AIR POLLUTION MITIGATION OF POISON GAS CO WITH CRUDE CHLOROPHYLL OF PAPAYA (*Carica papaya* L.) LEAF EXTRACT

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Abstract

The carbon monoxide (CO) is a toxic gas that results from incomplete combustion of carbon compounds that come from motor vehicle fuel. The presence of CO gas will be very dangerous if inhaled because it causes the formation of carboxyhaemoglobin. Based on the empirical approach is known that the structure of the chlorophyll molecule is consist of porphyrin which its structure is similar to the heme porphyrin of haemoglobin. Based on structural similarity between chlorophyll and hemoglobin, thought to chlorophyll can be used as an absorber of CO gas. Papaya plants (*Carica papaya* L.) are widely spread in Indonesia and have high leaf chlorophyll content. Therefore papaya leaf can be used as a source of chlorophyll that is easy to obtain. The purpose of this research is to know the ability of chlorophyll extract solution from papaya leaf on absorption against CO gas, knowing the optimum ratio of solvent composition in chlorophyll papaya leaf extract and to know the presence of physical changes that occur after the samples are treated with CO gas. This research used Completely Randomized Design (CRD) in one direction which consists of 6 treatments. The volume of each test solution was 500 ml with a ratio between acetone extract of papaya leaf 1% : distilled water : 85% acetone : distilled water extract of papaya leaf 1% in all solutions were A (0:5:0:0), B (1:4:0:0), C (3:2:0:0), D (5:0:0:0), E (0:0:5:0) and F (0:0:0:5). Each treatment contained CO and every 60 seconds was measured against the levels of CO gas. Data were analyzed using ANOVA, thus followed by a test DMRT (Duncan Multiple Range Test) and paired T test with a level 5%. The results showed that the extract solution of papaya leaf chlorophyll had the ability to absorb carbon monoxide (CO). Solution with 1:4 composition ratios between the solutions of acetone extract of papaya leaf 1% and distilled water was the optimum solution ratio to absorb CO gas. No color changes occured in each test solution. This indicated that the absorption process that occured was categorized as physical absorbtion. The proportion of time optimal absorption solution of acetone extract of papaya leaf chlorophyll against CO gas pollutants is 10 minute/1000ppm /Liter.

Keywords: **Absorption, CO gas, chlorophyll, papaya leaf.**

1.Introduction

One of the chemical compounds present in smoke is the result of incomplete combustion of carbon monoxide gas (CO) (Hadiyani, 2010). The presence of CO gas is very dangerous if inhaled by humans because the gas can bind to hemoglobin in the blood forming karboksihaemoglobin (Weaver, 2009) with higher affinity compared with oksihaemoglobin. Deaths from carbon monoxide poisoning caused by a lack of oxygen at the cellular level (cellular hypoxia) is often the case (Hadiyani, 2010), so efforts to mitigate air pollution in the CO gas is required. One way that can be used to reduce emissions of CO gas is by absorption method, the reaction of CO gas with an absorbent solution. Based on the empirical approach is known that the molecular structure of chlorophyll which is consisted of the same porphyrin heme porphyrin structure with which to form hemoglobin. Based on structural similarity between chlorophyll and hemoglobin, allegedly chlorophyll extract solution can be utilized as an absorbent solution of CO gas.

Papaya plants (Carica papaya L.) can be grown in almost all regions in Indonesia. Papaya

Leaf has a high chlorophyll content that is equal to 0.3726 mg / L (Rozak and Hartanto, 2008) and 29.5975 mg / g (Setiari and Nurchayati, 2009). Therefore papaya leaf can be used as a source of chlorophyll which is easily available and have high enough levels of chlorophyll. Chlorophyll in plants of papaya can be extracted by choosing the type and composition of the appropriate solvent. Acetone is a solvent commonly used in the process of extraction of plant pigments that have a polarity corresponding to the chlorophyll. This becomes a dilemma because it has no CO gas solubility in acetone but in aquades (Raub, 2009). While the chlorophyll which an ester compound is not soluble in aquades (Lehninger, 1990). Therefore, there should be a study of the absorption ability of papaya leaf extract chlorophyll with a variation of solvent composition on the CO gas as air pollution mitigation efforts.

2.Subject and Methods

The experiment was conducted in Sub Lab Biology Laboratory and the Laboratory Center for Mathematics and Science UNS and Petroleum and Coal Chemical Engineering Gadjah Mada University in October-November 2010.

