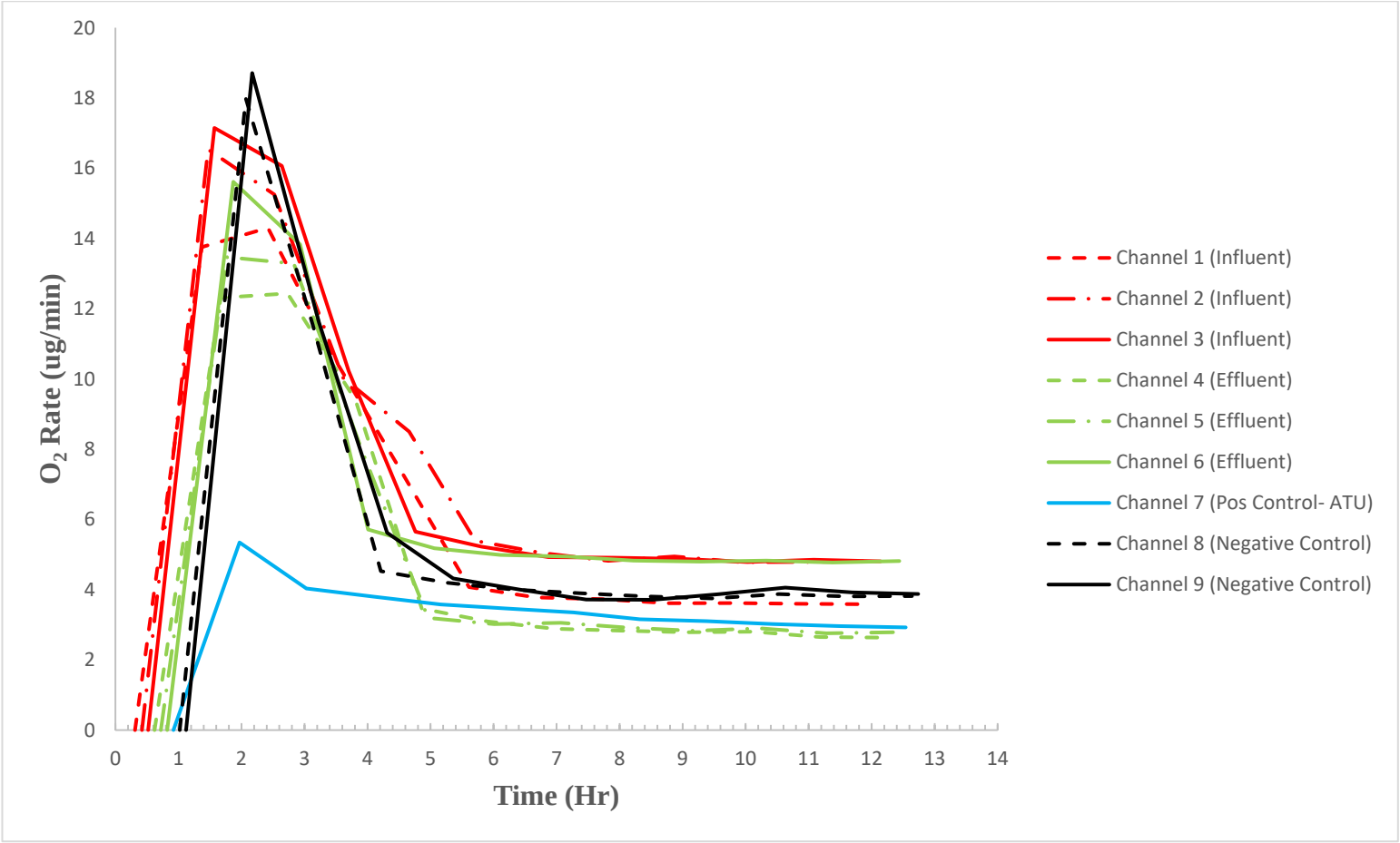

Figure 20: The Effect of AOP Treatment (70.5 g H_2O_2/g GG @ 200 mA) on the O_2 Uptake Rate of Activated Sludge

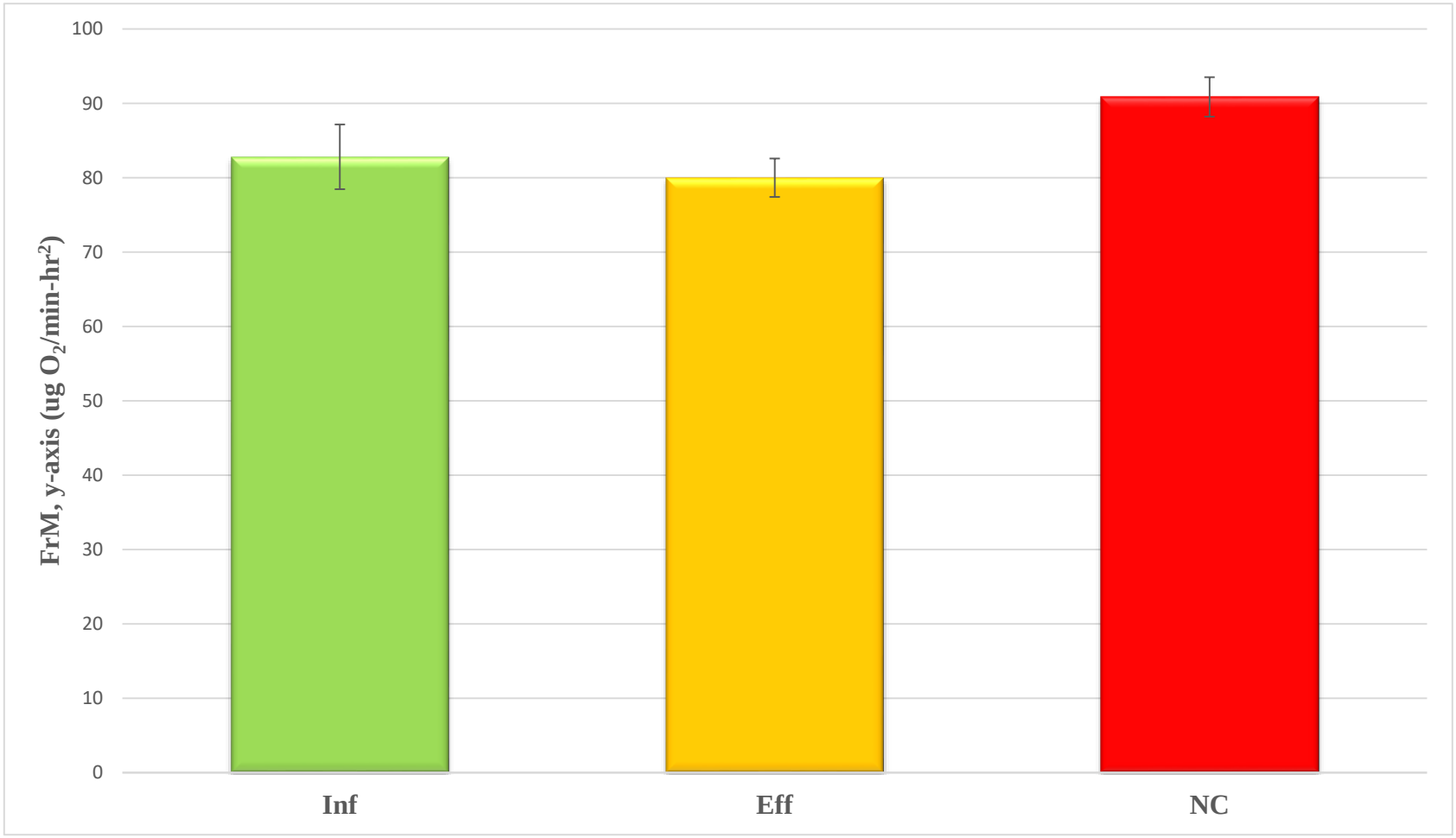

Figure 21: The Effect of AOP treatment (70.5 g H_2O_2/g GG @ 200 mA) on the FrM of Respirometry Profile.

Figure 22: The Effect of AOP treatment (70.5 g H_2O_2/g GG @ 200 mA) on the Skewness of Respirometry Profile.

