Evaluation of Chemical Oxygen Demand (COD) Reduction in Distillery Wastewater Treatment Using the Photocatalysis

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Abstract

The photo-catalysis technology has been effective and efficient in the reduction of chemical oxygen demand (COD) in wastewater. Titanium dioxide (TiO_2) is one of the most commonly used photo-catalyst and plays significant a major role in reducing COD concentration levels in wastewater. The polyaniline (PANI) was synthesized using an in-situ chemical oxidative polymerization method. This work focused on the reduction of COD in distillery wastewater using an annular rector under batch mode. The influent was diluted at different concentration levels of about 5 ml/l, 10 ml/l and 20 ml/l. The pH condition was adjusted at pH of 1.00, 2.00, 3.00, 4.00 and 5.00 in order to evaluate its effect on the COD reduction efficiencies. The TiO_2/PANI was prepared in different ratios and was allowed to mix with the wastewater for a good homogeneity mixture. The experiments were carried out at ambient temperature (± 25 ºC), whereby solutions were pumped into the photo reactor (annular) inserted with a 25 UVC lamp. The results indicated that the concentrations of all three solutions without the catalyst decreased from 355 mg/l, 655 mg/l and 837 mg/l to 325 mg/l, 572 mg/l and 820 mg/l, respectively. The solutions containing the catalyst also decreased from 325 mg/l, 572 mg/l and 820 mg/l to 344 mg/l, 475 mg/l and 752 mg/l, respectively. The results showed an increasing reduction trend of 2%, 2%, 19%, 20% and 26 % when the catalyst was used at pH of 6.0. It can be concluded that photo-catalysis can reduce COD in distillery wastewater when running under both recirculation and continuous. It can therefore be recommended that higher adjustments of pH can be done, and the process can be operated for more than 2 hours to further enhance the COD reduction in distillery wastewater.

Keywords:

Photo-catalysis, Chemical oxygen demand, Annular Photo-reactor, Distillery wastewater

1. Introduction

The effluents produced by most of the industries (gaseous or liquid) are harmful to health and the environment in general. The presence of undesired substances in liquid effluents can be disastrous as they pose serve threats to the immediate recipients. Wastewater from various factories, industries, laboratories, etc. are serious problems to the environment(Akpan and Hameed, 2009).

Different industrial effluents such as agrochemical, Kraft-bleaching, pulp and paper, and distillery wastes contains biological organic contaminants which are not easily removed by biological treatment (Susree et al., 2013). Distillery wastewater usually contains extremely high traces of Chemical Oxygen Demand (COD), Total Organic Carbon (TOC) and Biological Oxygen Demand (BOD) which cannot be released into the environment without treatment(Selvanathan and Deshpande, 2014).

The shortage of fresh water has led to the exploration of effective technologies for treatment of wastewater for reuse purposes. Conventional wastewater treatment is said to be inefficient when coming to the degradation of contaminants such as organic compound, since the micro – organic pollutants have the ability to avoid elimination in most wastewater treatment plants(Mecha et al., 2017).

Amongst the many techniques developed for wastewater treatment, the use of advanced oxidation processes (AOPs) has be implemented to refinement the effluents of wastewater to the required standards. The AOPs have been

investigated for their potential in large scale treatment due to their ease of operation, high efficiency in organic mineralization and inactivation of pathogens(Chong et al., 2012).

Advance oxidation processes can be applied to oxidize pollutants with a combination of oxidants. TiO_2 is the most used oxidant due to its high oxidizing potential of holes in the valence band formed by photoexcitation. Due to its excellent chemical stability, photocatalytic activity and superior oxidation ability, TiO_2 based photo-catalysts have been used in water purification and wastewater treatment(Jiang, 2004).

The study of photo-degradation has shown that majority of organic pollutants in water can be at least removed or mineralized. The photocatalytic treatment of many organic compounds has been successfully achieved. The photocatalytic activity is dependent on the surface and structural properties of the semiconductor such as crystal composition, surface area, particle size distribution, porosity, band gap and surface hydroxyl density(Segneanu et al., 2013, Jiang, 2004).

Ultra Violet (UV) photo degradation is said to have the ability to achieve color removal of 54% for distillery wastewater, with a COD reduction of <20% and a negligible BOD reduction. Solar radiation can be considered as an alternative, effective and economic energy carrier for the treatment of industrial effluent (Apollo et al., 2013, Vineetha et al., 2013).

