Sanitizing Waste Water from 12 MW Rice Hull Fired Power Plant by Functional Compound Agents

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Received:- 02 July 2025/ Revised:- 10 July 2025/ Accepted:- 16 July 2025/ Published: 31-07-2025

Abstract— *Wastewater (WW) produced by a 12 MW Rice Hull Fired Power Plant was analysed and then treated with organic based functional compound agents (FCA) to determine its sanitizing efficacy. Composite samples were analysed for Silica (SiO_2), Nitrates (NO_3^-), Biological Oxygen Demand (BOD), Total Suspended Solids (TSS) and heavy metals specifically lead (Pb) and mercury (Hg) concentration. In-situ properties, namely; pH, temperature, and dissolved oxygen (DO) were also determined by grab sampling. Correlation of these properties with other parameters was done as well.*

Results were compared with the permissible level of the country's environmental regulating body. Exceeding the permissible limit of Class C surface water based on the environmental regulating agency were Pb, temperature, DO, and BOD indicating that the water is slightly unfit for irrigation purposes. Treating the WW ($p < 0.05$) with the FCA resulted in the reduction of pH by 4.6%, in high increase of TSS by 3,315.64% and increase of Pb by 239.62%. Meanwhile, no change was observed in the temperature, DO, NO_3^-, SiO_2 and Hg. Therefore, the FCA tested had no sanitizing effect on the WW.

Keywords— Rice Hull Gasifier Plant, Wastewater, BOD, TSS, Organic Based Functional Compounds, Pb, Hg, SiO_2.

I. INTRODUCTION

Wastewater is produced from rice hull fired power plant which could generate electricity. Water treatment reject, cooling tower blown down, boiler, rain water, cleaning of vehicles and domestic waste are considered as the sources of effluent. Production of steam is an important component of any biomass fired power plant which requires water extracted from deep well ground water. This is done using submersible pump made possible by boring holes to reach the water source. This water resource is often high in mineral content [1] and is treated before using for steam production. Hence, minerals and ions in water must be removed to prevent corrosion of pipes.

Wastewater comes from rejected water during the process of regeneration and cleaning of water treatment plant [2]. Untreated or improperly treated wastewaters are the major sources of surface water body pollution especially when it contains sediments or fly ash. It is one of the most serious environmental problems resulting from industrial, domestic and agricultural activities [3]. Wastewater contaminated with even low concentration of heavy metals or other pollutants may affect the quality of soil, plants, aquatic life and human health. These metals affect soil quality by decreasing microbial processes or activities and may inhibit the physiological metabolism of plants.

Consequently, this condition could become potential threat to human and animal health because of the subsequent accumulation of heavy metals in the food chain [4]. Through the years, series of expensive chemical based treatment technologies have been developed for wastewaters but there is a dearth in the use of non-chemical and organic based treatment strategies. As such, this investigation explored the use of FCA to sanitize wastewater from a 12 MW Rice Hull Gasifier Plant in the Philippines.

FCA was constituted using the following: 7 bacteria for decomposition, enzyme production and nutrient transformation; 3 bacteria for decomposition of polysaccharides and enzyme production; 3 bacteria for enhanced decomposition, compost "Sweetening" and probiotics production; 5 bacteria for nitrogen fixation; 7 fungi composting microbes; aerobic and unaerobic methane producing bacteria; sulfate and ammonia consuming and heavy metal binding bacteria and emulsifiers.

II. METHODOLOGY

Wastewater samples were collected in three sampling stations from the open canal of the 12 MW rice hull fired power plant. Each sample had three replicates. Grab sampling was done for the in-situ parameters such as temperature, pH and dissolved oxygen (DO). Composite sampling was performed for biochemical oxygen demand (BOD), total suspended solids (TSS), silica (SiO_2), nitrates (NO_3^-), lead (Pb^{+2}) and mercury (Hg^{+2}).

A pole sampler was used in some inaccessible sites of the sampling station, which is a continuously flowing drainage canal for wastewater. Sample volumes collected ranged from 500 to 1000 ml. Immediate analysis was done for pH, DO and temperature because its values change quickly. Electrodes of pH and DO meter were immersed to a depth of 3 cm and at least 1 cm away from the sides and the bottom of a beaker. The wastewater samples were stirred gently to establish equilibrium between electrode and sample, to ensure homogeneity, and to minimize carbon dioxide entrapment. The pH level and DO concentration were recorded when the readings had become stable.

