

Systematic Biological Upgrade of a Urea Fertilizer Effluent Treatment Plant Using GPS

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Abstract

The use of modeling and simulation has developed into a critical tool for the sustainable management of wastewater, especially when it comes to replicating the complex biochemical procedures required for fertilizer effluent treatment, which calls for a significant amount of wastewater-related data. The biological improvement of a urea fertilizer effluent via GPS* simulation was carried out in this work using a methodical process. Using established analytical techniques, temperature, total suspended solids (TSS), biochemical oxygen demand (BOD), total phosphorus (T/PO₄⁻), chemical oxygen demand (COD), total nitrogen (TN), total nitrate (NO₃), electric conductivity (EC), turbidity, residual chlorine, urea, NH₃, and heavy metals (Cu, Cd, Cr, Pb, Ni, and Fe) were assessed. The research revealed that the measured values from the fertilizer factory outfall effluent had high concentrations of all the physicochemical water quality indicators, with the exception of TSS, PO₄⁻, SO₄⁻, and NO₃⁻. These concentrations are higher compared to the authorized limits or suggested values by the Federal Environmental Protection Agency (FEPA). To improve the therapy biologically, however, a modeling and simulation program (GPS-X, version 8.0) was used with the physicochemical information gathered from the studied sample. The results of the treated water simulation showed that the concentrations of BOD₅ and COD had been significantly reduced by 35% and 44%, respectively. Additionally, it was discovered that total phosphorus (TP), nitrate (N), and total nitrogen (TN) were all within the permitted FEPA limit. The results revealed good treatment performance of the wastewater with in-

creasing concentration of acetic acid and sodium hydroxide. Hence, the results of this research work identify the need for proper treatment of fertilizer industry effluents prior to their release into the environment.

Keywords

Fertilizer Wastewater Effluent, Discharge Basin, Outfall Basin, Physiochemical Analysis, GPS*, Modelling & Simulation

1. Introduction

The dangers of dumping hazardous chemicals, solid waste, heavy metals, and industrial effluent into rivers, lakes, and streams to aquatic life and ultimately to humans cannot be understated. With the advent of industrialization, many chemical firms have expanded and adapted to inadequate waste management procedures; typically, effluents wind up being diverted directly into the environment. Hence, this has adverse effect on the health of people, and the entire marine.

The quality of the water standard and the environment suffer severely if the residence time for microbial activity is insufficient to break down the contaminants and protects the habitats from deterioration [1]. In developing countries, particularly in African countries like Nigeria, a sizable portion of the rural population drinks water that they personally obtained from those sources. These water sources are exposed to pollutants from industrial activity because the industrial effluents are either not treated at all or only partially treated, making the water from those natural sources unsafe to drink. Because chemicals and pollutants are absorbed by aquatic species and then by humans, leading to a variety of health concerns, industrial effluent treatment becomes vital [1] [2].

Water contaminants that pose risks to people and the environment if discharged to surface and ground waters without effective treatments are what wastewater treatment processes aim to remove or reduce [3]. While industrialized nations continue to work on creating new technologies or setting up more effective treatment processes in WWTPs to fulfill the rising demand for water, the poorer nations are still struggling to put in place the necessary infrastructure for treatment. Even if the harm caused by a lack of such infrastructure is clear, public concern is still restricted as a result of a lack of public education programs on environmental issues as well as the impact of crises and political unrest in these nations [4].

In order of increasing degree of treatment, teams of preliminary, primary, secondary, and tertiary wastewater treatment stages are frequently used to describe the amount of water treatment. Activated sludge, contact stabilization, trickling filters, aerated lagoons, total oxidation, and waste stabilization ponds are also used in the secondary treatment process, which is the most important step in the sewage treatment process [5]. To remove particles, raw materials, and nutrients from effluent, physical and biological techniques are frequently com-

bined in wastewater treatment. The treatment of wastewater from manufacturing companies has been a challenge in the past; in the fertilizer industry, the anoxic process is the most frequently used biological process analog due to its ability to denitrify [3].

While biological treatment is frequently used to remove nitrates from wastewater used in the production of nitrogenous fertilizers, ion exchange can be utilized to remove ammonia and nitrates. However, it was advised to eliminate nitrogenous fertilizer effluents utilizing physical, chemical, and biological methods [6]. It is common knowledge that biological wastewater treatment requires the least amount of energy. It is the most eco-friendly method and doesn't require any xenobiotics. The characteristics of an effluent treatment system can be thoroughly understood using a mathematical model, lowering risk and operating costs.

Agriculture's support system unquestionably includes the industrial facilities that produce a wide range of fertilizer products [7]. On the other hand, by emitting gaseous, liquid, and solid pollutants, these businesses are also among the biggest offenders of environmental pollution. The main contaminants in effluents discharged by the fertilizer, pharmaceutical, tanning, and dyeing industries are toxic anions, organic and inorganic chemicals, dissolved gases, pesticides, and heavy metals [8] [9]. To ensure effective treatment before disposal, liquid effluents must be regularly and accurately characterized [10] [11] [12].

A "simulation" is a simple depiction of a chemical reaction that captures its operational circumstances throughout time. Simulation is frequently used in conjunction with scientific modeling of chemical systems to comprehend how a certain chemical system behaves or functions [13]. GPS*, a modular, versatile computer application, is used to construct and simulate wastewater treatment plants for both commercial and municipal uses. When constructing a new development or replicating an existing one, GPS* improves the design and operational efficiency of the process facility. This research's sole goal is to update fertilizer wastewater treatment facilities using GPS. GPS* is developed and distributed by Hydromantis Environmental Software Solutions, Inc., and is recognized for its accuracy, reliability, and user-friendly interface [14]. The key features of GPS* are process modeling, user-friendly interface, flexibility, simulation capabilities, data management, sensitivity analysis, reporting and visualization. Users can simulate the behavior of wastewater treatment plants under different operating conditions and scenarios, enabling them to optimize performance and identify potential issues. Hence, GPS* is a leading software tool in the field of wastewater treatment process modeling and simulation [14]. Its extensive features, accuracy, and user-friendly interface make it an indispensable asset for engineers, researchers, and operators working in the wastewater treatment industry. This research's sole goal is to upgrade Urea fertilizer wastewater using GPS*.

Solids, organic matter, and nutrients are removed from wastewater via physical and biological processes in traditional wastewater treatment methods. Preliminary, primary, secondary, and tertiary or advanced wastewater treatment me-

thods are general terminology used to represent various degrees of treatment, in sequence of increasing treatment [5] [15]. The secondary treatment procedure, which involves biological treatment methods using a variety of microorganisms in a controlled environment, is the main treatment method used in traditional sewage treatment methods. Activated sludge, total oxidation, contact stabilization, aerated lagoons, waste stabilization ponds, trickling filters, and anaerobic treatment are among the aerobic and anaerobic biological processes utilized for secondary treatment methods. In comparison to other biological processes, the activated sludge process is the most commonly used since its facility design is well known and it has specified operation characteristics [16].