This report focuses on the application of photo-catalysis, whereby a PANI/TiO_2 catalyst was used under UV light to reduce the amount of concentration of chemical oxygen demand (COD) in distillery wastewater. The catalyst was firstly prepared prior to its utilization during photo-catalysis.

2. Theoretical Background

There is always a demand of energy whenever there is a growth in population. All countries in the world are driven by natural energy policies such as energy security, economic growth and environmental protection. The enhanced lifestyle and energy demand creates a serious problem for both industries and societies which ultimately retards the economic growth. According to reports by the World Energy Council, energy demand will increase from 1990 to 2020 by at least 50 – 80%. This has a negative impact on the environment and creates health hazards (Vineetha et al., 2013, Susree et al., 2013).

The treatment of waste water is important because it will save large amount of water using for cleaning, washing, watering and industrial uses. Wastewater can be treated chemically, physically and biologically. However, these methods can be combined to achieve wastewater treatment(Ghaith et al., 2015).To achieve wastewater treatment, the implementation of the advance oxidation process (AOP) has been adopted. AOP is a set of chemical treatment procedure enhanced with a photo-catalyst to remove organic and inorganic matter from the wastewater(Ghaith et al., 2015, Segneanu et al., 2013).

Distilleries are one of the most polluting industries, generating large volumes of high strength wastewater. The effluent usually consists of extremely high Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD), strong odor and recalcitrant dark brown color (Satyawali and Balakrishnan, 2008). The recalcitrant color is called melanoidin, which can either be high or low molecular weight polymer formed as a one of the final products of Maillard reaction(Naik et al., 2010).

Few investigators have studied the treatment of distillery effluent for the removal of color and Chemical Oxygen Demand (COD) by different methods like biological and electrochemical methods(Kumar and Chandra, 2006). Distillery effluent contains high amounts of biodegradable organic contaminants which can be converted into biogas, therefore, the most suitable treatment for the effluent is anaerobic digestion. However, the major problem is that the anaerobic digestion process is incapable of removing the color associated with distillery wastewater(Pant and Adholeya, 2007, Apollo et al., 2013).

The highly-concentrated distillery wastewater has high COD in the range of 80 000 – 1000 000 ppm, the effluent has a low pH with a dark brown color contributed by the high COD. The COD reduction of wastewater is usually attained by a combination of physical and chemical methods(Vineetha et al., 2013).

Photo-degradation is the process of eliminating organic compounds in water by using the interaction between UV radiation and titanium dioxide (TiO_2) as a catalyst. This process has the ability to treat toxic organics in wastewater. The UV photo-oxidation is a method that uses UV radiation to activate a catalyst(MUTALIB, 2009). The oxidation process is determined by the very high oxidative potential of the HO. Radicals generated into reaction medium by different mechanisms.

There is no separation step required during UV photo – oxidation because organic contaminants are destroyed while still in the wastewater stream(Bahnemann, 2004). A variety of degradation products (DPs) are formed during photocatalytic processes. Nevertheless, in most cases, no attention is paid to the possible formation of these DPs which, on the other hand, allow the degradation processes to be better understood and evaluated. Cost-effective treatment to complete compound mineralization is usually not feasible and the generation of by – products appears to be unavoidable with photocatalytic degradation(Malato et al., 2002, Ghaith et al., 2015).

TiO_2 has been given the most attention as a semiconductor powder acting as a photo-catalyst. This is due to its high photocatalytic activity having a maximum quantum yields, its biological immunity, low cost and its resistance to photo – corrosion. The most promising method of solving problems concerning the photo-catalyst separation from the reaction solution, is to make use of photocatalytic reactors in which TiO_2 is immobilized on support. The immobilization of TiO_2 onto various support materials has been carried out largely either chemically or physically(Segneanu et al., 2013, Alfano et al., 2000).

3. Methodology

3.1 Materials and Reagents

500g TiO_2 (Degussa P-25, Aeroxide) was purchased from Acros Organics (South Africa). 1ℓ Aniline monomer (Reagent Plus, 99%) and 500g ammonium peroxodisulfate (APS, $(NH_4)_2S_2O_8$) were purchased from Sigma-Aldrich (South Africa). A 25 W Ultraviolet-C Germicidal Lamp from Philips (Ltd), was supplied by Technilamp (South Africa). All chemicals were used as received.