2.1. Research tools

The main tool used in this study is 4-brand motorcycle assembly year 2004, Horiba Automotive Emission Analyzer series MEXA-554J, the compressor, the bubble flow meter, a test tube, three-way tap, exhauster, magnetic Stirrer, stopwatch, brand spectrophotometer Perkin Elmer Lambda 25, cuvette and fleaker bottle.

2.2. Materials Research

Materials used in this study are two strands of papaya (Carica papaya L.), acetone 85%, aquades, liquid soap, motorcycle exhaust gas and air.

2.3. Research Procedure

2.3.1. Sampling leaf of Carica papaya L.

Papaya leaf collected from around the region of Surakarta, Indonesia. The selected leaf are leaf that have been stretched in a state of perfect and fresh (not wilted, not yellow and not attacked by pests) from the papaya plant age of 6 months.

2.3.2. Extraction of papaya leaf

Chlorophyll extraction process using a maceration method as proposed by Setiari and Nurchayati (2009) with some modifications. First, papaya leaf cut into pieces and weighed 10 grams. Pieces of crushed leaf in a mortar and then added 5 ml of acetone 85%. Results scours the leaf is inserted into the bottle fleaker 1000 ml acetone was then added 85% to the volume of 1000 ml solution. Solution was allowed to stand for 15 minutes until the chlorophyll dissolved. The solution was filtered with filter paper to scour the rest of the leaf behind. The solution that has been included in the 3 bottles of filtered fleaker different volumes of each solution of 100 ml (treatment B), 300 ml (treatment C), and 500 ml (treatment D). Each solution was added aquades until it reaches the volume of 500 ml. For treatment F, papaya leaf as much as 15 grams of crushed until smooth and then put in fleaker containing 1500 ml aquades. Solution was allowed to stand for 15 minutes and then filtered with filter paper. Solvent filtration results were then divided into three different bottles of each volume is 500 ml.

2.3.3. Analysis of leaf chlorophyll content of papaya

Chlorophyll content of leaf was calculated following the method proposed by Setiari and Nurchayati (2009) with absorbance (A) measured at a wavelength of 644 nm and 663 nm. Calculation of chlorophyll content (mg/L) is determined by the following formula:

Chlorophyll a = 1.07 (A 663) - 0094 (A 644)

Chlorophyll b = 1.77 (A 644) - 0:28 (A 663)

Total chlorophyll = 0.79 (A 663) + 1,076 (A 644)

2.3.4. Preparation of CO gases

Motorcycle engine ~~is~~ was turned on and left stationary for a while. Then the concentration of CO gas in the gas dump was measured. Exhaust pipe ~~is~~ was then connected with pipe peralon and directed at the compressor suction. Then the compressor was turned on. Charging CO gas in the tube compressor until the pressure showed the number level 4. The charging air pressure showed freely performed until the number 8. The compressor was turned off when the pressure reached level 8 and allowed to stand for a moment for a homogeneous gas.

2.3.5. Measurement of discharge and concentration of CO gas

CO gas detector instrument is turned on in advance to be calibrated. Then the detectors are connected to the tube 1. At the compressor outlet is connected to the inlet bubble flow meter. Measurements carried out by adjusting the gas discharge openings on the compressor valves and flow meter readings on the bubble. Discharge gas used in these experiments is 10 mL/sec. CO gas concentrations (vol%) was determined by reading the numbers on the detector when the instrument has reached stability.

2.3.6. Treatment of CO gas exposure

Close the tube 2 is opened, then extract papaya leaf chlorophyll of 500 ml in a test tube inserted. Magnetic Stirrer enter the tube, then cover tightly again the reaction tube. Turn on low speed Stirrer. Previous CO gas which will be presented have been measured concentration. Then the stream of CO gas into the reaction tube 2 by turning the taps T1 towards the tube 2. In the previous T2 faucets have been installed CO detectors that have been turned on to measure the amount of CO gas concentration after the treatment. CO gas concentration after the treatment are recorded every 60 seconds to obtain the saturation extract of papaya leaf chlorophyll in absorbing CO gas (concentration after treatment with concentrations before treatment).

2.3.7. Calculation of percentage absorption

Saturation solution of acetone extract of papaya leaf chlorophyll can be determined by calculating the percentage absorption every 60 seconds. The percentage of absorption is the comparative figures of the number concentration of CO gas is absorbed by the sample. The percentage of absorption can be determined by the following mathematical equation:

$$\text{The percentage absorption} = \frac{xo - xf}{xo} \times 100\%$$

Description: Xo = the concentration of CO gas before treated
Xf = the CO gas concentration after the treated

The lower the percentage absorption of the solution is closer to saturation point so that it can no longer absorb CO gas.