The purpose of this study is to biologically treat the effluents produced by various fertilizer plant operations, with the goal of reducing the following: Chemical Oxygen Demand (COD), Electric Conductivity (EC), Biochemical Oxygen Demand (BOD), Sulphates, Total Dissolved Solids (TDS), Turbidity, Total Phosphorus (T/PO_4^-), Residual Chlorine, Nitrate (NO_3), Total Nitrogen (TN), Total Suspended Solids related to this research include water recovery and reuse, economic savings (chemical, waste minimization), better management, and operator training. The biological treatment of fertilizer plant wastewater was evaluated in the study using the GPS*. The results of this study are anticipated to assist the pertinent companies and authorities in using biological treatment techniques for effluents and reduce the amount of hazardous waste released into the environment.

2. Materials and Methods

2.1. Collection of Samples

The wastewater from a fertilizer company was sampled in Epe, Lagos State, in southwest Nigeria. Two closed basins containing fertilizer wastewater at various concentrations were chosen for the collection of effluent samples. In addition to the outfall basin (Sample 2) because of the potential effects on aquatic life once it entered the lagoon, samples were also taken from the final discharge basin (Sample 1) because it comprises effluent from both the equalization basin and cooling tower blowdown. There is a fishing settlement along its banks.

2.2. Analysis and Calculations

The analytical procedures used to determine these parameters have been modified from Theoretical Aspects of Laboratory Analysis in 1992, Guidelines and Criteria for Water Quality Management in Ontario in 1967, the Laboratory Manual on Soil and Plant Analysis in 1995, and A.O.A.C. (Association of Analytical Chemists, Official Methods of Analysis, 1990). The wastewater quality characteristics of these effluents were measured, including temperature, total suspended solids (TSS), urea, total nitrogen, NH_3 , electric conductivity, color, nitrate, total dissolved solids (TDS), turbidity, residual chlorine, total phosphorus, sulphates, pH, and heavy metals.

2.2.1. Physicochemical Analysis of Effluents

As soon as the samples arrived, the pH was measured using a JENWAY 3020 pH meter using 100 ml of each sample. Total chloride was also measured using potentiometric titration. In order to prevent certain cations from being lost by absorption or ionic exchange with the walls of plastic containers as a result of storage effect, an additional 1.5 litres of each sample were collected in two distinct clean bottles and acidified with nitric acid to a pH below 2.0.

To analyze the other physicochemical parameters, the remaining samples were kept in the refrigerator overnight at a temperature of about 4°C. A mercury thermometer was dipped into each homogeneously mixed sample at each sampling location and left there for roughly two minutes to record the temperature. The mercury thermometer was cleaned in a buffer solution with a pH of 7 prior to reuse. The electrical conductivity of the samples was measured using a digital bench-top conductivity meter (JENWAY 4010 conductivity meter). The relationship between Total Dissolved Solids (TDS) and Electric Conductivity, however, is 2.2:1. To calculate the TDS measurement in mg/L, the electric conductivity value was divided by 2.2.

The spectrophotometric approach was used to calculate urea levels. P-dimethyl amino benzaldehyde (DMAB) and urea react to form a yellow complex in a Sulphuric acid medium. According to Obire, Ogan, and Okigbo (2008), the strength of the complex is closely correlated with the amount of urea contained in the sample. The organic nitrogen approach was used to calculate the amount of ammonia present in the effluent. Using a turbimetric method, the samples' sulphate (SO₄) content was measured. The total phosphate in the samples was determined using a spectrophotometric method based on sample digestion. A standard approach was used to analyze the sample color. Brucine reagent B was used to quantify the samples' nitrite (NO₂) level using spectrophotometry [7].

Titration was used to determine the chemical oxygen demand (COD), and then potassium permanganate was used as an oxidizing agent. The Winkler test was first used to gauge how much dissolved oxygen was present in the water samples. Iodometric titrations were used to calculate the BOD₅ of the effluent samples using the dilution method. MnSO₄ solution was used as the nutrient solution, and then the alkali-iodide reagent, sodium thiosulfate (Na₂SO₃), and sulfuric acid titration were used.

The metal concentration was measured using a Buck Scientific model 230 atomic absorption spectrometer with an air-acetylene flame and a wavelength range of 190 to 900 nm. Using calibration curves at specific wavelengths of 228.8 nm, 224.8 nm, 217 nm, 373 nm, 231.6 nm, and 522 nm, respectively, the concentrations of cadmium (Cd), copper (Cu), lead (Pb), nickel (Ni), chromium (Cr), and iron (Fe) were calculated.

2.2.2. BOD₅ Calculations

To determine the value of the BOD₅ in mg/l the following formula was used:

$$\text{BOD}_5 \text{ mg/l} = \frac{(\text{Initial DO} - \text{Final DO}) \times 300}{\text{sample volume (ml)}} \quad (1)$$

where DO is dissolved oxygen.

2.2.3. Final Discharge Basin (Sample 1)

$$D_{1fd} = \frac{13.5 \text{ ml} + 13.0 \text{ ml} + 14.0 \text{ ml}}{3} = 13.5 \text{ ml} \quad (2)$$

$$D_{2fd} = \frac{8.0 \text{ ml} + 7.8 \text{ ml} + 7.9 \text{ ml}}{3} = 7.9 \text{ ml} \quad (3)$$

$$\text{BOD}_{5fd} = \frac{(13.5 - 7.9) \times 250}{15} = 13.5 \text{ ml} \quad (4)$$

2.2.4. Outfall Effluent (Sample 2)

$$D_{1oe} = \frac{12.9 \text{ ml} + 12.9 \text{ ml} + 12.9 \text{ ml}}{3} = 12.9 \text{ ml} \quad (5)$$

$$D_{2oe} = \frac{7.3 \text{ ml} + 7.3 \text{ ml} + 7.4 \text{ ml}}{3} = 7.4 \text{ ml} \quad (6)$$

$$\text{BOD}_{5oe} = \frac{(12.9 - 7.4) \times 250}{15} = 91 \text{ ml} \quad (7)$$

2.2.5. COD Calculations

$$\text{COD mg/l} = \frac{(A - B) \times m \times 800}{\text{volume of sample}} \quad (8)$$

A = Titre volume of blank. B = Titre volume of sample. M = molarity of titer.