Before proceeding to another sample for analysis, the electrode was withdrawn gently and rinsed gently into a beaker with distilled water and was blotted with soft tissue. Container pre-treatment, maximum holding time, sample size, sampling method, preservation and storage were strictly followed in the collection and treatment of samples.

FIGURE 1: Open Canal of GIFT Corporation in Bacal II, Talavera, Nueva Ecija, Philippines (Photo credit from Google Earth 2018)

2.1 Collection and Analysis of Waste Water Samples:

Wastewater samples were collected in three sampling stations from the open canal of rice hull fired power plant. Grab sampling was done for *in-situ* parameters such as temperature, pH and dissolved oxygen. Each parameter had three replicates. DO meter was utilized to measure the dissolved oxygen concentration and temperature level while pH meter was used to determine the pH level. Composite sampling was performed for biochemical oxygen demand (BOD), total suspended solids (TSS), silica

(SiO_2), nitrates (NO_3^-), lead (Pb^{+2}) and mercury (Hg^{+2}) . These parameters were analyzed in the TransWorld Laboratory Incorporated. Requirements in the collection and methods of analysis used are indicated in Table 1.

TABLE 1
SUMMARY REQUIREMENTS IN THE COLLECTION AND ANALYSIS OF SAMPLES

Parameters	Container	Sample Size (mL)	Maximum Holding Time	Methods of Analysis
BOD	Plastic (polyethylene)	200	6 hr	5-BOD Test Azide Modification
TSS	Plastic (polyethylene)	200	7 days	Gravimetric
Silica	Plastic (polyethylene)	200	28 days	Molybdosilicate
Nitrates (NO_3^-)	Plastic (polyethylene)	100	2 days	Cadmium Reduction
Lead	Glass	100	6 months	Wet Digestion & AAS
Total Mercury	Teflon/ Glass	200	6 months	AAS Cold Vapor

Source: Standard Methods for Examination of Water and Wastewater 20th Edition (1998) and laboratory protocol.

2.2 Statistical Analysis:

The experiment was carried out using Completely Randomized Design and comparison among means using t-test. The probability level for significance was ≤ 0.05. Furthermore, Pearson's Correlation Coefficient was used to correlate the different *in-situ* factors while Post-hoc analysis using Tukey's HSD determined the significant difference among the sampling points.

III. RESULTS AND DISCUSSION

3.1 Concentration of the Physico-chemical Parameters before the Addition of FCA:

Differences in concentration of the physico-chemical parameters were determined before and after the addition of the FCA (Figure 2). Also, temperature, pH, and dissolved oxygen of the wastewater were taken from different sampling points before the addition of FCA. The recorded water temperature ranged from 31.77°C to 34.53°C. Sampling Point 3 obtained the highest mean temperature while Sampling Point 1 recorded the lowest mean temperature. This observed range of water temperature surpassed the permissible limit of Class C water body; that is 25^0C- 31^0C. Hence, it could become problematic in the long run when using these surface water bodies. The increasing rate of wastewater temperature from Sampling Point 1 to Sampling Point 3 might be due to the boiling process of the power plant and the exposure of the wastewater to direct sunlight. This result conformed to the results of an earlier study [5].

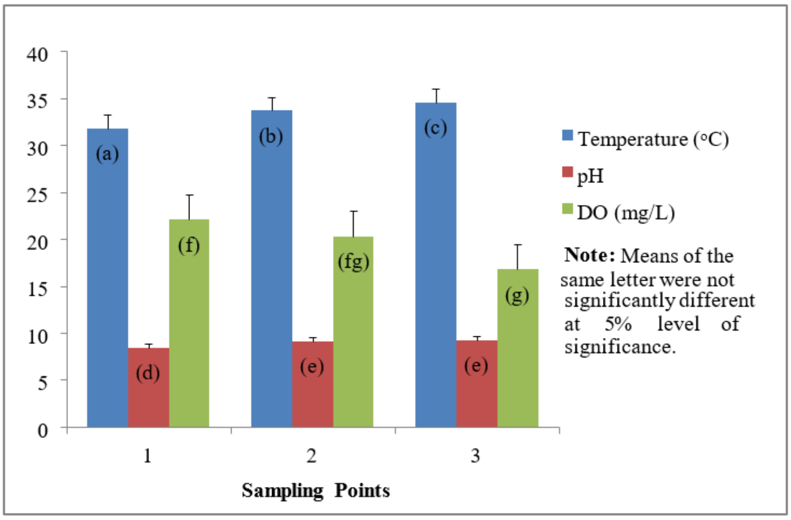

FIGURE 2: Variations in the level of temperature, pH, and dissolved oxygen of wastewater from different sampling points before the addition of FCA