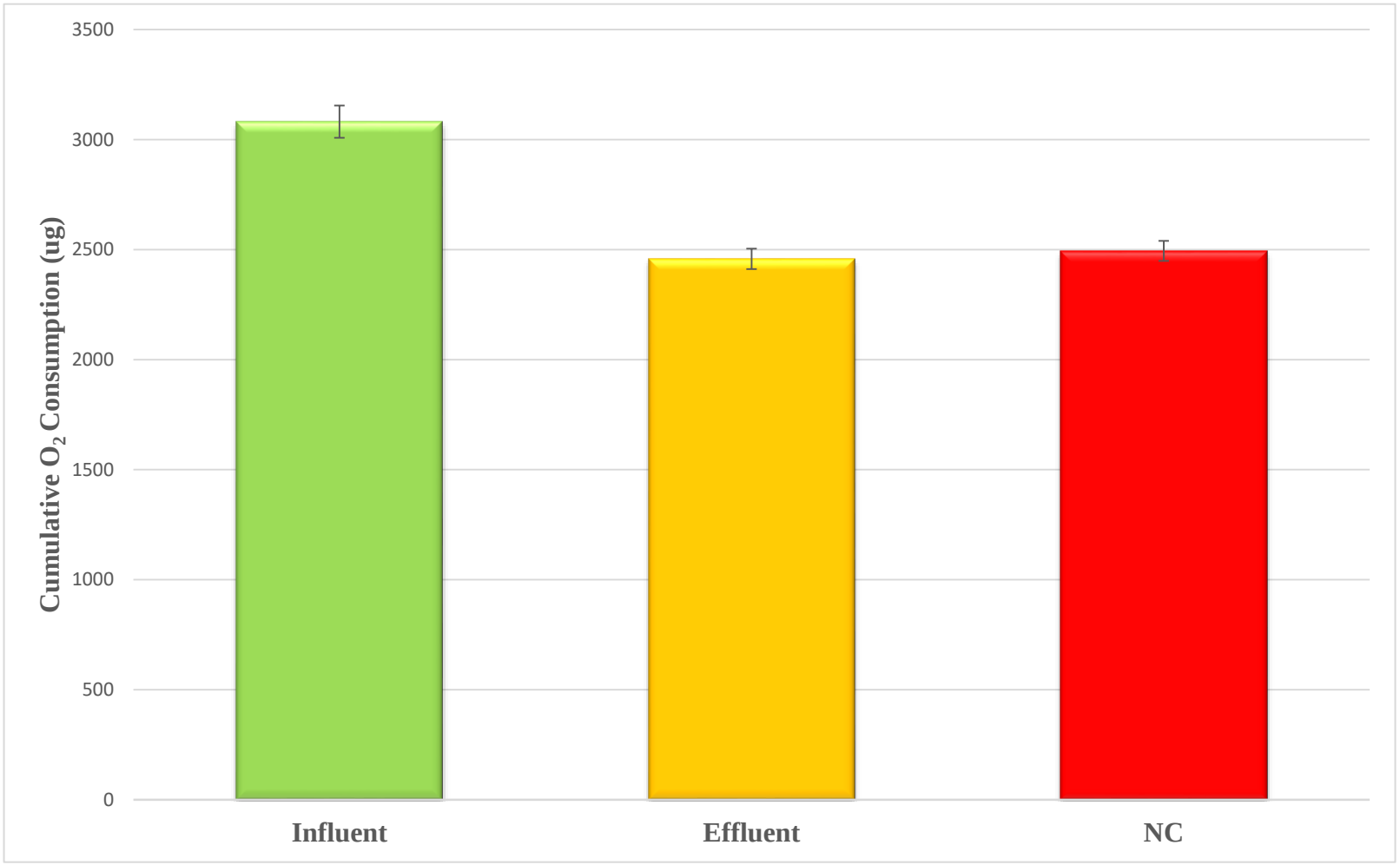

Figure 23: The Effect of AOP treatment (70.5 g H_2O_2/g GG @ 200 mA) on the Cumulative O_2 Consumption.

Appendix D

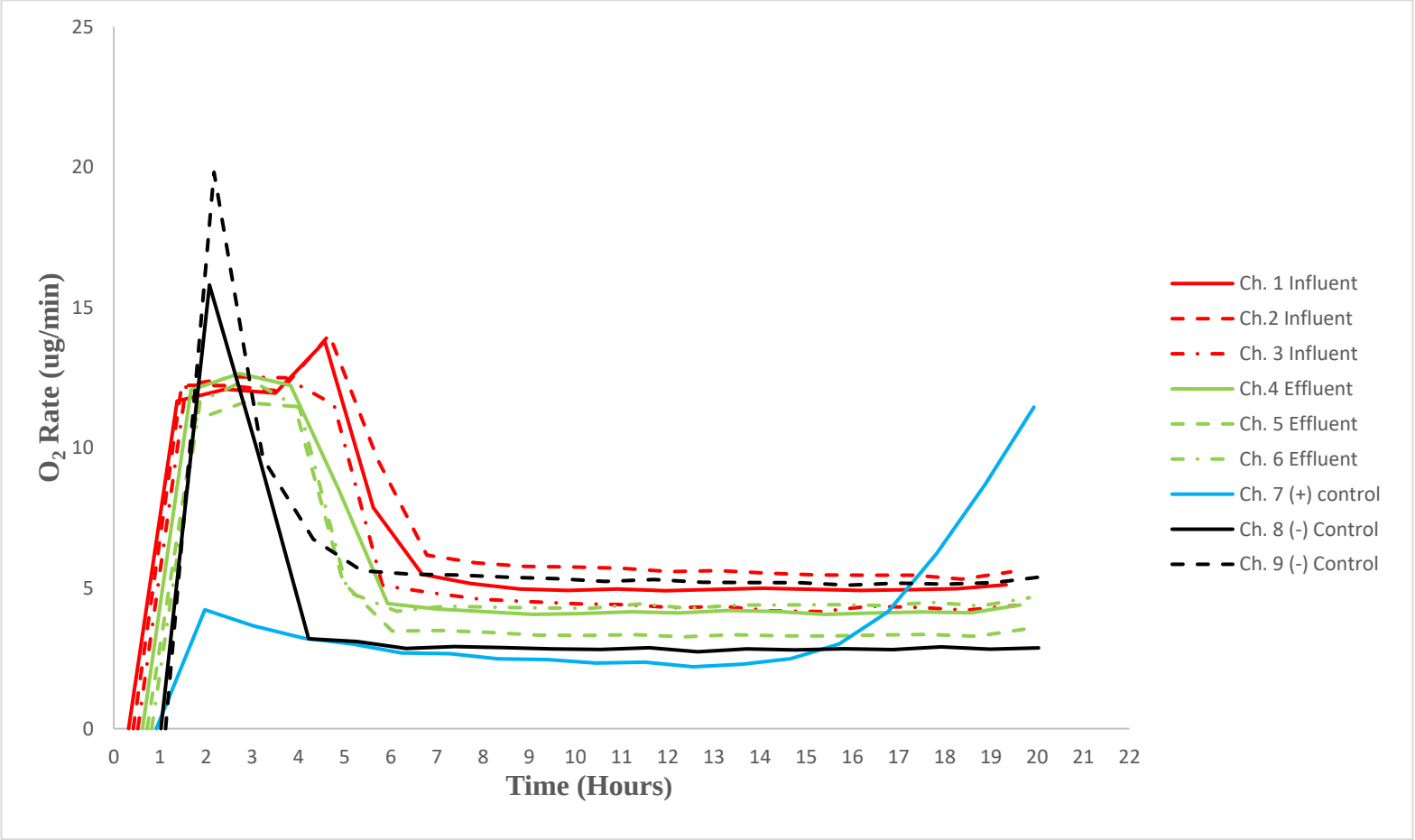

Figure 24: The Effect of AOP Treatment (176.3 g H_2O_2/g GG @ 200 mA) on the O_2 Uptake Rate of Activated Sludge.

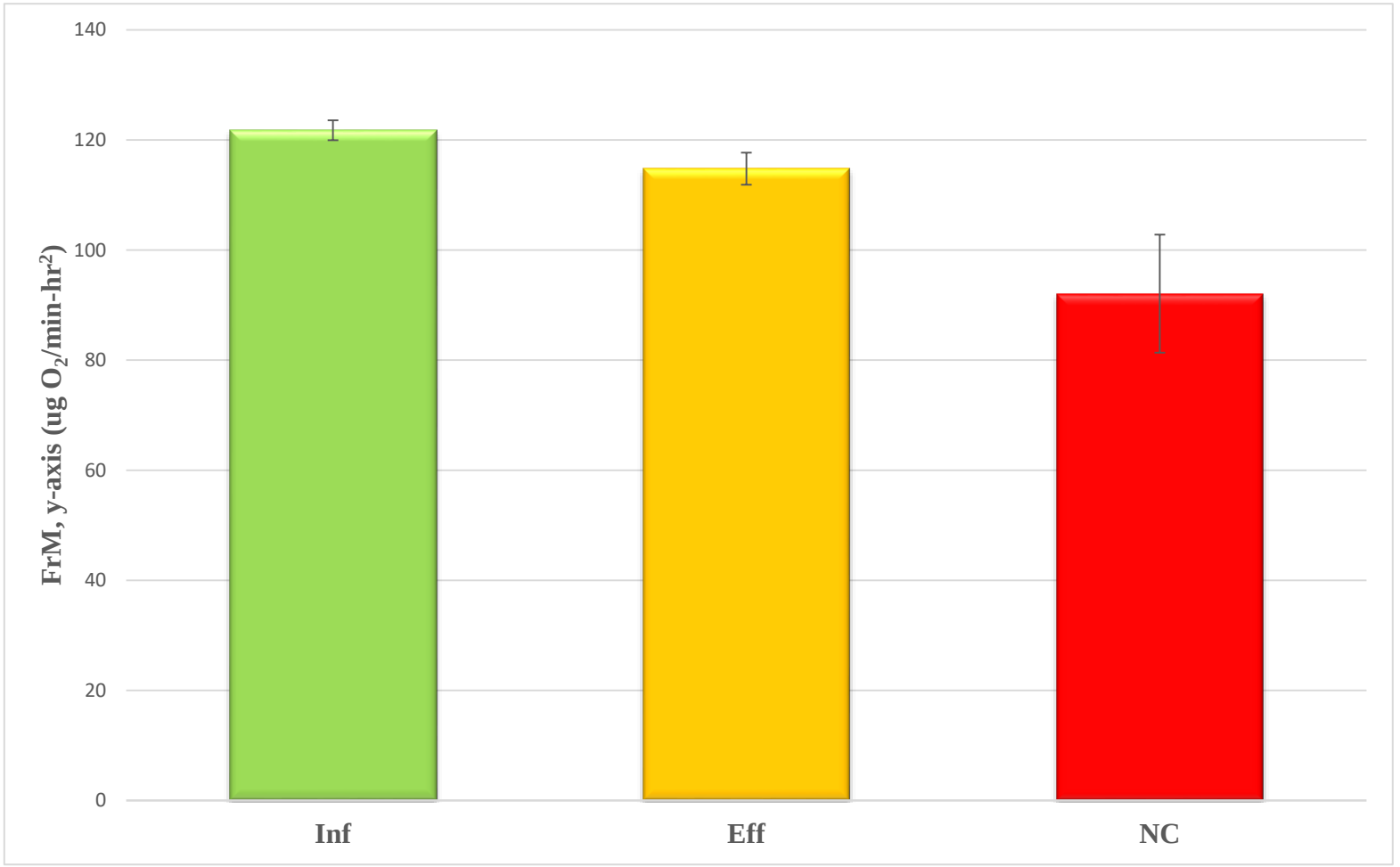

Figure 25: The Effect of AOP treatment (176.3 g H_2O_2/g GG @ 200 mA) on the FrM of Respirometry Profile.