2.2.6. Final Discharge Basin (Sample 1)

Titre value of blank = 22.1 ml; Titre value of sample = 21.5 ml.

$$\text{COD} = \frac{(22.1 - 21.5) \times 0.5 \times 800}{12} = 100 \text{ mg/l}$$

2.2.7. Outfall Effluent (Sample 2)

Titre value of blank = 22.1 ml; Titre value of sample = 21.7 ml.

$$\text{COD} = \frac{(22.1 - 21.7) \times 0.25 \times 800}{12} = 116.7 \text{ mg/l}$$

Using an atomic absorption spectrometer with an air-acetylene flame and a wavelength range of 190 to 900 nm, Buck Scientific's model 230 was used to measure the metal concentration. Cadmium (Cd), Copper (Cu), Lead (Pb), Nickel (Ni), Chromium (Cr), and Iron (Fe) concentrations were determined using calibration curves at particular wavelengths of 228.8 nm, 224.8 nm, 217 nm, 373 nm, 231.6 nm, and 522 nm, respectively.

2.3. Simulation

The biological treatment of fertilizer effluent made it possible to install and use GPS*, version 8.0, a modelling and simulation program developed by Hydro-mantis Environmental Software Solutions Inc., the most advanced tool currently

accessible for the mathematical optimization, modelling, and management of wastewater treatment plants [17].

The software was started, and the process water treatment library (proc water lib) option was selected. After finding the process table, a plant layout was made utilizing its icons. On the drawing board, every element of the process model was moved, arranged, and labelled. The process table was especially used to build all of the flow connections between the components of the process model. After adjusting the flow connections, stream labels were chosen using the labels button on the main toolbar. Following that, all process model object flow lines were given new names and labels.

2.3.1. Selection of Object Model and Mathematical Analysis

The primary unit processes and control points are the sole fundamental objects chosen to be modelled in our plant. The layout's numerous objects weren't given mathematical models. Therefore, several equations were established by the GPS* as one of the most crucial qualities to define the dynamic behavior of the process model objects. The models of the process elements that were utilized to construct the treatment scheme were examined, and decisions were taken for each element as indicated in **Table 1**.

Table 1. Process model utilization for each equipment.

S/N	Process Model Objects	Available Model (s)	Selected Model
1	Wastewater Influent point	states, tsstoc	Tsstoc
2	Anoxic Tank 1 & 2	pw2	pw2
3	Aeration Tank 1 & 2	pw2	pw2
4	Air Blower	Interchange	Interchange
5	Clarifier	empiric, point, simple1d, tss-sor-slr	Empiric
6	Sludge Buffer Sump	pw2	pw2
7	Sludge Thickener	empiric, simple1d	Empiric
8	Sludge Centrifuge	asce, point, simple1d, press	Empiric
9	Solutions from Side Filter & Oil Sludge	Interchange	Interchange
10	Sludge Disposer	Default	Default
11	Outfall Effluent point	Default	Default
12	Acetic Acid Doser	Codfeed	Codfeed
13	Sodium Hydroxide Doser	Alkalifeed	Alkalifeed
14	Sodium Hypochlorite Doser	Watchem	Watchem
15	Polymer Doser	Metaladd	Metaladd
16	Ferric Chloride Doser	Metaladd	Metaladd

The created layout was saved as “Fertilizer Effluent Biological Treatment GPS* Modelling Layout” using the file browser, which was chosen from the file menu.

Empiric Model was selected due to the following advantages;

- It's easily the most-used solids separation model for thickening and dewatering.
- It's easy to use and calibrate.
- No differentiation between different types of particulate COD.
- It is not predictive at very low/high concentrations due to the constant removal rate. One exception to the generic empiric model in the primary clarifier:

$$\text{Efficiency}(\%) = \frac{\left(\frac{T_{\text{det}}}{A+B}\right) \times T_{\text{det}}}{100} \quad (9)$$

where, T_{det} = Detention time (h). $A \& B$ = Solids removal parameters [17].

The data from sample 1 (the effluent sample), which were received following the laboratory analysis, were used to characterize the influent on the influent advisor by selecting influent characterization from the influent composition menu. The information for all chosen process model objects, such as initial conditions, input variables, flow, output variables, source data, etc., was also chosen and filled using menus and sub-menus based on information obtained from the Biological Treatment and Sludge Handling Package design manual and data sheet used in the fertilizer plant. The model's construction process is depicted in **Figure 1** [17].

The values of the variables used to describe the GPS-X Modelling Layout for the characterization of the wastewater influent and characterization of process model objects are presented in **Table 2** and **Table 3**, respectively.

2.3.2. Modelling and Simulation Procedure

To transition from modelling mode to simulation mode, click the Simulation button in the upper-right corner of the main window. This started the compilation and linking processes and produced an executable model. Upon completion, the simulation environment was available and the building model window vanished. The simulation proceeded in a steady state when the start button on the tool bar was pressed. Values were output in tabular form in the output section after completion. A rapid display screen allowed users to evaluate the simulation results, simulation parameters, and mass flows for each unit process in the layout [17].

1) Creating Input Controls

To investigate the effects of changes in the influent flow rates on the plant effluent qualities, the saved built layout was opened via file menu, new input controls were created. The flow rate setup was selected on the acetic acid and sodium hydroxide dosage object thereby accessing their parameters. The flow rate variables for both were moved from the flow rate setup to the empty input control space directly above the layout. The input control properties were changed