Meanwhile, the pH values of the wastewater ranged from 8.40 to 9.20, which indicated slight alkalinity, thereby safe for irrigation purposes as it is within the national allowable limit. However, Sampling Points 2 and 3 surpassed the permissible limit of 6.59 set by DAO 08-2016. Todd (1980) as cited [1] and Todd and Mays as cited in [6] claimed that the basicity of wastewater could be due to the extracted groundwater as main source for steam production which is often high in mineral content or dissolved salts such as calcium (Ca^{+2}), magnesium (Mg^{+2}), and sodium (Na^{+}). Moreover, preliminary water treatment reject contains these metal ions and is considered as one of the sources of wastewater in a power plant [2].

Data showed that the level of dissolved oxygen (DO) of wastewater varied across the sampling points. Recorded level ranged from 16.77 mg/L to 22.03 mg/L (Figure 5) which was above the national permissible level of 5 mg/L provided by DAO 08-2016 for class C surface water. The lowest reading for dissolved oxygen was recorded in Station 3 while Station 1 recorded the highest reading. According to Metcalf and Eddy (2003) and EPA (1996) as cited [7], DO is required for the respiration of all aerobic life forms in water and its quantity can be governed by temperature, solubility, atmospheric pressure, and concentration of impurities like salinity and suspended solids. Very high and abrupt changes in DO concentration can also be harmful to aquatic life specifically by inducing stress that subsequently makes fish more susceptible to disease. This was confirmed in the study done by Yilmaz (2014) [8].

The concentration of the parameters in Figure 3 was assessed without the addition of FCA. Composite sampling of wastewater samples was done for the analysis. TransWorld Laboratory Inc. started to analyze the samples five days after collection. Analysis for nitrates, BOD, TSS, and silica was performed on April 11-18, 2018. Composite sample was sub-divided into three replications. Each parameter concentration was compared to the national permissible limit set by DAO 08-2016.

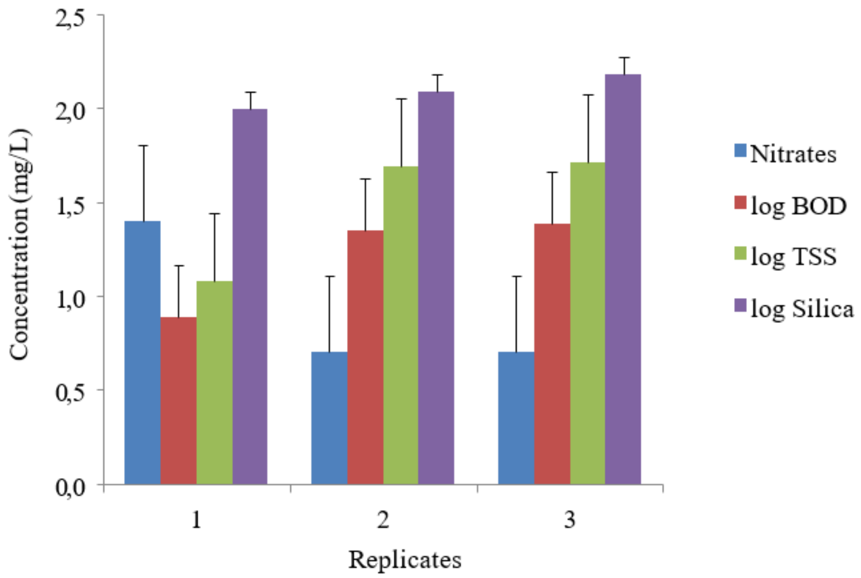

FIGURE 3: Concentration of the different physico-chemical properties before the addition of FCA. Data and deviation are presented with three replications and expressed in mg/L. Most parameters are plotted on a logarithm scale base 10.