2.3.8. The calculation of gas absorption of CO

CO gas absorption is known by calculating the difference between the concentration of CO gas concentration of CO gas before and after treatment in each 60 seconds of observation.

Data analysis was performed using analysis of variance (ANOVA) to determine the significance of differences between treatments. Then further tests using the test DMRT (Duncan Multiple Range Test) at 5% level test to find out the real difference between treatment and paired T test to determine the significance of the differences before and after treatment.

3.Results

Methods of chemical analysis of contaminants in the air in this study using the technique impinger (Agustini et al., 2005), with modifications. Sources of CO emissions were derived from vehicle exhaust 4 stroke motorcycle brand assembly year 2004. CO gas emission measurements performed on a stationary engine speed due to the concentration of CO gas will be higher when the condition of the vehicle in a stationary state (Basuki et al., 2008). Previous vehicle exhaust gas is sucked and accommodated in a compressor to homogenize the CO gas is dissolved in the vehicle exhaust gas, so that when the concentration of CO gas treatment remained stable. Gas flow rate determined for the treatment of 10 ml/sec, equivalent to 0.6 l/min. This is because the smaller the flow rate of gas containing contaminants in the gas residence time of absorption to the longer tube so that the higher level of efficiency (Basuki et al., 2008). CO gas concentration before and after treatment were measured with a measuring instrument Automotive Emission Analyzer Horiba MEXA-554J.

Before the leaf of papaya was extracted, first done slicing, weighing and destruction of papaya with comminution. Furthermore, papaya leaf extract was diluted with acetone to menvariasikan aquades solvent composition in each treatment. Each treatment was tested with a spectrophotometer to determine absorbance values. Absorbance values were then converted by the formula according to Setiari and Nurchayati (2009) in order to get the numbers in any solution the chlorophyll content (mg / L).

Table 1. Chlorophyll concentrations before treatment (mg / L)

Treatment	A	B	C	D	E	F
Total Chlorophyll Total (mg/L)	0,0000[a]	0,4502[b]	1,2483[c]	2,1195[d]	0,0000[a]	2,3888[d]

Description: The volume of each solution is 500 ml of acetone in the ratio between the papaya leaf extract 1%: aquades: 85% acetone: aquades papaya leaf extract 1% of each treatment, A (0:5:0:0), B (1:4: 0:0), C (3:2:0:0), D (5:0:0:0), E (0:0:5:0) and F (0:0:0:5).

Table 1 shows the chlorophyll concentrations of papaya leaf before treatment. From the ANOVA test can be known that variations in the addition of water to the treatment produced a significant difference in chlorophyll levels ($p < 0.05$). After further testing with known DMRT treatments A and E are not significantly different. This is due to treatments A and E is the control treatment so that the analysis did not produce a spectrophotometer absorbance values because there is no chlorophyll dissolved. Results of treatment B, C and D are significantly different, while for treatments D and F are not significantly different. Increased levels of soluble chlorophyll is proportional to the increase in the comparison between the solution of acetone extract of papaya leaf and aquades. Treatment B produced the lowest levels of dissolved chlorophyll (0.4520 mg/l) when compared with treatment C (.2483 mg/l), D (2.1195 mg/l) and F (2.3888 mg/l). Low levels of total chlorophyll in the treatment of B due to the comparison solution of acetone extract of papaya leaf chlorophyll a small 1% of aquades (1:4). The addition of the extract aquades pigment can also lead to aggregation. According to research conducted by Nugrohadi et al., (2008) additional of water caused the aggregation of pigment in the crude extract of alfalfa leaf. The process occurs because the water as an electron donor can bind to the metal center chlorophyll. Aggregation process caused bathochromic shift of spectra towards. In addition, the aggregation process also leads to decreased absorbance (hypochromic) on the tape Qx, Qy and Soret.

Test the ability of CO gas absorption by chlorophyll solutions extracts using the basic concepts of gas absorption by using an absorbent solution.