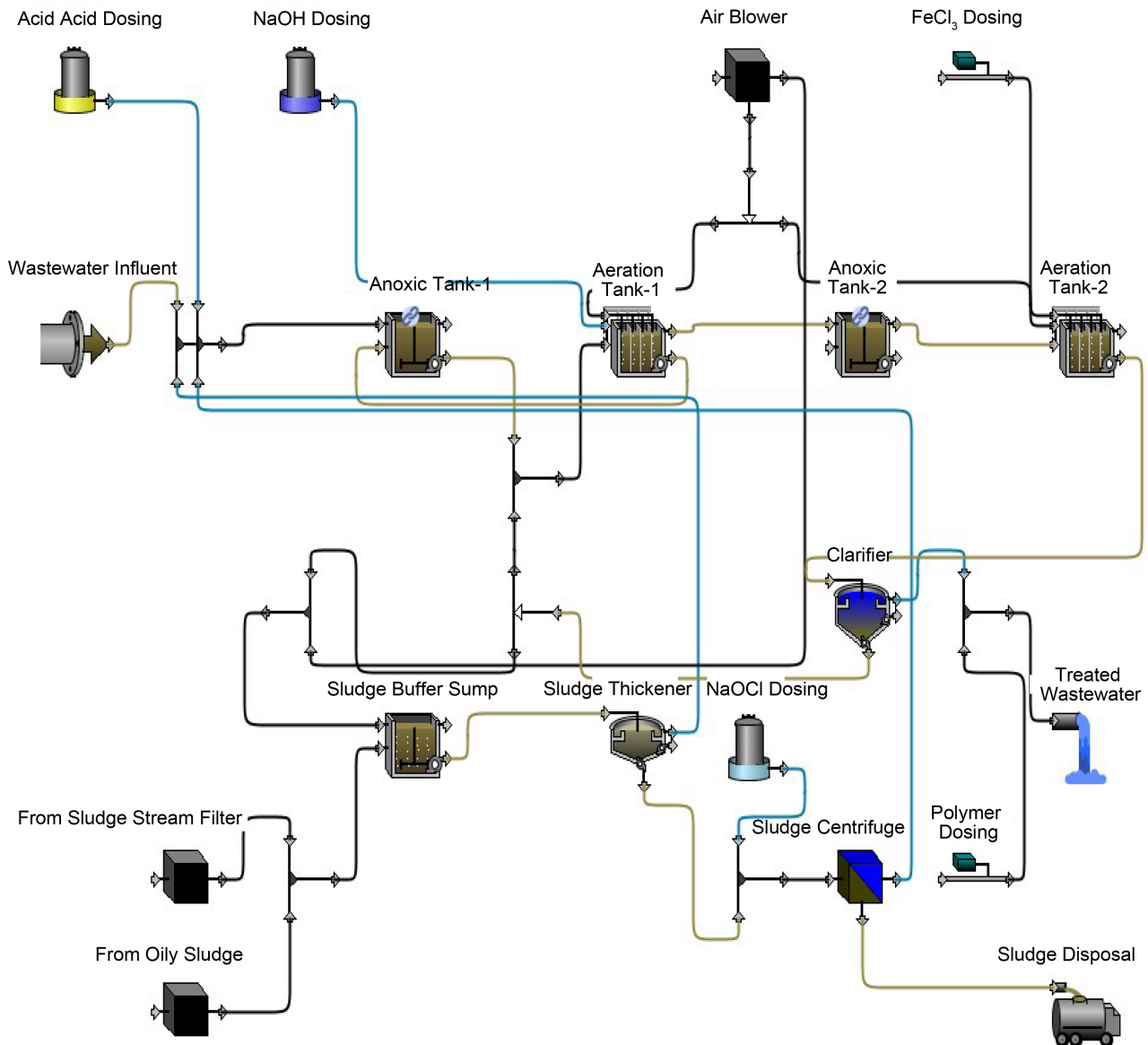


Figure 1. Fertilizer Effluent biological treatment GPS* modelling layout.

on the control toolbar to 45 L/hr, 60 L/hr, 75 L/hr, and 90 L/hr for acid dose and 9 m³/hr, 12 m³/hr, 15 m³/hr, and 18 m³/hr for alkali dose. Simulations were then run in accordance with the changes, the results of which were generated, and the impact on the treated water quality was examined. Additionally, the cost summary, energy usage summary, mass balance diagram, and Sankey diagram were generated by clicking on additional output displays on the output tool bar, as illustrated in **Figures 2-5**, respectively.

3. Results and Discussion

3.1. Effluent Characterization

The collected fertilizer effluent samples were evaluated in reference to temperature,

Table 2. Simulation data sample for the characterization of wastewater influent.

Variable	Unit	Default	Value
[winf] pH	-	7.0	11.48
[winf] total BOD	g/m ³	87.0	93.3
[winf] turbidity	NTU	78.0	108.0
[winf] total nitrogen	mgN/L	43.0	112.9
[winf] fraction inert soluble organic nitrogen	gN/gCOD	0.05	0.24
[winf] fraction inert soluble organic phosphorus	gP/gCOD	0.01	0.0167
[winf] nitrate	gNO ₃ -N/m ³	0.0	2.3
[winf] sulfatesulfur	gSO ₄ -S/m ³	0.0	50.311
[winf] chloride	gCl/m ³	0.0	8.6
[winf] copper	gCu/m ³	0.0	6.0
[winf] other cations	eq/m ³	3.0	42.0
[winf] ammonia nitrogen	gNH ₄ ⁺ -N/m ³	25.0	5.6
[winf] unit price of water	\$/m ³	2.0	6.5
[winf] influent flow	m ³ /hr	83.3333	45.0

Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD), Total Dissolved Solids (TDS), Electric Conductivity (EC), Sulphates, Turbidity, Total Phosphorus (T/PO₄⁻), Residual Chlorine, Nitrate (NO₃), Total Nitrogen (TN), Total Suspended Solids (TSS), Colour, pH, Urea, NH₃ and heavy metals (Cu, Cd, Cr, Pb, Ni and Fe). Results are shown in figures that compare the outfall effluent of the urea fertilizer business to Federal Environmental Protection Agency (FEPA) criteria from 1991.

Sample 1's color was a pale shade of blackish white, while sample 2 was found to be colorless. The fertilizer factory outfall effluent (sample 2) recorded high concentrations for all the water quality physicochemical parameters, and these concentrations are higher than the FEPA (1991) standard, with the exception of TSS, PO₄⁻, SO₄⁻, and NO₃⁻. Temperature and pH were determined from sample 2 analysis to be 41 °C and 9.7, respectively. Because it has an impact on aquatic life, the outfall effluent temperature is a crucial variable. An abrupt change in temperature may lead to a high mortality rate for aquatic species [1]. In rivers, streams, and canals, high pH wastewater has the potential to reduce the solubility and toxicity of pollutants, which could have an impact on aquatic life (Umer *et al.*, 2017) [7]. High pH wastewater can also promote the solubility of many important elements, such as Selenium (Se), in place of Mn, Cd, Al, B, Hg, and Cd. Additionally, high urea and NH₃ concentrations of the process condensates from the urea plant, ammonia plants, and from the sanitary sewage system following organic matter decomposition are connected with high pH values of the

Table 3. Simulation value for variables used in characterization of process model objects.