Nitrate concentration of wastewater without FCA in the three replications recorded a range of 0.7 mg/L to 1.4 mg/L. This nitrate level in the wastewater was lower than 7 mg/L, the national standard limit set by DAO 08-2016. This is not risky to the aquatic organisms found in the water body. Stendahl (1990) and Liu (1999) were cited [9] as having asserted that the amount of nitrate on wastewater depends on the availability of oxygen for oxidizing bacteria and ammonia to nitrate.

Biochemical oxygen demand (BOD) value of wastewater was recorded as above 7 mg/L, the recommended limit for BOD of class C surface water provided by DENR. This concentration means the wastewater had high content of organic matter. Accordingly [10], the amount of BOD depends on the amount of organic matter and the activity of the bacterial species present in wastewater.

Total suspended solids (TSS) are the solids in the water retained by the filter [11]. The recorded values were within the permissible level at 80 mg/L set by DAO 08-2016. The concentration of all the particles suspended in the wastewater ranged from 12 mg/L to 52 mg/L as shown in Figure 3. This result indicated that the wastewater appearance was clear to cloudy.

In terms of silica concentration, it ranged from 99.2 mg/L to 152.4 mg/L. Its national allowable level was not yet available in the general effluent guidelines by DENR. However, according to the available data in the power plant, 85 mg/L of silica in wastewater was the basis of allowable level. This concentration might be due to the amount of silica present in the rice husk fly ash that mixed with the water [12] and in the extracted groundwater [13].

3.2 Correlations between Temperature and the other Parameters:

Table 2 reveals a highly significant relationship between temperature and the other parameters tested. This means that temperature can influence the rate of pH and DO. Results showed that temperature and DO had a negative substantial correlation in which as temperature increased, the DO decreased and vice versa, confirming the results of previous similar studies [9-14]**.**

Also, temperature and pH showed strong but negative correlation wherein as the temperature increased, the pH level rapidly decreased and vice versa. This result supported the data gathered in a previous study [15]. Similarly, pH was inversely proportional to temperature as stated in Le Chatelier's Principle. This was confirmed by a previous study [16] in which it showed that as temperature level increased, more molecular vibrations or dissociation of hydrogen ions were formed, thereby eventually decreasing the tendency of forming hydrogen bonds and causing a decrease in the pH value of water.

In contrast, DO and pH were strongly correlated to each other positively. Similar result was revealed by a previous study [17] wherein both values of DO and pH rapidly increased or decreased.

TABLE 2
PEARSON CORRELATION OF EACH *IN-SITU* PARAMETERS

Correlation Coefficient Parameters	Temperature	Dissolved Oxygen	pH Values
Temperature		-0.866*	-0.937*
Dissolved Oxygen	-0.866*		0.922*
pH Values	-0.937*	0.922*	

Correlation Scale: 0.01 – 0.20 = very weak 0.41 – 0.70 = moderate
0.21 – 0.40 = weak 0.71 – 0.90 = substantial
0.91– 0.99 = strong

3.3 Heavy Metal Concentrations in the Wastewater:

The data on heavy metals concentration (Figure 4) were analyzed from April 13 to May 2, 2018 by Transworld Lab Inc. Accordingly [18], the presence of such inorganic contaminants in water specifically lead and mercury could pose deleterious effect in the environment. Studies conducted [19,20,21] showed that accumulation in the soil and in the plant of these given elements may occur. In addition, it was revealed [22] that physical factors such as temperature and biological factors such as species characteristics, biochemical/physiological adaptation and trophic interactions can influence the bioavailability of heavy metals.

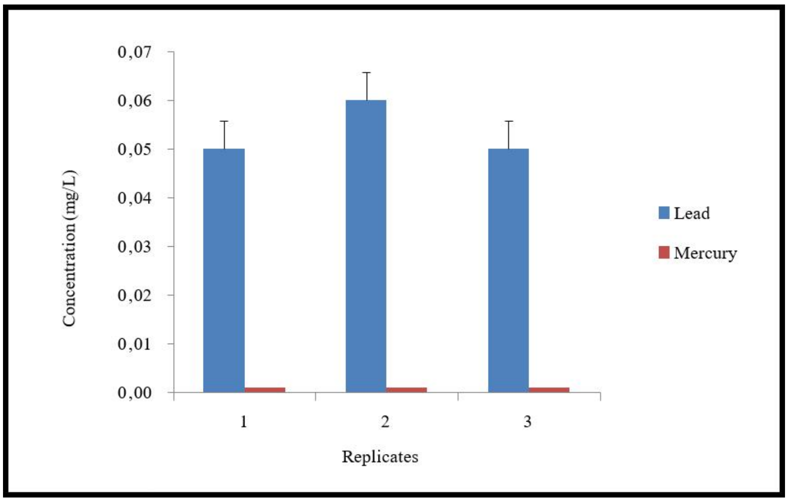

FIGURE 4: Concentration of heavy metals in wastewater before the addition of FCA Data and standard deviation are presented with three replications