3.2 Experimental Set-Up

The total capacity of the photo-reactor (annular) was 450 mL (Figure 1). The reactor height was 330 mm, internal diameter was 26 mm, with a wall thickness of 2 mm. The capacity of the UV lamp was 25 W UV-C. The inner (length, 451.6 mm, diameter, 28 mm) shield was made of quartz glass to allow full penetration of the UV-rays, while the entire outer fabrication was made of Perspex. The distribution compartment in the annular photo-reactor were fitted with a distribution plate which had 34 evenly distributed holes, each of 1 mm in diameter, and it was located at the bottom of the reactor (the inlet section). The radial length of the annular space was 8 mm. The horizontal irradiation distance of the photo-reactor was 1.2 mm.

Total recirculation volume of the feed solution was 1 L. Before irradiation, dark adsorption experiments were conducted, and the suspension was stirred magnetically for 1h until adsorption-desorption equilibrium was established. The recirculation flow of the solution through reactor was regulated by a peristaltic pump (Masterflex, Head 77916-20, Cole-Parmer instruments, Canada) and operated under ambient temperature. The suspension of varying concentration of distillery wastewater with photo-catalyst was stirred at 360 rpm using a magnetic stirrer (Heidolph MR 1000) with a stirrer bar 40 mm in length and 5 mm in diameter to keep the mixture homogeneous. Aliquots were withdrawn and filtered using 0.45µm nylon membrane filters at predetermined time intervals for all experiments.

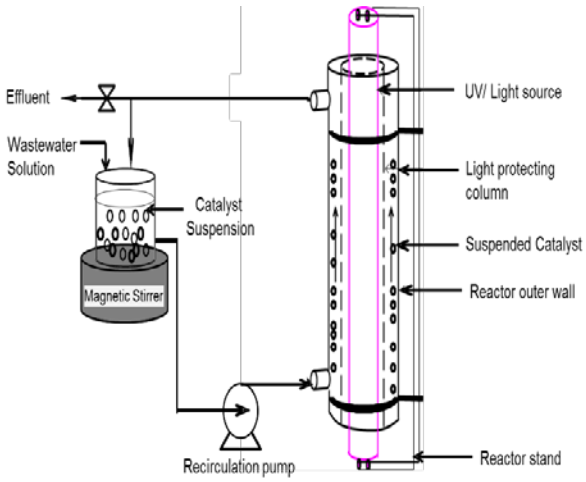

Figure 1: Schematic diagram of the set-up for recirculation flow of annular photo-reactor.

3.3 **Preparation of PANI modified TiO_2**

For polymerization, five catalysts were prepared. All catalysts contained 0.5 ml of aniline and 0.5 g of ammonium persulfate (APS), which were dissolved in 10 ml (0.5M) of hydrogen chloride (HCl). The first catalyst was taken as a blank since there was no addition of TiO_2. For the other four catalysts, the mixture of APS, aniline and HCl were stirred at 250 rpm. An addition of TiO_2 with different masses was made (0.1g, 0.2g, 0.25g and 0.5g).

Once the TiO_2 was added, the solution was then added to 200 ml of deionized water under stirring. The solution was then stirred for 2 hours for polymerization to take place. A polyaniline salt precipitate formed, and the solution was centrifuged to separate the salt and the water. The polyaniline was then dried at 55°C for 24 hours.

3.4 **Procedure**

Three diluted distillery wastewater solutions were prepared as follows; 5 ml/l, 10 ml/l and 20 ml/l, with initial COD concentrations of 335 mg/l, 655 m/l and 837 m/l, respectively. Without the addition of a catalyst, each wastewater solution was placed on a magnetic stirrer, stirring at 360 rpm. The solutions were then pumped using a peristaltic pump (55 ml/min) to recirculate the solution through the photo-reactor, which consists of a 25W UVC lamp. The solutions recirculated for an hour, sampling was done after ever 15 mins. Sampling was done after another 2 hours to measure the final COD concentration.

A PANI/TiO_2 catalyst consisting of 0.5 ml of aniline, 0.5 g APS and 0.5 g of TiO_2 was added to each diluted wastewater solutions. 0.3 g of the catalyst was added to each solution and conducted under the same conditions using a pump for recirculation and passed through the UV light. Sampling was done every 15 mins for an hour, and the final sample was taken after 2 hours for analysis.

3.5 **Adjustments of pH**

To investigate the effect of pH on the reduction of COD, five solutions of 10 ml/l of distillery wastewater were prepared and pH was adjusted to 1, 2, 3, 4, and 5. A PANI/TiO_2 catalyst consisting of 0.5 ml of aniline, 0.5 g APS and 0.5 g of TiO_2 was added to each diluted wastewater solutions. 0.5 g of the catalyst was added to each solution and was operated under the same conditions as the first trials.