Process Model Objects	Variable	Unit	Value	Process Model Objects	Variable	Unit	Value
Anoxic Tank-1	Maximum Volume		307.2	Air Blower	Solids Capture Rate Flowrate	%	95.0
	Tank Depth	m ³	6.0				
	Pumped Flow	m	170.0				
	Initial Reactor Volume	m ³ /hr	270.0				
	Start with Full Tank	m ³	Off				650
Aeration Tank-1	Tank Depth	M	6.0	Clarifier	Surface Area	m ²	44.8
	Maximum Volume	m ³	328.0		Depth	m	3.5
	Pumped Flow	m ³ /hr	70.0		Pumped Flow	m ³ /hr	70.0
					Sludge Disposal Cost	\$/m ³	553.6
CH ₃ COOH Dosing	Chemical Purity	%	45.0	Polymer Dosing	Use Local Temperature		On
	Cost of Chemical	\$/kg	1.03		Local Liquid Temp.	C	21.0
	Flowrate	L/hr	31.0		Chemical Type		PAC-Al ₂ (OH) _n cl(6n)
					Chem. Dosage, in Mass	Kg/hr	450.0
NaOH Dosing	Use Local Temperature		On	Sludge Buffer Sump	Chemical Purity	%	0.2
	Local Liquid Temp.	C	21.0		Chemical Purity	\$/ kg	2.0
	Chemical Purity	%	50.0		Cost of Chemical		
	Cost of Chemical	\$/KG	0.42		Maximum Volume		230.0
	Flowrate	L/hr	6.0	Tank Depth	m ³	6.0	
Anoxic Tank-2	Maximum Volume	m ³	153.6	Sludge Thickener	Pumped Flow	m	70.0
	Tank Depth	m	6.0		Initial Reactor Volume	m ³ /hr	192.0
	Initial Reactor Volume	m ³	140.0		Volume	m ³	Off
	Start with Full Tank	m ³	Off		Start with Full Tank		
Aeration Tank-2	Tank Depth	M	6.0	Sludge Centrifuge	Surface Area	m ³	18.5
	Maximum Volume	m ³	140.0		Depth	m	3.5
	Pumped Flow	m ³ /hr	170.0		Pumped Flow	m ³ /hr	19.0
					Sludge Disposal Cost	\$/m ³	553.6
FeCl ₃ Dosing	Chem. Dosage, in Mass	Kg/hr	7197	NaOCl Dosing	Use Local Temperature		On
	Chemical Purity	%	40		Temperature	C	22.0
	Cost of Chemical	\$/kg	0.26		Local Liquid Temp.		Sodium Hypochlorite
					Chemical Type	%	10.0
Treated Wastewater Sludge Disposal	Chemical Purity			Chemical Purity	\$/kg	0.16	
	Cost of Chemical			Cost of Chemical	L/hr	10.0	
	Flowrate			Flowrate			
System	Maximum TDS	mg/L	30.0				
	Max. Total Hardness	mg/L	120.0				
	Sludge Disposal Cost	\$/tonne	55.36				
	Ratio of Soluble BOD to soluble COD	%	93.3				
	Liquid Temperature	C	43.0				
	Blower Inlet Air Temp.	C	32.0				

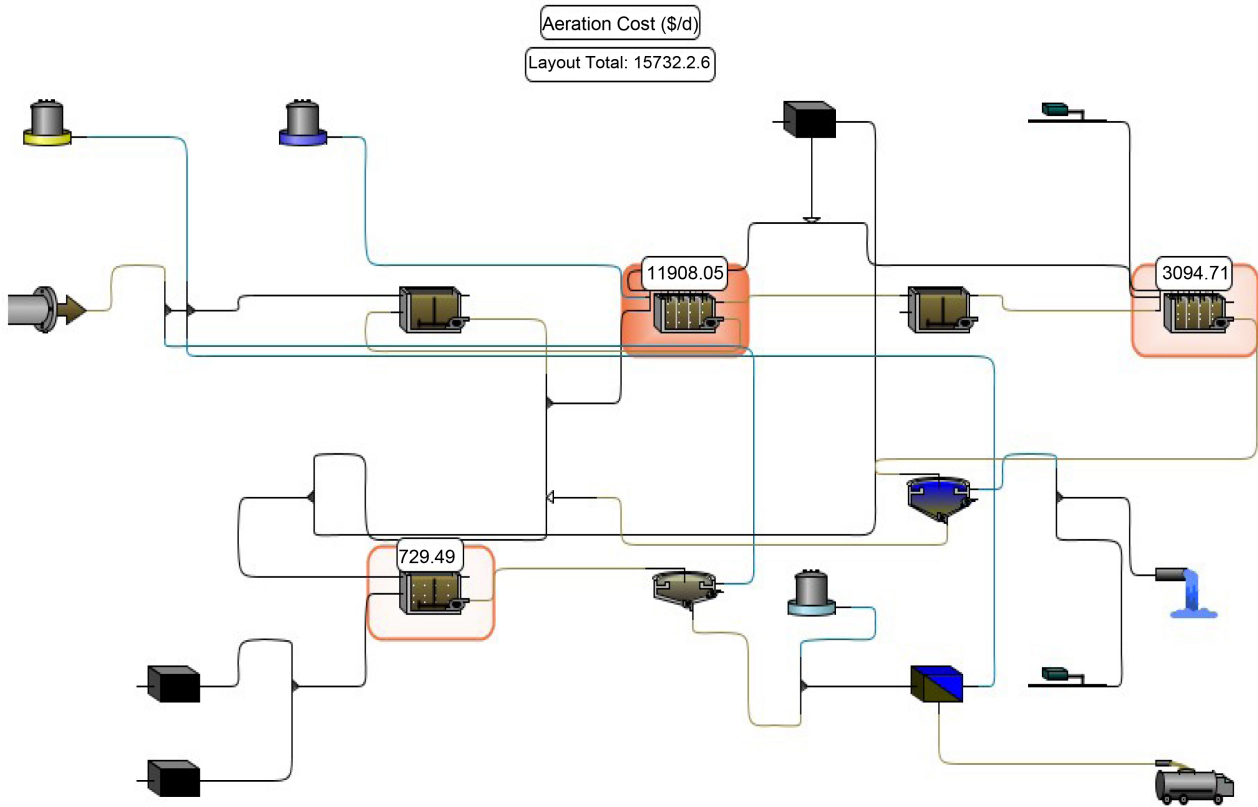


Figure 2. Fertilizer effluent biological treatment operating cost summary, Source: (GPS*, version 8.0).