The concentration of lead in industrial wastewater limit is 1.0 mg/L according to the Environmental Protection Agency (EPA 2002) while the maximum permissible limit of lead in inland surface water is 0.1 mg/L as set by CPCB. In this investigation, the concentration of lead in the wastewater ranged from 0.05 mg/L to 0.06 mg/L, which is way below the EPA standard for industrial water and CPCB maximum permissible limit of lead in inland surface. This concentration might have been caused by the exhaust from automobiles [23] and additives in gasoline, burning, and factory chimneys [24]. Meanwhile, mercury, a non-essential element, had recorded concentration of 0.001 mg/L which was lower than 0.002 mg/L, the national permissible level provided by the DAO 08-2016.

It was claimed [4] that high or even low concentration of heavy metals may affect the natural soil quality, aquatic life, plants and human health. Heavy metals affect the soil quality by decreasing microbial processes or activities, and may inhibit the physiological metabolism of plants. Eventually, potential threat to human and animal health may occur due to uptake of heavy metals by the plants and subsequent accumulation in the food chain (Schickler and Hadar, 1999) as cited [4]-[28].

3.4 Comparative Concentration of the different Parameters before and after FCA Application:

The comparison on the concentration of the different physico-chemical parameters before and after the addition of FCA (Table 3) revealed a statistically significant difference in pH, TSS and lead across the treatments. The pH values decreased by 4.6% while the total suspended solid abruptly increased by as high as 3,315.64%. Lead increased to 239.62%. These results imply that the FCA failed to sanitize the wastewater, specifically binding the heavy metals present in the wastewater.

TABLE 3
EFFICACY OF FUNCTIONAL COMPOUND AGENT (FCA) IN TREATING WASTEWATER IN 12 MW RICE HULL FIRED POWER PLANT

Elements	Initial Readings	Final Readings	Difference	Significance	% Change
Temperature	33.31	37.41	4.10	0.063^{ns}	12.31
pH	8.91	8.50	0.41	0.003*.	-4.6
DO	19.69	16.84	-2.85	0.868 ^{ns}	-14.47
Nitrates	0.93	3.67	2.74	0.405 ^{ns}	294.62
BOD	18.10	203.53	185.43	0.093 ^{ns}	1,024.48
TSS	37.67	1286.67	1249	0.030*	3,315.64
Silica	124.67	124.93	0.26	0.706 ^{ns}	0.21
Lead	0.053	0.18	0.127	0.000*	239.62
Mercury	0.001	0.0018	0.0008	0.117 ^{ns}	80

Note: * significant at 5% level of significance using t-test.

IV. CONCLUSIONS AND RECOMMENDATION

The FCA was effective in reducing the pH and dissolved oxygen level while inefficient in reducing the temperature level, amount of BOD, TSS, silica, nitrate, lead and mercury. The possible increase in heavy metals in the wastewater, particularly "lead", could have been due to the proximity of the rice hull fired plant (being adjacent) to a paddy field where inorganic fertilizers and insecticides are being applied. The rice hull gasifier fired plant continuously extract groundwater that serves as cooling agent and can be reprocessed to be a part of the wastewater.

Nevertheless, these results can serve as precautionary measure to minimize the potential risk to the environment. The apparently alarming concentration of pollutants, particularly the heavy metals, could result in the deterioration of nutrient soil quality and bio-accumulation by the plants thereby rendering serious environmental problems.

Moreover, the wastewater quality parameters documented may serve as benchmark data in predicting the cumulative toxicity it would bring to nearby vegetation over a certain period, through algorithm equations. More research efforts should therefore be done on other similar or modified FCA to make it an effective sanitizing agent for wastewater from Rice Hull Fired Power plants considering their growing use globally and long term adverse effects to the environment, humans, and animals.

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