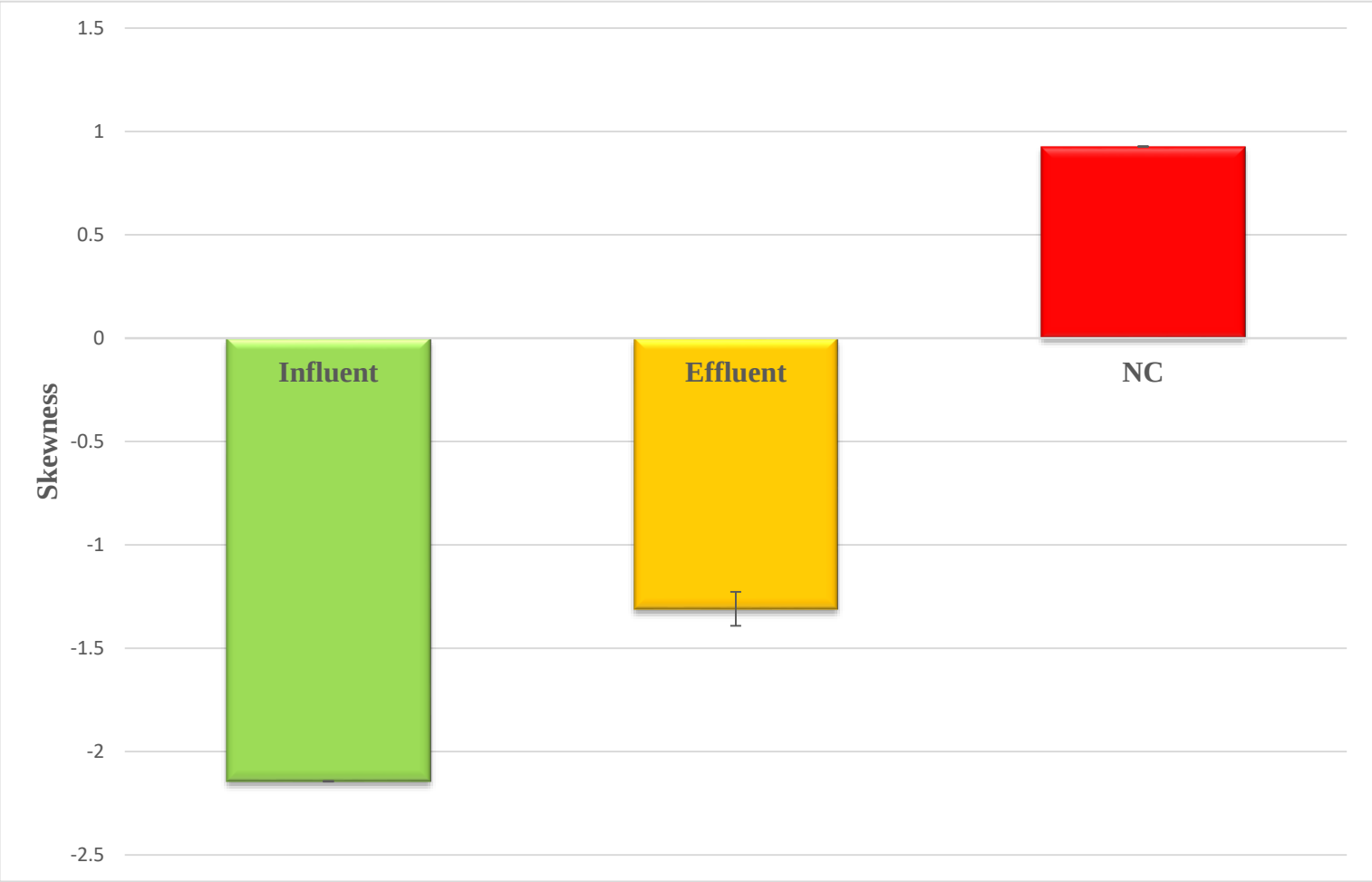

Figure 26: The Effect of AOP treatment (176.3 g H_2O_2/g GG @ 200 mA) on the Skewness of Respirometry Profile.

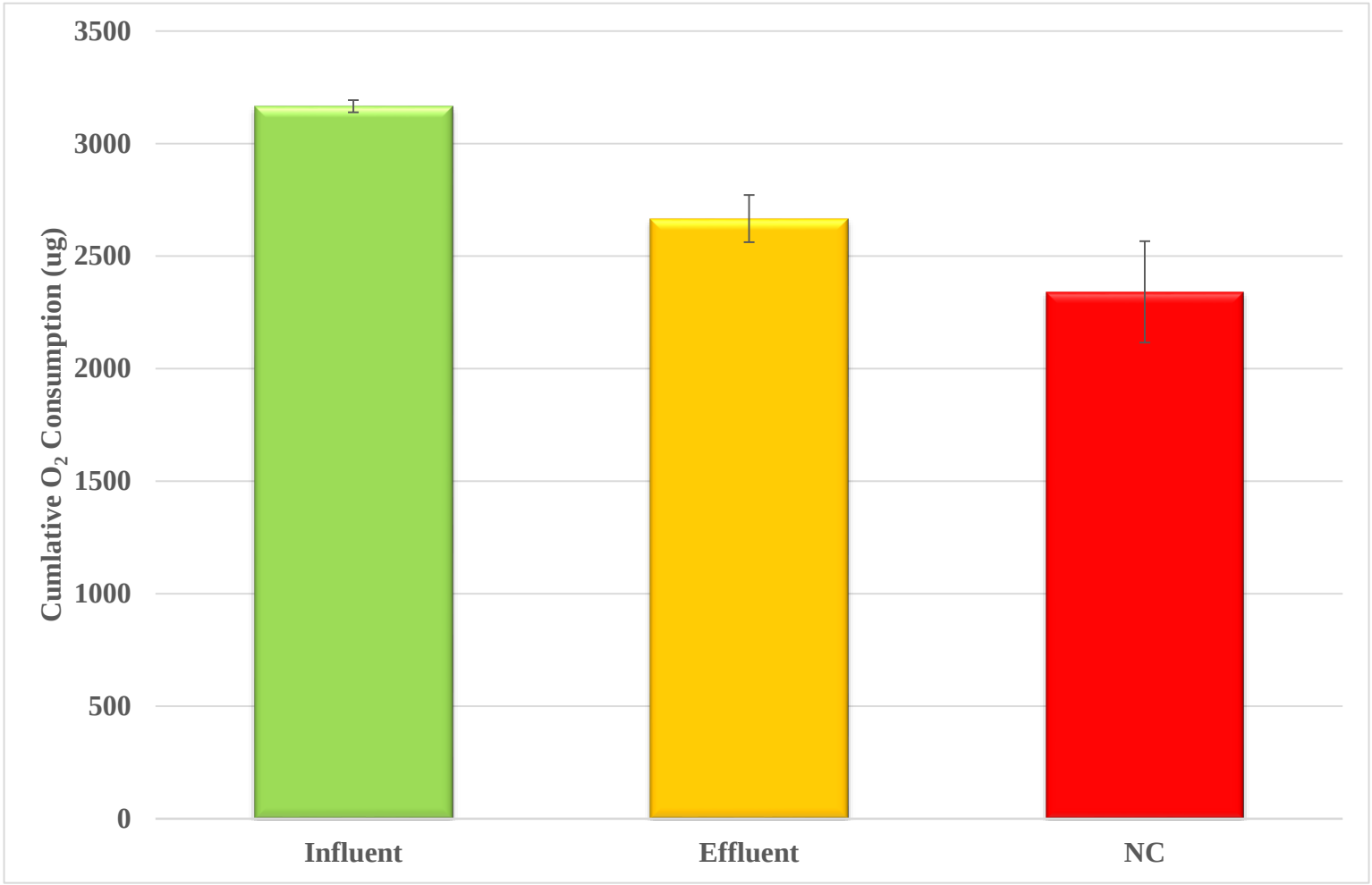

Figure 27: The Effect of AOP treatment (176.3 g H_2O_2/g GG @ 200 mA) on the Cumulative O_2 Consumption.