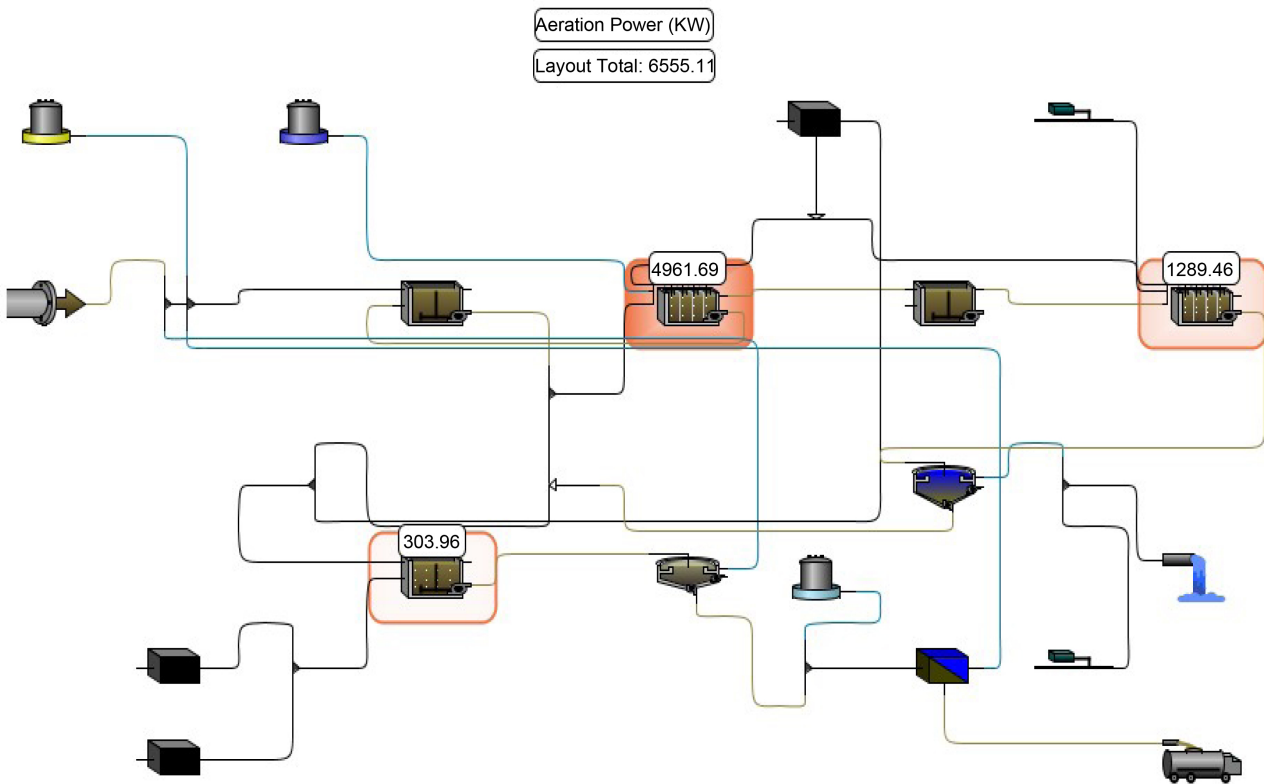


Figure 3. Fertilizer effluent biological treatment energy usage summary, Source: (GPS*, version 8.0).

outfall effluent. The pH of natural waters is a crucial quality indicator [1]. Salts are present in the samples, as determined by the measurements of EC and TDS. The EC and TDS values of the outfall effluent were measured to be 5848 S/cm and 2658.18 mg/l, respectively. These values are higher than the FEPA standard of less than 1000 μ S/cm and 2000 mg/l in reported in the [7], indicating their propensity to increase the salinity level of water bodies, which can have detrimental ecological effects on aquatic biota. High solubility compounds in aquatic environments may also slow down the rate of sunlight penetration into aquatic microsystems, which would otherwise have been a key factor in the emergence of photosynthetic organisms [7]. However, a high concentration of conducting particles in the effluent from production processes and chemical spills may be to blame for the small rise in EC and TDS [1]. The outfall effluent's turbidity was estimated to be 267 NTU, exceeding the FEPA requirement of 100 NTU. High turbidity can affect aquatic life, raise the expense of treating drinking water, and have a negative effect on tourism and recreation, greater turbidity of wastewater correlated with greater conductivity, and vice versa.

Figure 6(a) and **Figure 6(b)** shows that the outlet effluent's concentrations of urea, ammonia, phosphates, sulfates, nitrates, and total nitrogen were 219 mg/l, 20 mg/l, 0.358 mg/l, 26.80 mg/l, 1.70 mg/l, and 2.80 mg/l, respectively. The results of the current analysis show that the effluent quality of fertilizers is poor and that inorganic elements are present in considerable concentrations. The levels of urea, ammonia, and T/N are over the FEPA's acceptable limits of 100 mg/l, 0 - 5 mg/l, and 0.6 mg/l, respectively. The lagoon's water quality has greatly decreased as a result of this. High quantities of $(\text{NH}_2)_2\text{CO}$ and NH_3 in process condensates from the urea plant and the ammonia plant, which were improperly hydrolyzed or stripped, are linked to the high values. Excretory materials from the sanitary sewage system and seal leakage from ammonia pumps may both cause a high level of NH_3 to appear in the outfall effluent. (Obire, Ogan, & Okigbo, 2008) stated that high concentrations of $(\text{NH}_2)_2\text{CO}$ and NH_3 may have an effect on available trace metals that brings about detrimental or beneficial effect and also cause eutrophication issues on water. These activities include urea synthesis, housekeeping activity, and granulation section cleaning that dispose/discharge urea granules into open drains. When nitrogen is released into the environment above the necessary level, it may have undesirable consequences on the environment's ecology and human health [18]. In order to maintain oxidation (degradation) of the available nutrients and support the typical spectrum of aquatic life, the available dissolved oxygen (DO) must be used [1].

The calculated biological and chemical oxygen demands were 91.7 mg/l and 116.7 mg/l, respectively. **Figure 6(c)** demonstrates that despite the normally low amounts, both samples have BOD and COD levels that are greater than the FEPA's recommended limits of 30 mg/l for each.

According to Umer *et al.* (2017), high BOD and COD of effluent samples indicate that organic and inorganic matter is present in the fertilizer effluent