Table 2. CO gas concentration before treatment

Treatment	A	B	C	D	E	F
CO Concentration (% vol)	0,245[a]	0,25[a]	0,37[a]	0,325[a]	0,235[a]	0,275[a]

Description: The volume of each solution is 500 ml of acetone in the ratio between the papaya leaf extract 1%: aquades: 85% acetone: aquades papaya leaf extract 1% of each treatment, A (0:5:0:0), B (1:4: 0:0), C (3:2:0:0), D (5:0:0:0), E (0:0:5:0) and F (0:0:0:5)

From the Anova test results can be known that CO gas inputs assigned to each treatment did not differ significantly ($p > 0.05$). This is because CO gas in the exhaust of vehicles accommodated in advance in compressor run into the homogenization tube so that the concentration is stable over exposed to the test solution of each treatment.

To find the optimal time to absorb the gas saturated CO performed ANOVA analysis. The results of ANOVA analysis of the saturated solution is presented in Table 3.
Table 3. Saturation Time of CO Gas Solution

Treatment	A	B	C	D	E	F
Saturation Time (second)	180[a]	240[a,b]	150[a]	150[a]	120[a]	360[b]

Description: The volume of each solution is 500 ml of acetone in the ratio between the papaya leaf extract 1%: aquades: 85% acetone: aquades papaya leaf extract 1% of each treatment, A (0:5:0:0), B (1:4: 0:0), C (3:2:0:0), D (5:0:0:0), E (0:0:5:0) and F (0:0:0:5).

From the ANOVA test, the length of time saturated chlorophyll in absorbing CO gas showed significant results ($p < 0.05$). Having tested further by DMRT, treatments A, B, C, D, E are not significantly different. While the F treatment was not significantly different with the fate B but significantly different from treatment A, C, D and E. This means the treatment of B with the composition of the comparison between the solution of acetone extract of chlorophyll and aquades (1:4) is the optimal composition of CO in absorbing gas. That is because the treatment of B have the same ability with treatment F.
After experiencing the absorption of CO gas in a given time, the test solution will not be able anymore to absorb the CO gas.

4.Discussion

Stage of the process is gas absorption of CO by the test solution is a solution of papaya leaf extract chlorophyll a varied composition of the solvent. To determine the absorption process that occurs then the CO gas concentration is recorded every 60 seconds until there is saturation of the solution to absorb CO gas. The data can be seen that known long time tend to be shorter saturated from treatment A to treatment E and increased sharply in treatment F. These results indicate that the saturated solution is not only influenced by the levels of chlorophyll contained in the solution but is also influenced by the type of solvent used. Increasing the volume of test solution addition of aquades in proportion to the length of time saturated solution of CO in absorbing gas. This result is due to one of the factors that affect the absorption of gases by liquid solubility (solubility) of gas in the solvent in equilibrium (Kartohardjono et al., 2006). It is in accordance with the references obtained that CO gas has a solubility in aquades (Raub, 2009). CO gas can be dissolved in aquades because CO gas molecules are slightly polar (Sukardjo, 1990). The presence of CO gas solubility properties in aquades is why treatment A, B and F have saturated much longer time compared with treatment C, D and E. But conversely, the more the addition of acetone solvent in the test solution saturated shorter lead time. Saturated short time seen in treatment C, D and E. This was caused by the high volume ratio between the solvent acetone and aquades in treatment C, D and E, causing more rapid solution of saturated to absorb CO gas. This is caused by the decomposition of acetone solvent to the air containing CO gas (ATSDR, 1995). Acetone solvent that is volatile (easily evaporated) caused the accumulation of CO gas in the first in a test tube before the gas exposed to CO, making the solution more quickly burn out. Presence of chlorophyll extract dissolved in the test solution also affects the timing of saturated and CO gas absorption. This event is visible from the time differences are significantly different saturated between treatments A and F. Both of these treatments using the same solvent that is aquades. Differences both the presence or absence of chlorophyll aggregates that are suspended in solution. With the chlorophyll aggregates that are suspended in a solvent aquades (treatment F) have saturated the time twice as long compared with the control aquades (treatment A). These results indicate that the aggregate of chlorophyll suspended in solution aquades contribute to prolong the absorption of saturated solution of CO gas.