Appendix E

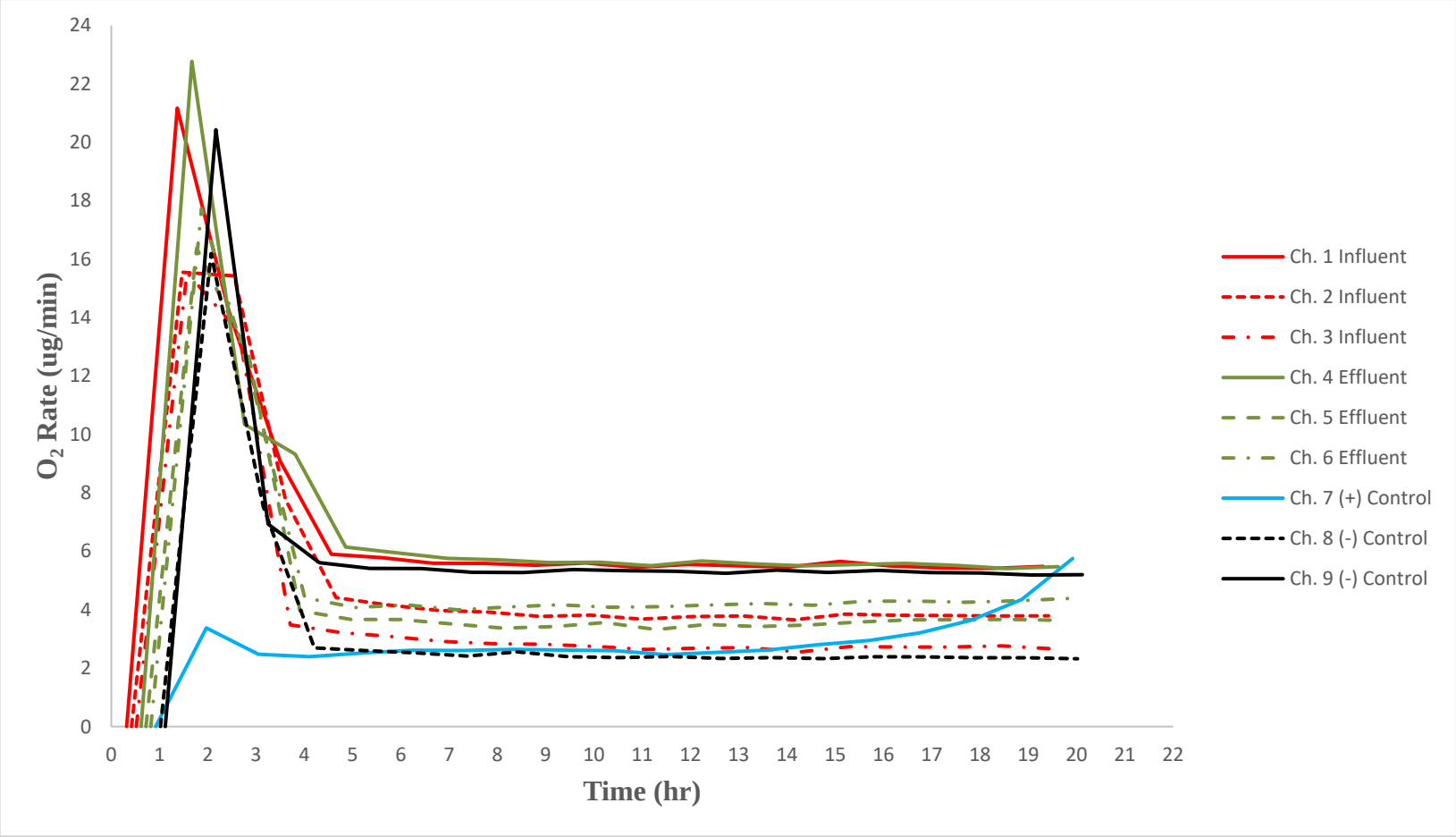

Figure 28: The Effect of AOP Treatment (17.6 g H_2O_2/g GG @ 100 mA) on the O_2 Uptake Rate of Activated Sludge.

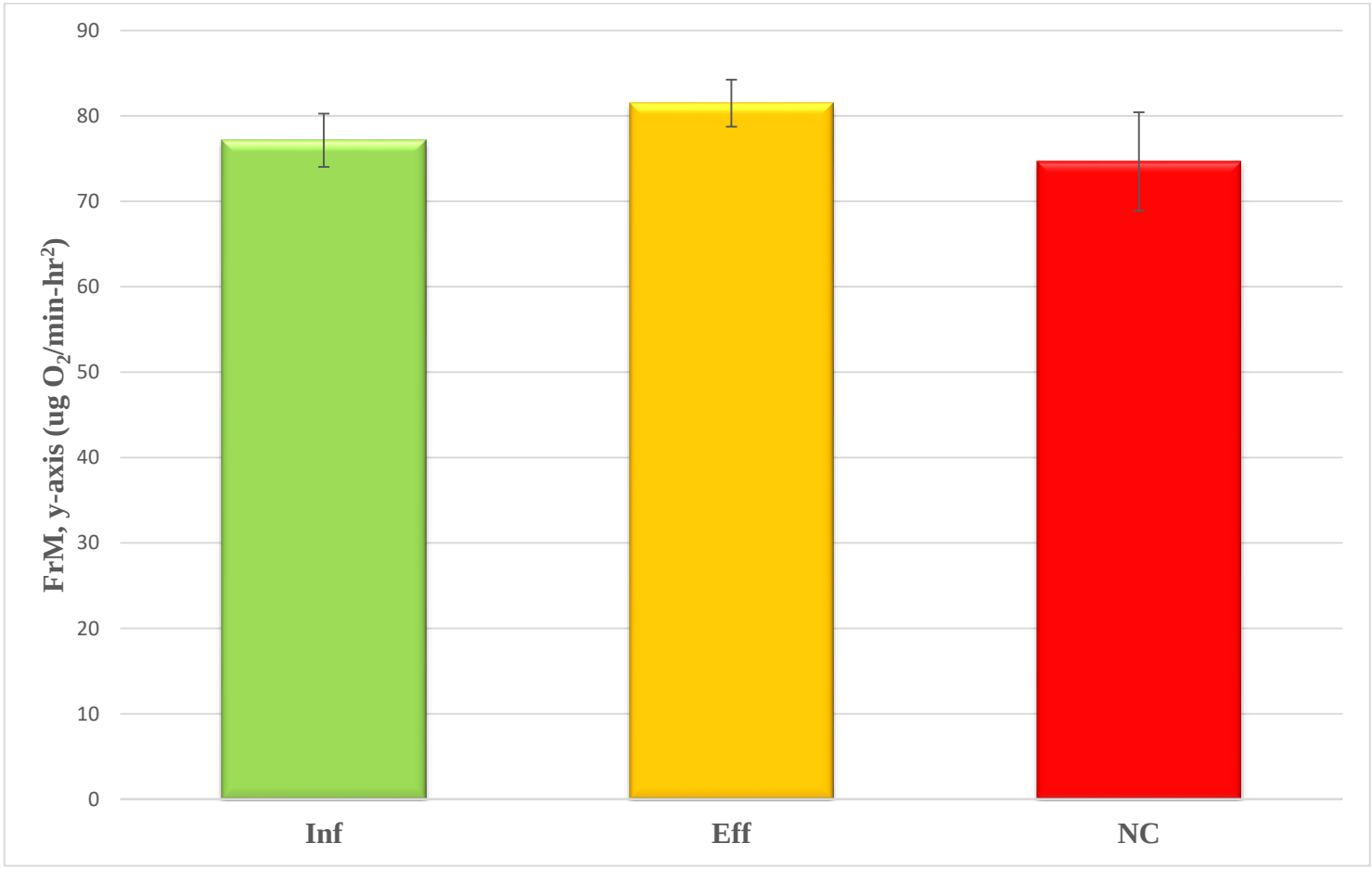

Figure 29: The Effect of AOP treatment (17.6g H_2O_2/g GG @ 100 mA) on the FrM of Respirometry Profile. .