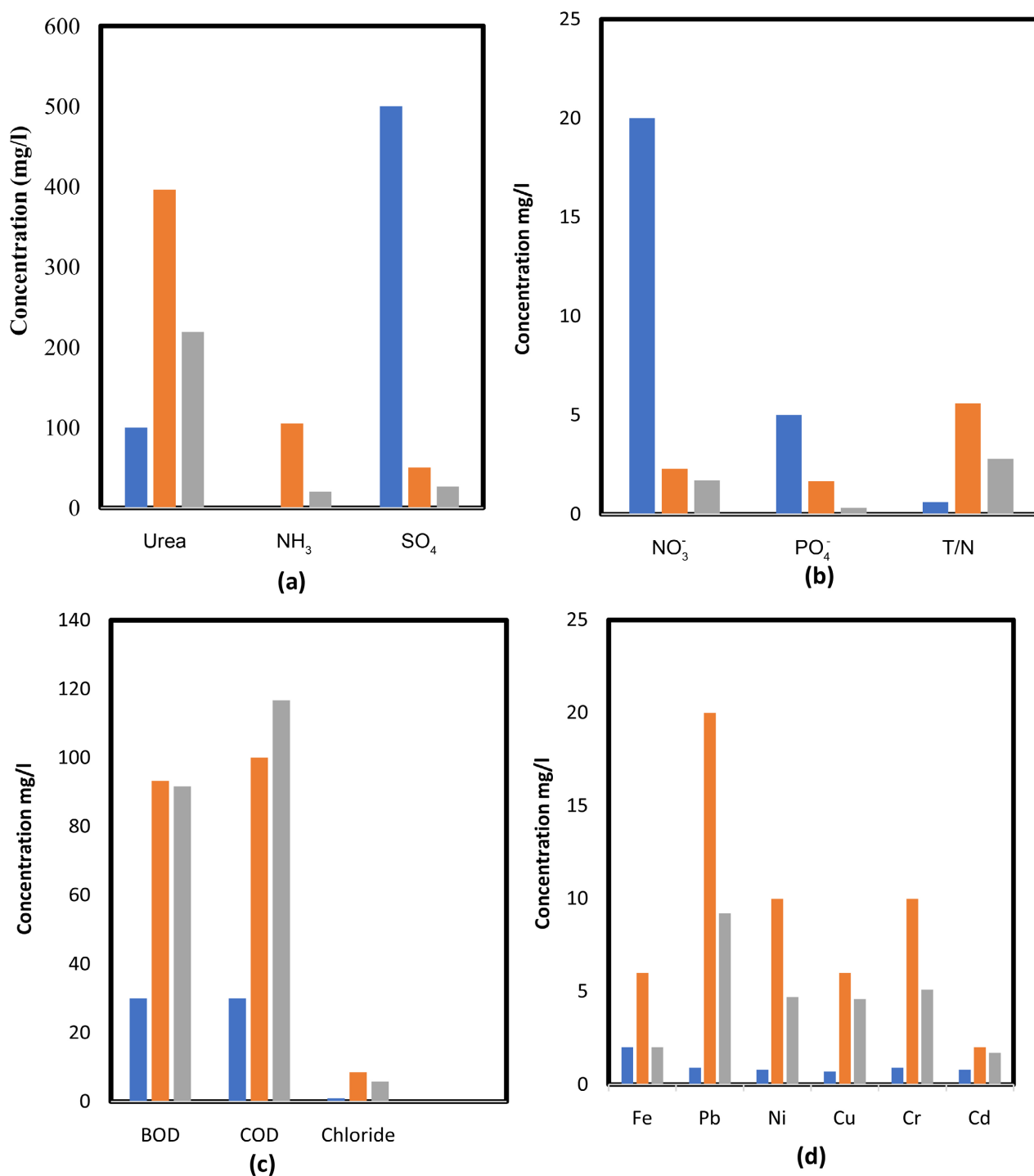


Figure 6. (a) Urea, ammonia and sulphate concentration in the fertilizer wastewater; (b) Nitrate, phosphate and total nitrogen concentration in the fertilizer wastewater; (c) Biological Oxygen Demand, Chemical Oxygen Demand and Chloride (mg/l) content of the fertilizer wastewater; (d) Metal ions (mg/L) contents of the fertilizer wastewater. The symbols represent FEPA (□), Sample 1 (◻) and Sample 2 (◻).

sample in high concentration, suggesting the possibility that the sample could enhance algal blooms and destabilize aquatic systems due to the high amount of nutrients present. The rate at which oxygen is used up in the stream increases

with BOD. Similar to low dissolved oxygen levels, too much BOD stresses aquatic life, suffocates it, and ultimately kills it.

According to **Figure 6(d)**, the amounts of Cd, Cr, Cu, Fe, Pb, and Ni in the fertilizer outfall effluent sample were 1.7 mg/l, 5.1 mg/l, 4.6 mg/l, 2.0 mg/l, 9.2 mg/l, and 4.7 mg/l, respectively. Except for the Fe concentration, which was not as high as observed in other detected heavy metals, the results of all heavy metals detected show concentrations exceeding the FEPA recommended values of the release of heavy metals into the environment. This suggests that the fertilizer plant's piping system is sufficiently protected from corroding by chemical and biological actions. Metal and non-metal ion concentrations in aquatic environments have been shown to impact the metabolism of higher creatures and bacteria in seawater. These ions, particularly cations, are hazardous to aquatic life at varying levels. This can be caused by the impact of soluble elements in the effluent generated by the overall functioning of the fertilizer plant. Lead is a toxic metal that can harm the liver and kidneys. Chromium in its hexavalent form is extremely toxic because it has the ability to cross cell membranes and interact with genetic materials after being reduced to trivalent form, which is what causes its mutagenic and toxic effects. As a result, the effluent from the fertilizer outfall can be deemed inappropriate for environmental release (Umer *et al.*, 2017). When applied to the soil, high iron concentrations in wastewater can cause soil acidity and lower the amount of molybdenum and phosphorus that is readily available. When copper concentrations rise slightly over those needed as a micronutrient, they become hazardous, especially to marine invertebrate larvae [19].

3.2. GPS* Modelling and Simulation Result

The model layout was built due to what is obtainable from **Figure 1**, the process model objects were calibrated as per the data extracted from the Biological Treatment and Sludge Handling Package design manual and data sheet used in the fertilizer plant, and the influent was characterized using the physicochemical parameters got from the analyzed influent sample. From the process simulation of the wastewater treatment, the analysis of results revealing the chemical analysis of the effluents is shown in **Table 4**. Hence, the treated water simulation results clearly showed high reduction in BOD and COD concentration by 36% and 54.5% respectively, total nitrogen (TN), Nitrate-N and total phosphorus (TP) were also seen to be within the permissible FEPA standard as can be seen in **Table 4**. Acetic acid and sodium hydroxide flow rates were used as the output variables to investigate the effects of changes in the influent flow rates on the plant effluent qualities. On increasing the acetic acid dosage at 45 L/hr, 60 L/hr, 75 L/hr and 90 L/hr into anoxic tank-1 and keeping sodium hydroxide flow at 6 m³/hr, some changes in the treated water simulation results were observed.

As the acid flow rate increases and more simulations are run, a continuous concentration decrease was seen in the TSS, BOD, COD, Volatile Suspended

Table 4. Treated wastewater simulation results. Source: (GPS*, version 8.0).

Variable	Unit	Value
Flow	m ³ /d	2400
TSS	mg/L	3570
VSS	mg/L	1.166
cBOD ₅	mg/L	33.37
COD	mg/L	63.64
Ammonia N	mgN/L	3.342
Nitrite N	mgN/L	2.233
Nitrate N	mgN/L	2.029
TKN	mgN/L	81.67
TN	mgN/L	85.93
Soluble PO ₄ -P	mgP/L	1.964e-10
TP	mgP/L	0.576
Total Alkalinity	mgCaCO ₃ /L	62,590
pH	-	14.0
DO	mgO ₂ /L	0.0

Solids (VSS), Ammonia-N, Total Kjeldahl Nitrogen (TKN), Nitrate-N and Total Phosphorus in the treated water simulation results as shown in **Table 5** below. Hence, this indicates a proportional relationship with acid flow rate and the waste-water treatment performance.

Similarly, on increasing the sodium hydroxide dosage at 9 m³/hr, 12 m³/hr, 15 m³/hr and 18 m³/hr into the aeration tank-1 and keeping acetic acid flow at 31 L/hr, some changes on the treated water simulation results were observed. As the sodium hydroxide flow rate increases and more simulations are run, even though, continuous concentration decrease was observed in total alkalinity but, a continuous concentration decrease was sighted in the TSS, BOD, COD, Volatile Suspended Solids (VSS), Ammonia-N, Total Kjeldahl Nitrogen (TKN), Nitrate-N and Total Phosphorus in the treated water simulation results as shown in **Table 6**.