3.6 **Analysis**

For the COD analysis, 2.5 ml of each solution was mixed with 1.5 ml of potassium dichromate ($K_2Cr_2O_7$) and 3.5 ml of sulfuric acid (H_2SO_4). The samples were then left in a thermos-reactor/digester for 2 hours. After 2 hours, the samples were then analyzed or COD using a spectrophotometer, the obtained results were then recorded and documented.

4. **Results and Discussions**

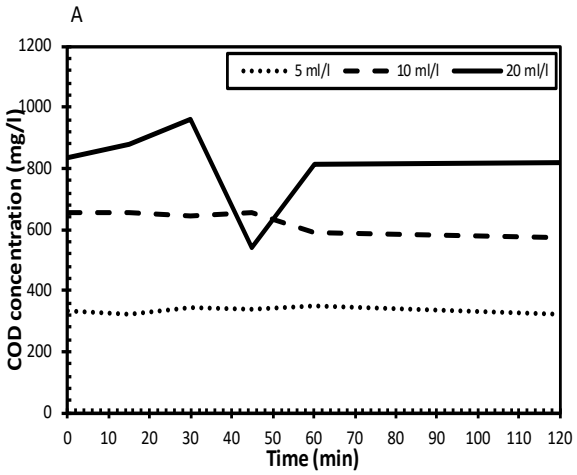

Figure 2: The concentration of COD in diluted distillery wastewater without a catalyst (25°C,360 rpm and 55 ml/min)

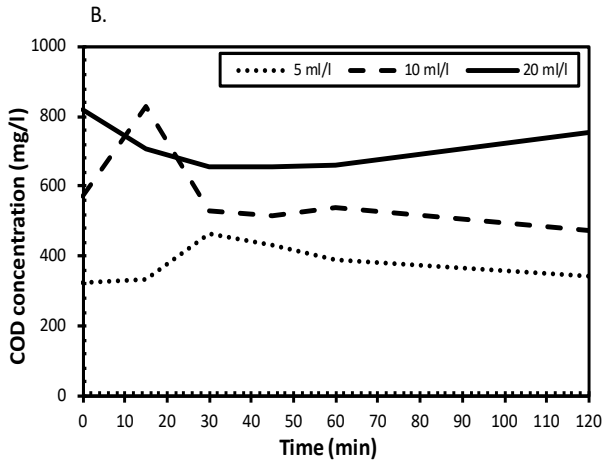

Figure 3: The concentration of COD in diluted distillery wastewater with PANI/TiO_2 catalyst (25°C,360 rpm and 55 ml/min)

The results obtained illustrates that the concentration of COD in diluted distillery wastewater decrease with time when exposed through a photo-reactor. However, there is no consistence in the decrease, as one can see graphs in figure 2.

In figure 2(a), is the graph of COD concentration in diluted distillery wastewater against time without the presence of a catalyst. There is no stable decrease in concentration, however, after 2 hours of the conduction of the experiment, the final concentration is less than the initial concentration. The results show about 3%, 13% and 2% reduction of COD for the 5ml/l, 10 ml/l and 20 ml/l distillery wastewater solutions respectively.

Figure 2(b) illustrates the results of COD concentration is distillery wastewater with time in the presence of a catalyst. By observation, one can tell from the line graphs that the amount of catalyst in the solution might not be enough. The results show some fluctuation during the process. About 2% and 6% increase in COD for 5 ml/l and 20 ml/l solutions, respectively. However, for the10 ml/l solution, there was a 43 % reduction in COD.

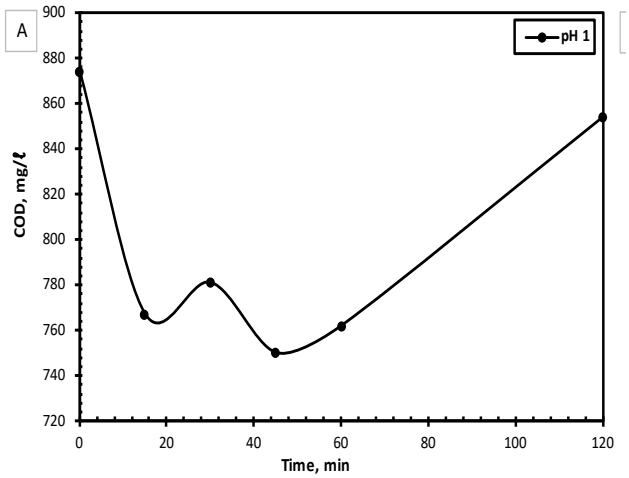

Figure 4: The adjusted pH distillery wastewater solution at pH 1.00(25°C, 360 rpm and 55 ml/min)