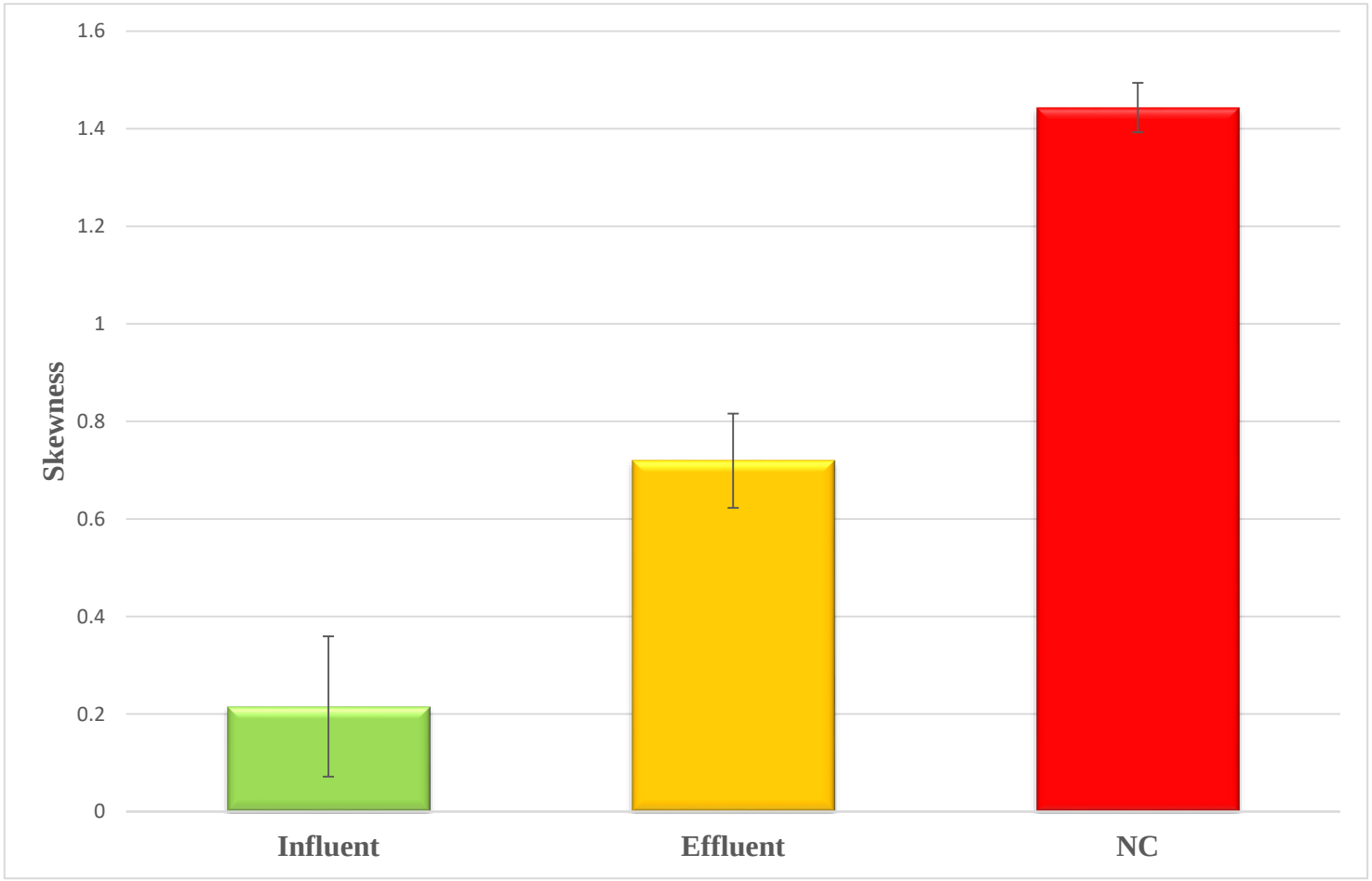

Figure 30: The Effect of AOP treatment (17.6 g H_2O_2/g GG @ 100 mA) on the Skewness of Respirometry Profile.

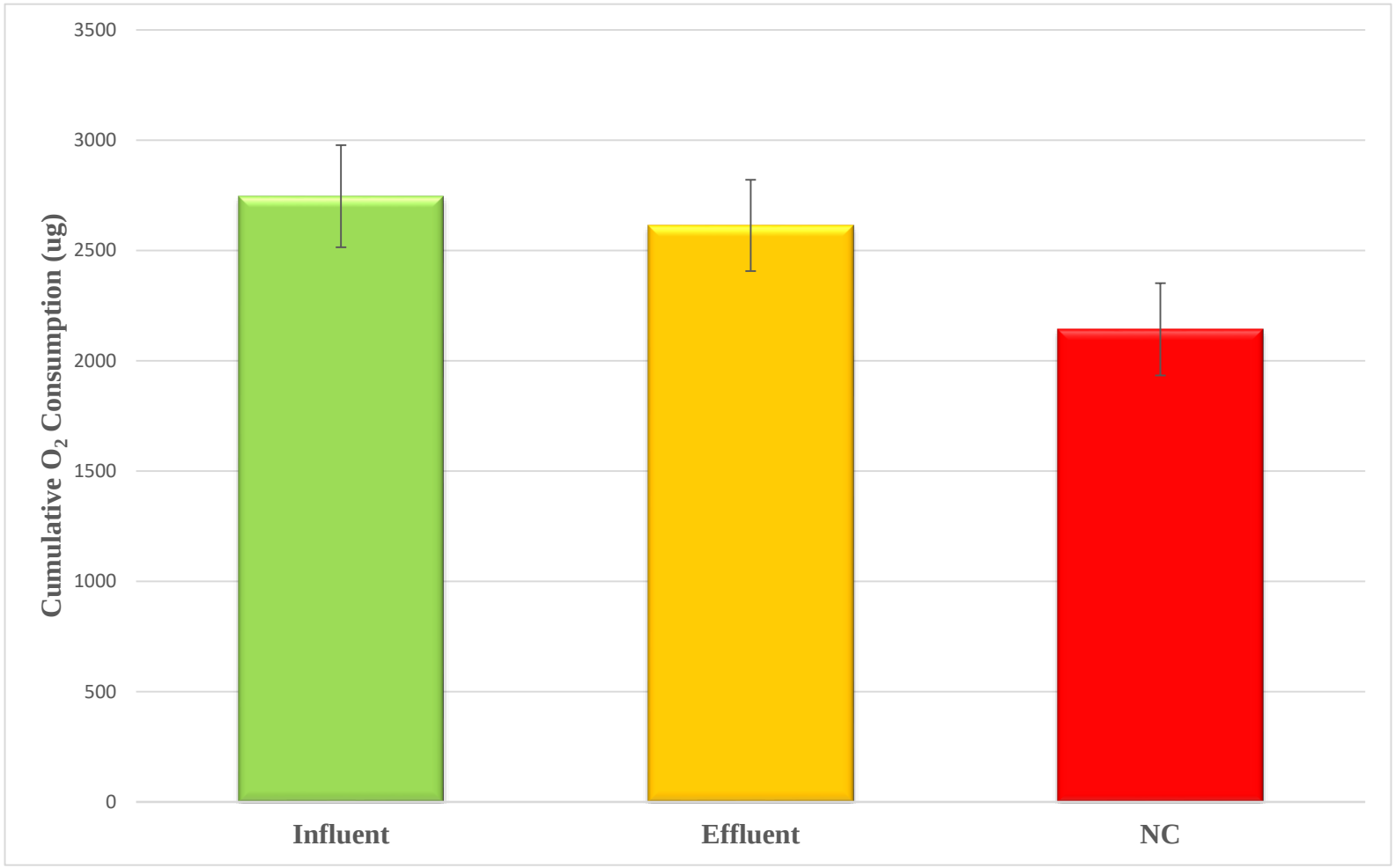

Figure 31: The Effect of AOP treatment (17.6 g H_2O_2/g GG @ 100 mA) on the Cumulative O_2 Consumption.

Appendix F

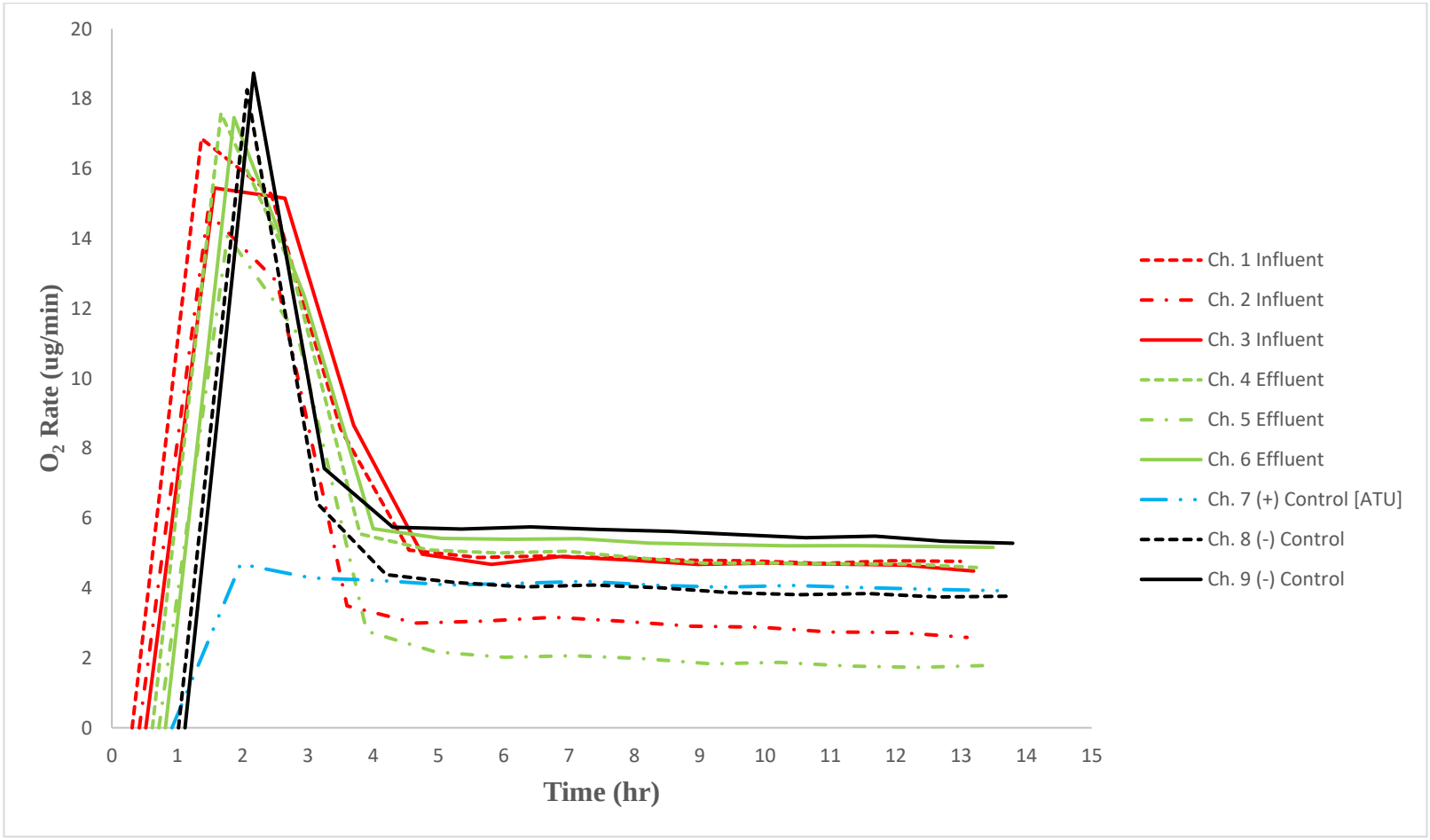

Figure 32: The Effect of AOP Treatment (17.6 g H_2O_2/g GG @ 50 mA) on the O_2 Uptake Rate of Activated Sludge.