Also, on increasing both sodium hydroxide dosage at 9 m³/hr, 12 m³/hr, 15 m³/hr and 18 m³/hr into the aeration tank-1 and acetic acid flow at 45 l/hr, 60 l/hr, 75 l/hr and 90 l/hr into anoxic tank-1, some changes on the treated water simulation results were observed. As the flow rate of both chemicals increases with corresponding values and more simulations are run, even though, continuous concentration decrease was sighted in total alkalinity and Nitrate-N but, a continuous concentration decrease was observed in the TSS, BOD, COD, Volatile Suspended Solids (VSS), Ammonia-N, Total Kjeldahl Nitrogen (TKN) and Total Phosphorus in the treated water simulation results as shown in **Table 7**.

However, no significant change was observed in all the three scenarios as

Table 5. Treated water simulation results with increasing acetic acid dose at 6 m³/hr dose of sodium hydroxide.

Acetic Acid Flow (L/hr)	31.0	45.0	60.0	75.0	90.0
pH	14.0	14.0	14.0	14.0	14.0
Total Alkali (mgCaCO ₃ /L)	62,590	64,490	62,980	63,150	63,100
TSS (mg/L)	3570	3560	3995	3990	3988
cBOD ₅ (mg/L)	33.37	33.36	33.35	33.34	33.33
VSS (mg/L)	1.166	1.162	1.161	1.161	1.160
COD (mg/L)	63.64	63.62	63.60	63.58	63.56
DO (mgO ₂ /L)	0.0	0.0	0.0	0.0	0.0
Ammonia-N (mgN/L)	3.342	4.936	4.934	4.933	4.932
TKN (mgN/L)	81.67	83.23	83.20	83.18	83.16
Nitrite-N (NO ₂ ⁻) (mgN/L)	2.233	5.23 × 10 ⁻¹⁰	1.10 × 10 ⁻¹⁰	1.01 × 10 ⁻¹⁰	1.10 × 10 ⁻¹⁰
TN (mgN/L)	85.93	85.26	85.23	85.21	85.18
TP (mgP/L)	0.5760	0.5757	85.5755	0.5753	0.5751
Nitrate-N (NO ₃ ⁻) (mgN/L)	2.029	2.027	2.027	2.026	2.025
Soluble PO ₄ -P (mgP/L)_	0.0	0.0	0.0	0.0	0.0

Table 6. Treated water simulation results with increasing sodium hydroxide dose at 31 L/hr dose of acetic acid.

Sodium Hydroxide Flow (m ³ /hr)	6.0	9.0	12.0	15.0	18.0
pH	14.0	14.0	14.0	14.0	14.0
Total Alkali (mgCaCO ₃ /L)	62,590	87,080	108,700	127,900	145,400
TSS (mg/L)	3570	4207	3895	3627	3393
cBOD ₅ (mg/L)	33.37	31.50	29.83	28.32	26.96
VSS (mg/L)	1.166	1.046	0.9513	0.872	0.8049
COD (mg/L)	63.64	60.02	56.79	53.90	51.30
DO (mgO ₂ /L)	0.0	0.0	0.0	0.0	0.0
Ammonia-N (mgN/L)	3.342	4.663	4.418	4.197	3.997
TKN (mgN/L)	81.67	78.62	74.48	72.48	67.39
Nitrite-N (NO ₂ ⁻) (mgN/L)	2.233	1.01 × 10 ⁻¹⁰	0.0	0.0	1.42 × 10 ⁻¹⁰
TN (mgN/L)	85.93	80.54	76.30	72.48	69.03
TP (mgP/L)	0.576	0.532	0.505	0.476	0.451
Nitrate-N (NO ₃ ⁻) (mgN/L)	2.029	1.915	1.815	1.724	1.642
Soluble PO ₄ -P (mgP/L)_	0.0	0.0	0.0	0.0	0.0

regard Dissolve oxygen (DO), soluble PO₄-P and P^H, this could be owing to the fact that limited parameters were used in characterizing the influent causing most required parameters to run on default. Another factor may be that the acid dosage flow rate is not sufficient enough to bring down the P^H and alkalinity concentration of the treated water.

Table 7. Treated water simulation results with increasing both sodium hydroxide and acetic acid dose.

Acetic Acid Flow (L/hr)	31.0	45.0	60.0	75.0	90.0
Sodium Hydroxide Flow (m ³ /hr)	6.0	9.0	12.0	15.0	18.0
pH	14.0	14.0	14.0	14.0	14.0
Total Alkali (mgCaCO ₃ /L)	62,590	87,740	110,200	127,800	145,400
TSS (mg/L)	3570	4205	3892	3315	3389
cBOD ₅ (mg/L)	33.37	31.49	29.81	28.30	26.94
VSS (mg/L)	1.166	1.046	0.9504	0.8709	0.8037
COD (mg/L)	63.64	60.00	56.76	53.86	51.25
DO (mgO ₂ /L)	0.00	0.00	0.00	4.07	0.00
Ammonia-N (mgN/L)	3.342	4.662	4.416	4.194	3.994
TKN (mgN/L)	81.67	78.60	74.45	70.71	67.33
Nitrite-N (NO ₂ ⁻) (mgN/L)	2.233	1.04 × 10 ⁻¹⁰	3.34 × 10 ⁻¹⁰	4.16 × 10 ⁻¹⁰	1.04 × 10 ⁻¹⁰
TN (mgN/L)	85.93	80.52	76.26	72.43	68.97
TP (mgP/L)	0.576	1.915	1.814	1.723	1.640
Nitrate-N (NO ₃ ⁻) (mgN/L)	2.233	1.915	1.814	1.723	1.640
Soluble PO ₄ -P (mgP/L)	0.0	0.0	0.0	0.0	0.0

4. Conclusion

The physicochemical characterization of influent and outfall effluent samples collected from a urea fertilizer plant was conducted and the parameters measured from outfall effluent were compared with Federal Environmental Protection Agency (FEPA) standard. While TSS, PO₄⁻, SO₄⁻ and NO₃ values were found within the permissible limits, the pH, temperature, COD, BOD, TDS, EC, Turbidity, Residual Chlorine, TN, Colour, Urea, NH₃ and heavy metals ions (Cu, Cd, Cr, Pb, Ni and Fe) recorded concentration values higher than recommended standards. Results showed that a proper treatment of fertilizer industries effluents is required prior to discharge into the environment. However, using modeling and simulation software (GPS-X, version 8.0), a biological treatment upgrade of the physicochemical parameters obtained from the analyzed influent sample was performed. The treated water simulation results clearly showed a high reduction in cBOD₅ and COD concentration by 35% and 44% respectively. A continuous concentration decrease was also observed in the TSS, Volatile Suspended Solids (VSS), Ammonia-N, Total Kjeldahl Nitrogen (TKN), Nitrate-N and Total Phosphorus on increasing the acetic acid and sodium hydroxide dosage and running more simulations. Results showed that a proper treatment of fertilizer industries effluents is required prior to discharge into the environment.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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