The data can be seen that the absorption of CO gas by the test solution of each treatment is optimal at 60 seconds first and tend to decrease until it reaches saturation point. The highest uptake of CO gas in the first 60 seconds of the treatment F (0.225 vol%) and lowest in treatment E (0.06 vol%). While the absorption rate of CO gas in the first 60 seconds between treatment A and treatment D as large as the 0.15% vol. This event caused by the solvents used in the treatment of F is aquades. While the solvent used in the treatment of E is 85% acetone. These results are in accordance with the references obtained that CO gas has a solubility in aquades (Raub, 2009) but not in acetone. This suggests that the type of solvent used affect the absorption of CO gas. CO gas absorption figures in the first 60 seconds between treatment A and treatment D as large as the 0.15% vol. This figure shows that in the first 60 seconds of treatment D had the same absorption capacity with solution A. This event indicates that the presence of chlorophyll extracts in solution affects the absorption of CO gas. This is evident by comparing between treatments D and E. Both of these treatments using the same solvent is acetone 85%. The difference lies in the presence or absence of chlorophyll extract dissolved in the solution. Presence of chlorophyll extract dissolved in D treatment led to absorption of CO gas in solution is greater than the treatment of E and be able to match the absorption treatment A. This event indicates that the presence of chlorophyll extracts can affect the absorption of CO gas in the solvent acetone. However, the volatile solvent acetone which is causing this volatile solvent. According to the Material Safety Sheet Datas CO gas which was published by ATSDR (1995), decomposition of acetone solvent to the air containing CO gas. Therefore, the treatment using acetone solvent in this study is faster experience boredom so boring even shorter time compared with treatment using a solvent aquades. From the above description shows that the chlorophyll is not the sole factor that plays a role in the process of gas absorption properties of CO but the suitability of gas solubility in solvents that are used as CO gas that has a solubility in aquades also played a role in achieving optimal results.

A similar note of CO gas concentration before treatment ranged from 0.235 to 0.37 vol%. While the concentration of CO gas after treatment ranged from 0.25 to 0.385% vol. From the t-test results of against concentration before and after treatment showed a significant result ($p < 0.05$). This means that each treatment is given differences in the ability to absorb the CO gas so that the final concentration obtained from each different treatment with initial treatment.
Measurement of total chlorophyll levels at the beginning and end of treatment aims to determine whether there is change in chlorophyll levels before and after treatment with CO gas. Changes in total chlorophyll levels may indicate the occurrence of a reaction that causes the degradation of chlorophyll derivatives formed through a process that is feofitin feofitinisasi. Feofitinisasi process will affect change in the pattern spectrum of chlorophyll (Kusmita and Limantara, 2009) so that absorbance values were also changed.

T test results of total chlorophyll content before and after treatment showed no significant results ($p > 0.05$). This indicates that during the process of CO gas exposure did not change levels of total chlorophyll. This further strengthens indications that the absorption process that occurs when treatment classified as physical absorption. This event is also marked by no apparent change in color of a solution of acetone extract of chlorophyll and leaf extracts of papaya aquades both before and after exposure to CO gas. In addition, physical absorption events between chlorophyll extract solution with CO gas can also be analogous to a study conducted by Kartohardjono et al., (2006) is the absorption of CO_2 from biogas using water solvent. CO_2 reacts with water via the following equation:

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$

The reaction of CO_2 with water is an equilibrium reaction, where the equilibrium constant is so small that the formation of H^+ and HCO_3^- is also very small. Hence, CO_2 absorption process with more water absorption is expressed as a physicist, not a chemical absorption (Kartohardjono et al., 2006). This is what strengthens the assumption that the absorption process that occurs between the solution of chlorophyll extract with CO gas is classified into physical absorption.

5.Conclusion

Solution of chlorophyll leaf extract papaya (Carica papaya L.) has the ability to absorb the gas carbon monoxide (CO). Comparison between the composition of the solvent acetone extracts of chlorophyll and the optimal aquades absorb CO gas is 1:4. No changes color on each test solution. The proportion of time optimal absorption solution of acetone extract of papaya leaf chlorophyll against CO gas pollutants is 10 minute/1000 ppm / Liter. This indicates that the absorption process that occurs in the form of physical absorption.