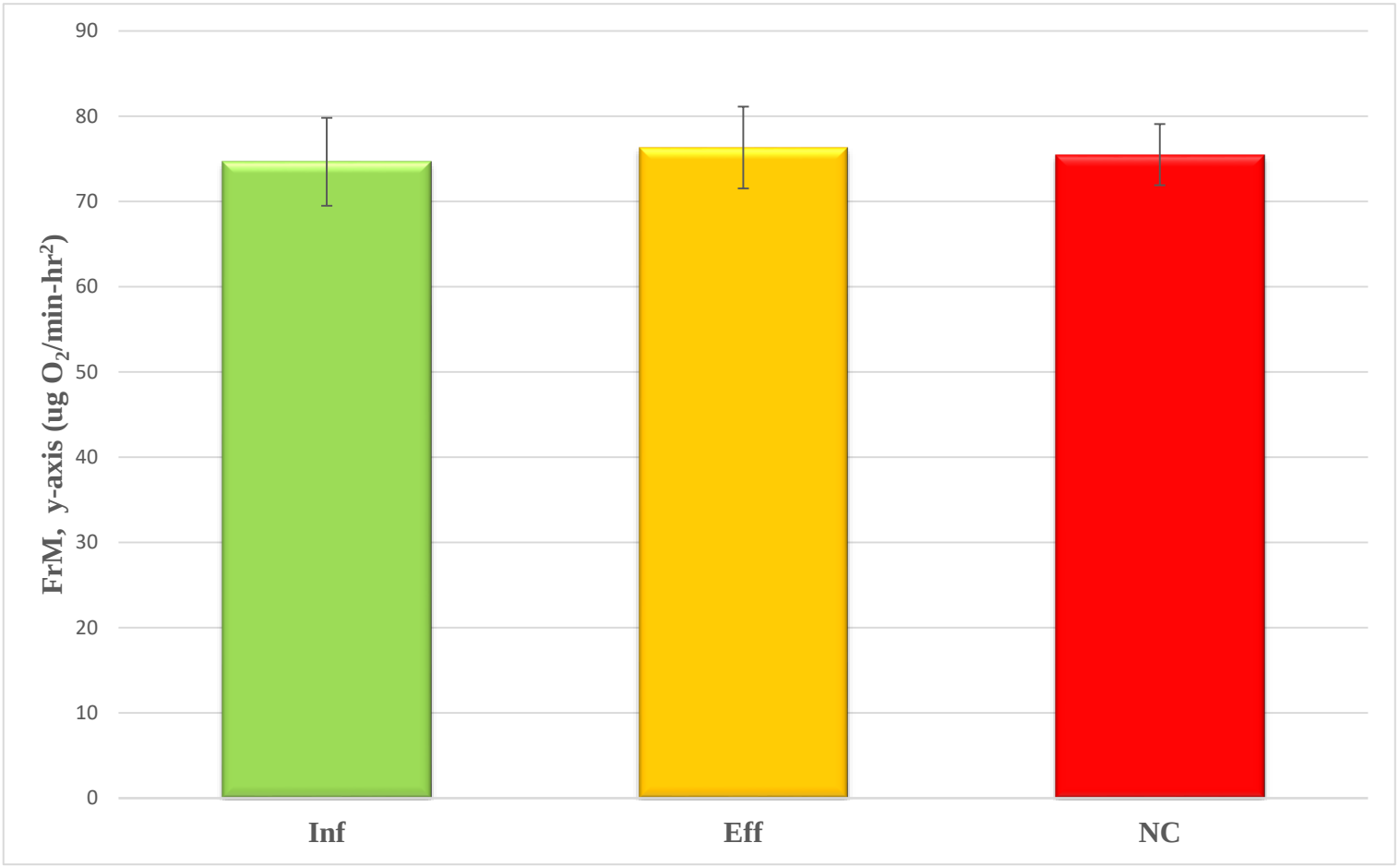

Figure 33: The Effect of AOP treatment (17.6 g H_2O_2/g GG @ 50 mA) on the FrM of Respirometry Profile.

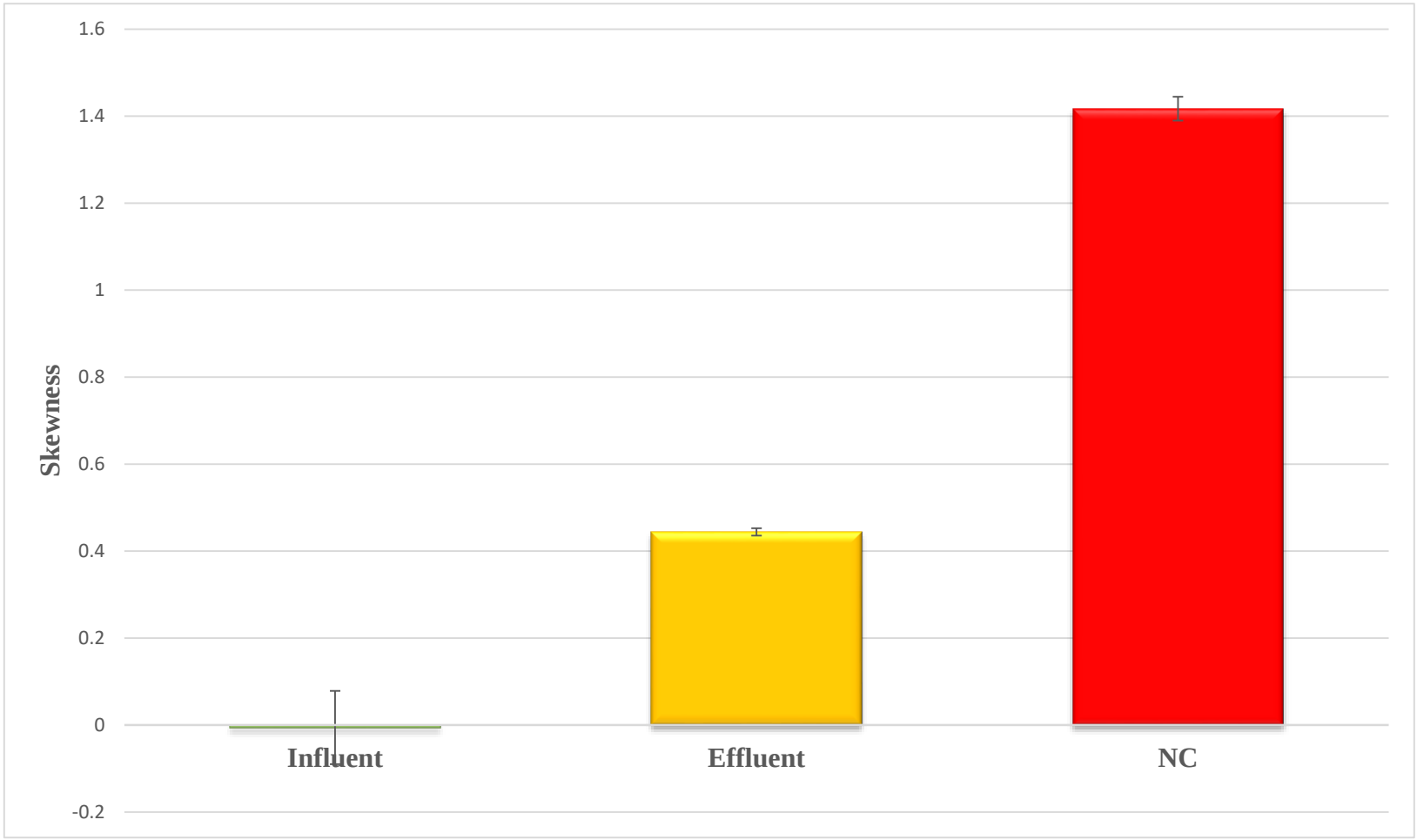

Figure 34: The Effect of AOP treatment (17.6 g H_2O_2/g GG @ 50 mA) on the Skewness of Respirometry Profile.