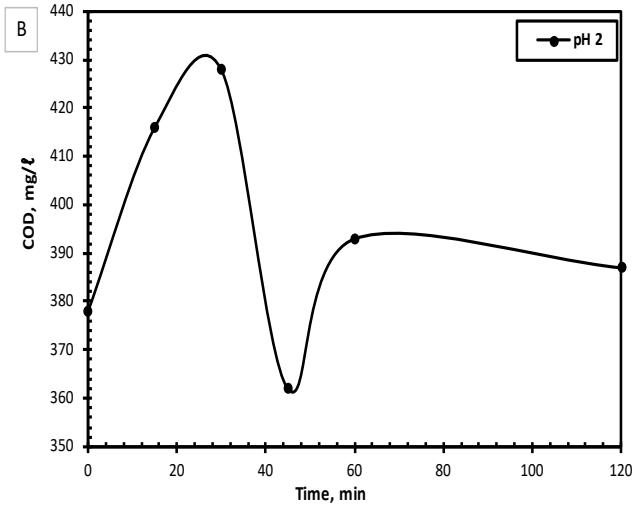

Figure 5: The adjusted pH distillery wastewater solution at pH 2.00 (25°C, 360 rpm and 55 ml/min).

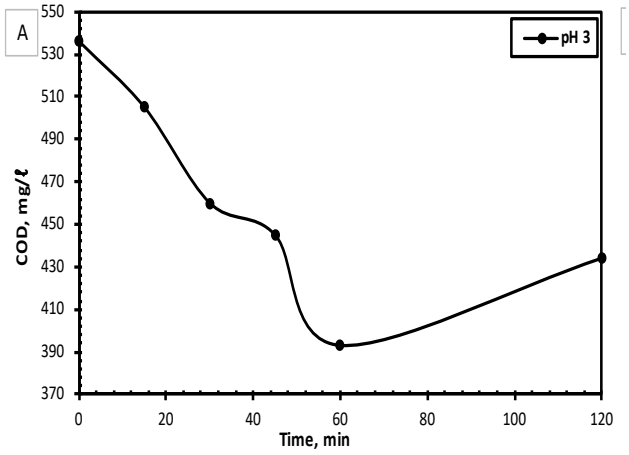

Figure 6: The adjusted pH distillery wastewater solution at pH 3.00 (25°C, 360 rpm and 55 ml/min)

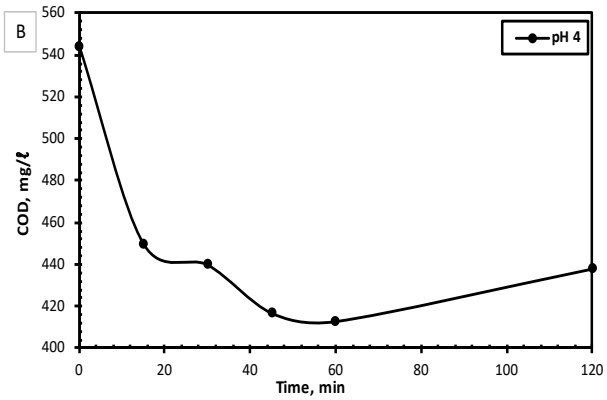

Figure 7: The adjusted pH distillery wastewater solution at pH 4.00 (25°C, 360 rpm and 55 ml/min).

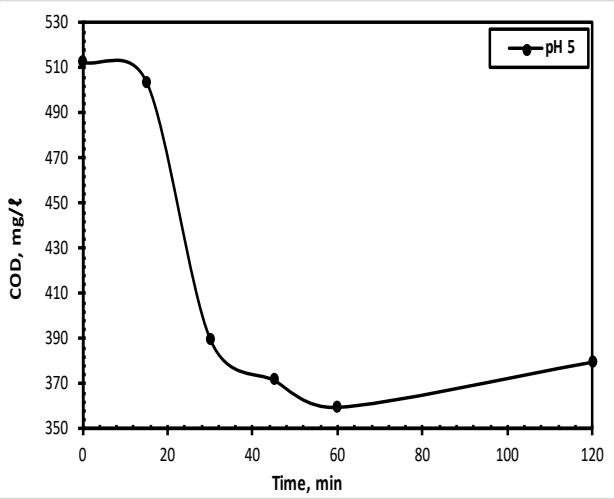

Figure 8: The adjusted pH distillery wastewater solution at pH 5.00 (25°C, 360 rpm and 55 ml/min)