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Figure 1. Histogram of saturated long each treatment

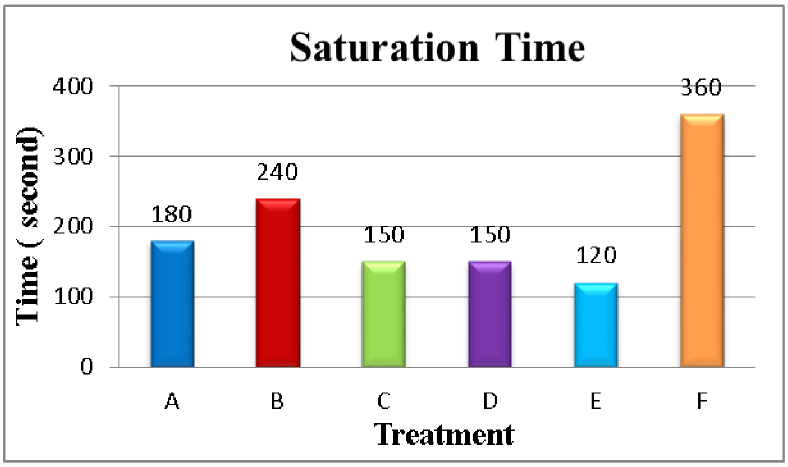

Figure 2. Graphic of gas absorption of CO every 60 seconds

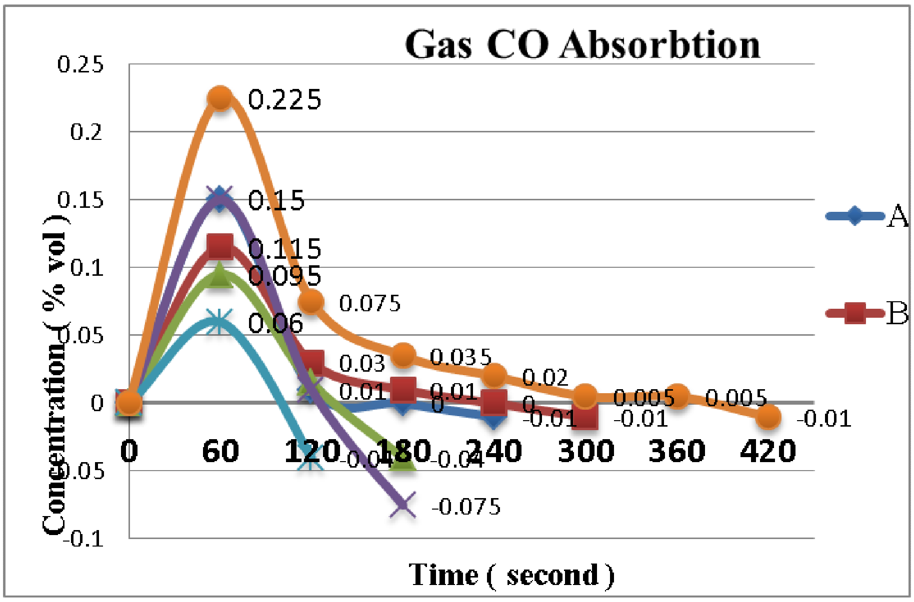

Figure 3. Saturated concentration of CO gas before and after treatment

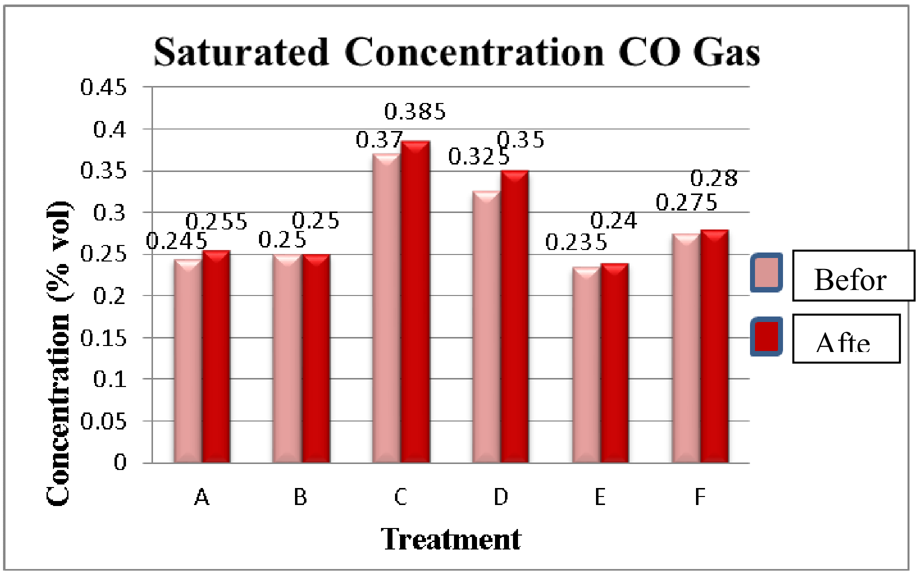

Figure 6. Total chlorophyll levels before and after treatment