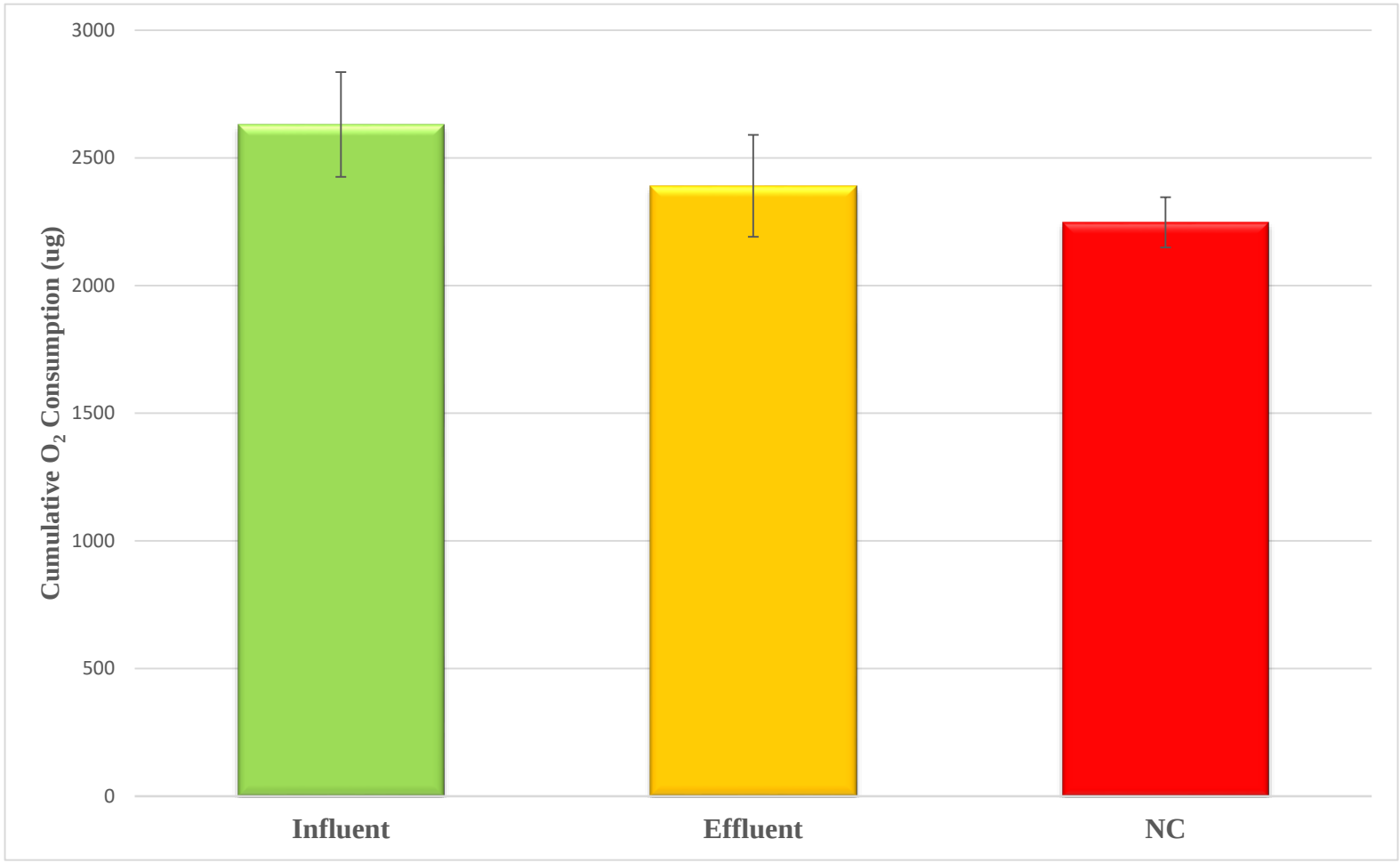

Figure 35: The Effect of AOP treatment (17.6 g H_2O_2/g GG @ 50 mA) on the Cumulative O_2 Consumption.

Appendix G

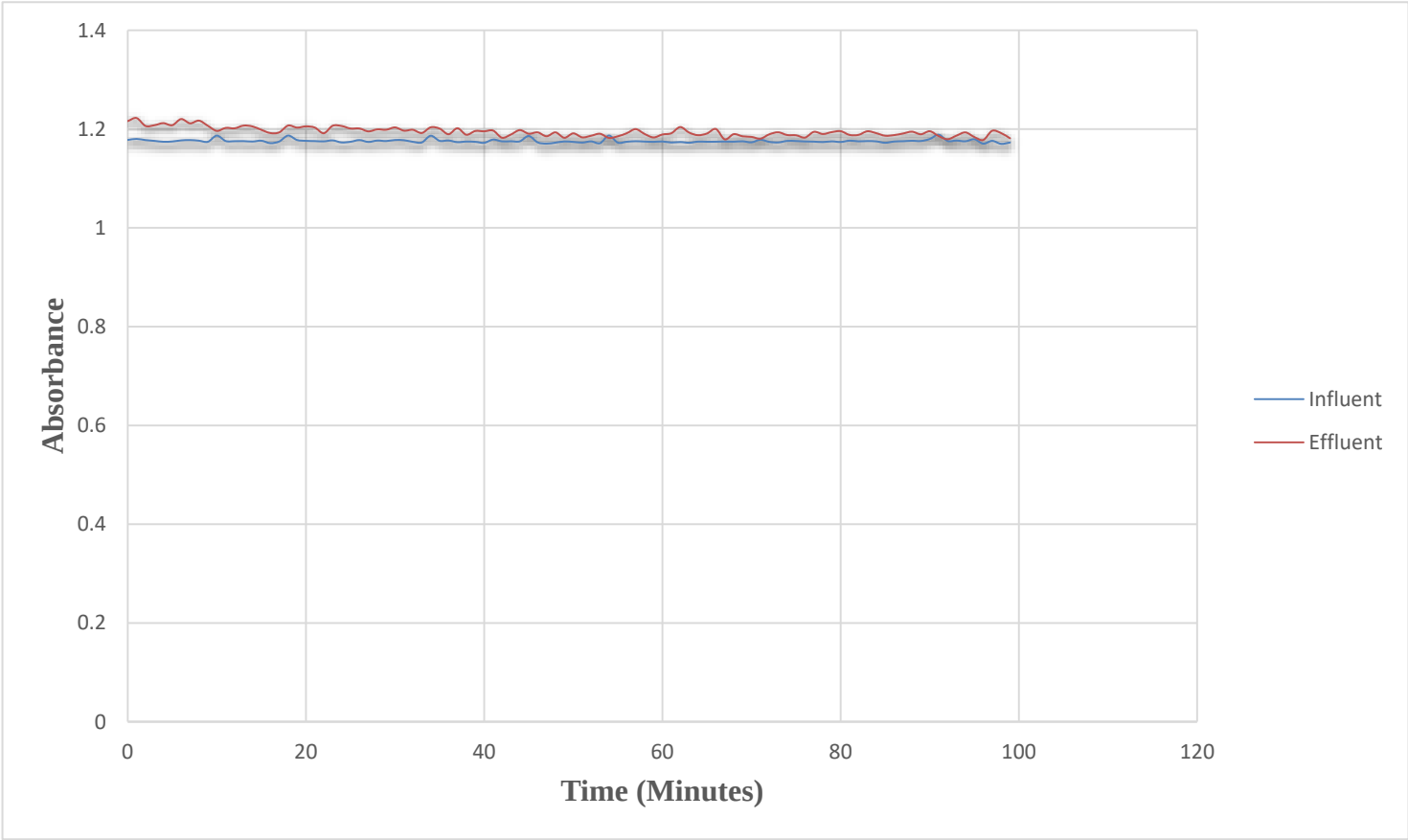

Figure 36: Influent vs Effluent Absorbance Profiles at 265 nm. Treatment Condition: 70.5 g H_2O_2/g GG, 200 mA.

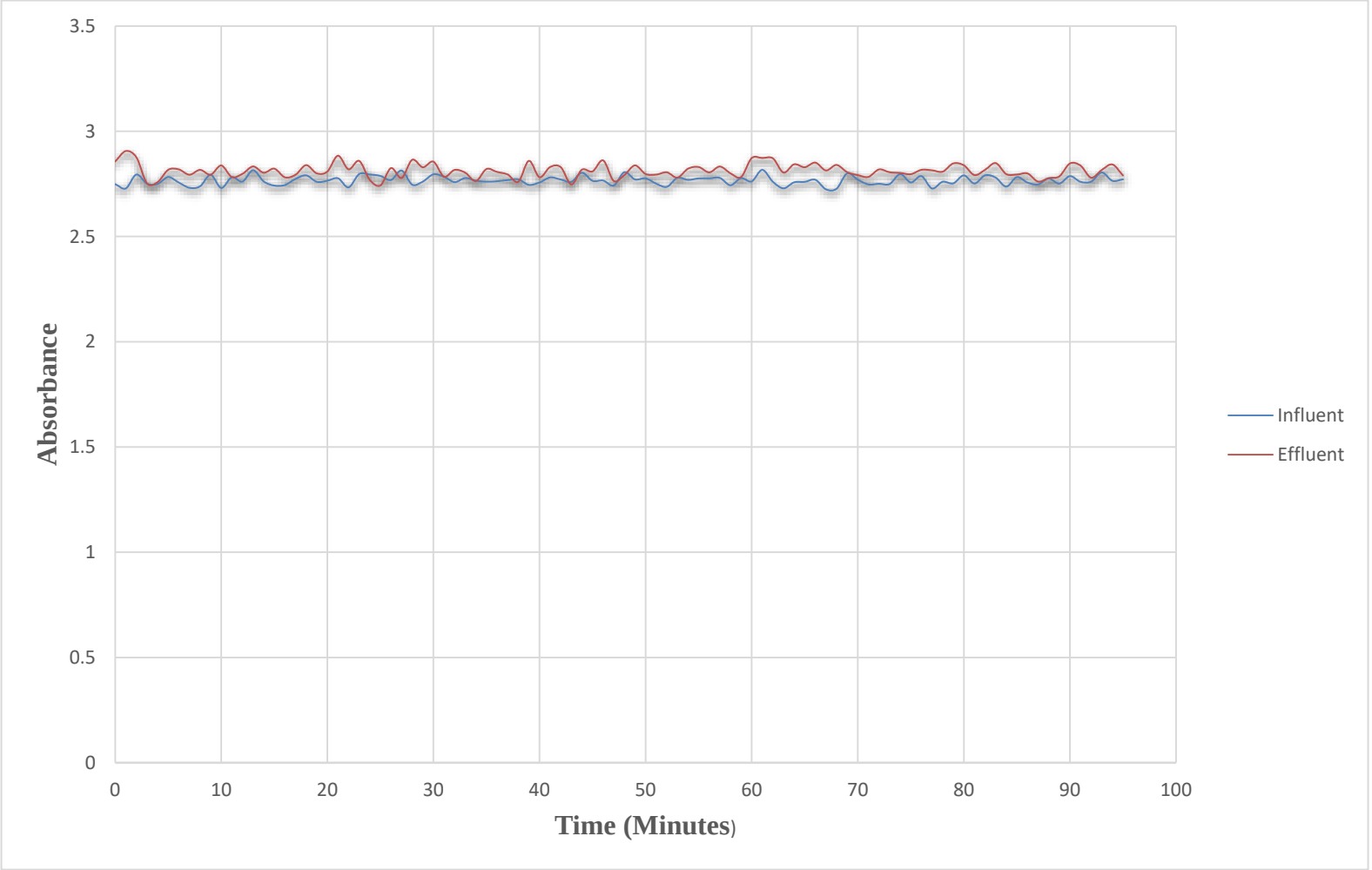

Figure 37: Influent vs Effluent Absorbance Profiles at 265 nm. Treatment Condition: 176.3 g H_2O_2/g GG, 200 mA.