Figure 3 – 5 demonstrates the reduction of COD in distillery wastewater at different adjusted pH, all solutions were operated under the same conditions and the same catalyst mass (0.5 g PANI/TiO_2). Figure 3(a) illustrates the COD reduction at adjusted pH of 1.00, the graph shows fluctuation. After 2 hours the final pH increased massively in comparison to the first hour of operation. There was a reduction of 2% of COD. Figure 3(b) illustrates the results obtained for the solution adjusted at pH 2.00, results also showed fluctuation and instead of a reduction, there was a 2% increase in COD.

Figure 4(a) shows the resulting COD reduction when the pH was adjusted to 3.00, the graphs shows a massive decrease in COD for the first hour in operation. Though the was an increase in COD after 2 hours, the final concentration was 19 % less than the initial COD concentration. Figure 4(b) shows the reduction of COD at pH 4.00, the results obtained showed a similar trend as the ones obtained at pH 3.00. the COD reduction was at 20%.

Figure 5 demonstrates the results obtained when the pH was 5.00, the was a massive decrease in concentration for the first hour of operation, however, the concentration increase after 2 hours. The final COD reduction was 26% less than the initial concentration.

5. Conclusions and Recommendations

5.1 Conclusions

The study was conducted to evaluate the reduction of COD in distillery wastewater using the PANI/TiO_2 catalyst. From the experiments conducted, it can be seen that photo-catalysis of distillery wastewater was an efficient process of degrading COD, the results showed the process is effect with and without the addition of a catalyst. However, an addition of a catalyst increases the efficiency. Results showed that the reduction of COD in distillery wastewater can be done using photo-degradation, however, the process requires more processing time and an addition of a catalyst to be efficient.

The results obtained the from the 5 ml/l diluted distillery wastewater, for both the solutions (without and with the catalyst) showed no consistence in decrease of the COD concentrations. The results for the 10 ml/l and 20 ml/l diluted distillery wastewater showed a decrease in concentration. Therefore, the UV light had an effect on the concentration with the assistance of the catalyst.

One can conclude that pH has a great effect on the reduction of COD, as seen from results in figure 3-5. The results showed COD reduction of 2%, 2%, 19%, 20% and 26 % when pH was adjusted to 1, 2, 3, 4 and 5 respectively, all operated under the same conditions (room temperature, stirring speed = 360 rpm, pumping speed = 55 ml/min).

5.2 Recommendations

Results showed the reduction of COD in distillery wastewater, proving that photo-catalysis is one of the process that can be used to treat this type of effluent. However, the study recommends that the process should be conducted for more than 2 hours and be conducted under isolation (the beaker containing the solution should be closed) to prevent any sort of contamination.

In addition, the hypothesized 50% reduction of COD could have been achieved if the pH was adjusted to be more basic (< 7), by observing the obtained results. The result might show a different deviation if the process was conducted in both batch and continuous mode. Due to time constraints and lack of distillery wastewater, the process was conducted only in batch mode.

Acknowledgements

I like to thank Mr. Thabo Brooms for supervising this project. I would also like to thank Mr V.T Mhlanga, Mr M.J Mosesane and Tshwane University of Technology for granting me permission to utilize their Chemical Engineering Laboratories and for the provision of consumables and facilitation of this project.

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Dr Thabo Brooms is an academic acquiring a PhD in Chemical Engineering at Tshwane University of Technology. His specially includes renewable energy and wastewater treatment and have published more than 4 articles from accredited Journals. I have a passion in exploring biogas opportunities though disadvantaged communities and enhancing the skill to both academic and non-academic institutes.

Molelekoa James Mosesane holds a Master's Degree in Chemical Engineering and a B-Tech Project Management Degree. He is currently employed by Tshwane University and studying towards a Master's of Business Administration Degree. He lectures laboratory classes and design experiments for undergraduates; supervise WIL (P1 and P2), B-Tech and Masters chemical engineering, students. His expertise includes, project management, laboratory management and maintenance, commissioning of pilot plants, liaising with industry, research collaborations and working on different projects for his students.