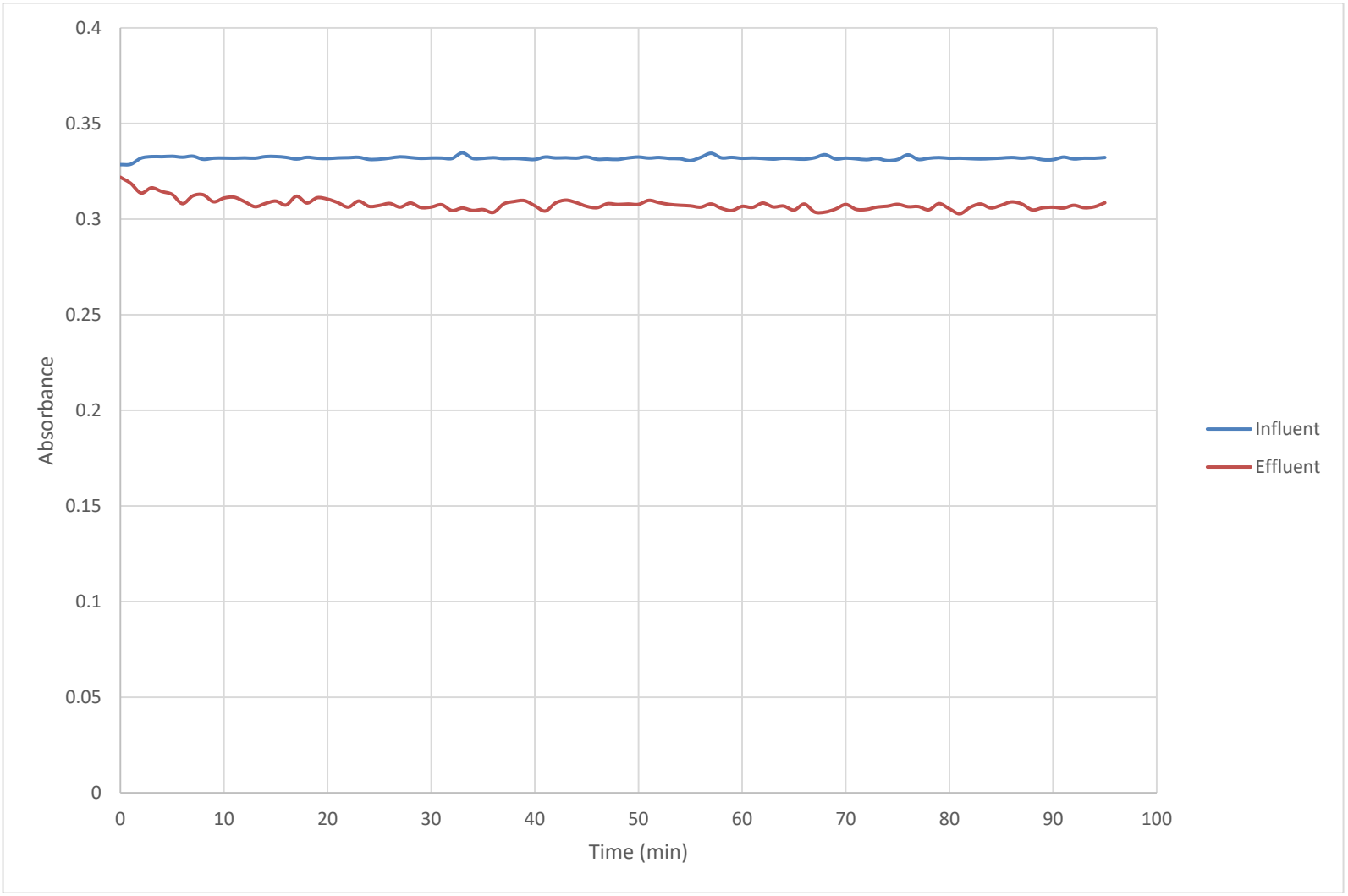

Figure 38: Influent vs Effluent Absorbance Profiles at 265 nm. Treatment Condition: 17.6 g H_2O_2/g GG, 100 mA.

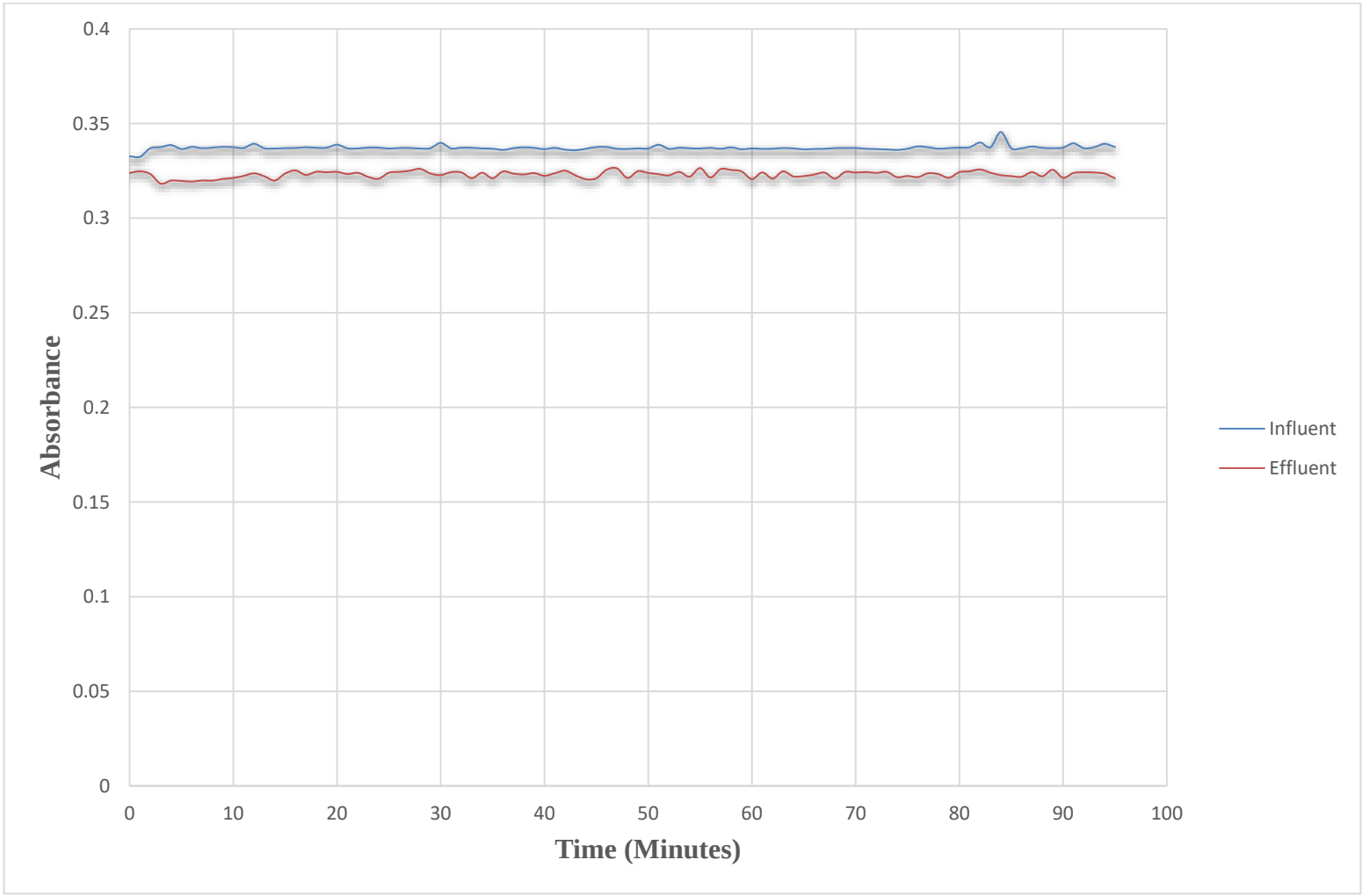

Figure 39: Influent vs Effluent Absorbance Profiles at 265 nm. Treatment Condition: 17.6 g H_2O_2/g GG, 50 mA.

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14. ABSTRACT

Guar Gum (GG) is one of the problematic water pollutants connected to hydraulic fracturing. There is a pressing need to investigate appropriate unit operations that can be employed to protect the aquatic environment. This study investigated the use of light-emitting diodes (LEDs) in the advanced oxidation process (AOP) of GG. Chemical oxygen demand (COD) removal provided mixed results, depending on the concentration of hydrogen peroxide (H_2O_2) in solution, and was between (0-95%) for H_2O_2-to-GG ratios between 7.0 and 176.3g $H_2\neg O_2$/g GG. COD removal was greatest at the lowest H_2O_2-to-GG ratio of 7.0g H_2O_2/g GG. Additionally, the COD removal was near 0% at the higher H_2O_2-to-GG ratio of 176.3 H_2O_2/g GG. These results were explained by the measured relative absorbance of GG and H_2O_2, which showed that H_2O_2 absorbed 8 times more UV light than GG. This means that the hydroxyl radicals were not inhibited by the absorbance of the GG. The AOP effluent was not chemically identical to the influent and a small pool of transformation byproducts were likely present in the effluent. UV LED/H_2O_2 AOP treatment of GG had no statistically significant effect on microbial respiration.

15. SUBJECT TERMS

Advanced oxidation, guar gum, water

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