The Concept of Examination of Biochemical and Chemical Oxygen Demand in Stagnant Water System

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Abstract Predictive model on the rate of biochemical and chemical oxygen demand concentration diffusion in a stagnant water environment was investigated in this paper. The mathematical model was formulated based on the basic principle of mass and momentum concept which was resolved to obtain an ordinary differential equation. A mathematical tool known as the least square method was applied to resolve the differential equation to a quadratic equation. The samples collected were analyzed to predictive the model on the rate of biochemical and chemical oxygen demand concentration diffusion in a stagnant water environment as presented in this paper. Experimental data obtained from the analysis were fitted into the model to obtain their diffusivities and velocities of the parameters upon the influence of contaminants. Concentrations of the BOD and COD at the various depths were simulated and the polynomial of the curve was also established to ascertain the validity of the developed model. Simulated results from the model were compared analytically and graphically with the experimental and validated result as presented in the work. The results obtained show a reasonable level of agreement which is an indication of the reliability of the developed model for predicting the diffusion of BOD and COD in a stagnant water environment.

Keywords Concept, examination, biochemical, chemical Oxygen Demand, Stagnant Water, System

Introduction

There are various physiochemical parameters which can be used to measure the quality of water, of which turbidity is a common one. Turbidity refers to the amount of suspended matter dirt, organic particulates, planktons, etc. in water. It determines the visibility in the water (how far down into the pond you can see through). Whether turbidity indicates a real problem depends on the type of particulate matter suspended in the water. Water turbidity in freshwater ponds is caused by phytoplankton and zooplankton (microscopic plants and animal) and suspended or colloidal particle in the water column of pond. Green water is due to planktonic algae. Tea-colored water is the result of leaching from decomposing leaves in the pond. Unless leaves are removed promptly, this coloring is unavoidable. Brown-colored water has several possible causes' dead and dying planktonic algae produces a brown coloration that appears once the material settles out, and suspended clay or silt can also produce brown colors [1-6]. Another important physiochemical parameter for measuring the quality of water is dissolved oxygen (DO) concentration. It is a common indicator of the health of aquatic ecosystem. It tells the amount of oxygen present in the water mass. DO is important because it is used by aquatic living organism for survival. The sources of dissolved oxygen in water body include re-aeration from atmosphere, photosynthetic oxygen production from aquatic plants,

denitrification and DO inputs. DO can be measured in terms of percentage saturation and level less than 80 percent saturation in drinking water can usually be detected by consumers as a result of poor odor and taste [7-10].

Odor is caused by biological contaminants of the water mass of pond by organic decays, feaces, urine etc. [11-15]. Biological respiration including that related to decomposition process reduces DO concentrations. Other physiochemical parameters for assessing the quality of water include pH, temperature, conductivity, COD and BOD, nutrient etc.

Biodegradation process typically results from microorganism activity that causes the transformation or breakdown of organic materials. Chemical conversion associated with biodegradation include: (1) Organic to inorganic (2) Toxic compounds to innocuous compounds and (3) Non-toxic to toxic compounds. Biodegradation of organic substances can be carried out by aerobic or anaerobic organism. Aerobic organism utilizes oxygen to metabolize organics. Anaerobic organisms do not use oxygen to metabolize organics. Therefore, when an organic waste is discharged into an aquatic ecosystem, a biological oxygen demand (BOD) is created. BOD is a measure of the oxygen required to breakdown organic compounds. High BOD levels significantly deplete the amount of dissolved oxygen (DO) in water surface. Consequently, high BOD level can have a detrimental effect on health of aquatic species that requires elevated (DO) level, such as fish. This happens when for example, an algae reproduces rapidly within the reservoir in responds to input of phosphorus or of other contaminants that happens to be nutrient for algae. The algae biodegrades the nutrients at the same time decreasing the amount of available oxygen. Thus, the increased amount of algae creates a high BOD, which depletes the DO, possibly resulting in the death of fishes in the reservoir [16].

The study of the physiochemical analysis of water is of great significance in removing the constraints in the pond. Effluent quality evaluation is also based on physicochemical parameters. The physiochemical parameters in the pond have been shown to influence the rate of biodegradation in the pond [5].

The present research is aimed at developing a model that would be helpful in the future to determine the quality or portability of water taking the physiochemical parameters of the water such as COD, BOD, and pH etc. as input data.

The investigation is targeted to derive an empirical model that can monitor and predict pollutant deposition and transport (diffusion) in stagnant water. The developed model is an effective tool for monitoring and predicting pollutant transport in water environment, the developed model will serve as a tool for identifying pollution, and the fate and behavior of pollutant in water environment, the result obtained from the model through analysis of the physiochemical parameters of stagnant water can be a very important component of environmental impact assessment and also used for providing technical support for water environmental protection agencies.

The scope of study of the research work covers the following areas as stated below**:** Collection of samples of stagnant water around the Asphalt Company in Ahoada-West local government area of Rivers State and transporting the samples to the Department of Pure and Applied Chemistry, Niger Delta University for examination and analysis. Experimental methods was carried out which includes: physiochemical analysis on reliability and portability of the water, influence of diffusion on the stagnant water, turbidity, total dissolved solid and total suspended solid analysis, development of mathematical model based on first and second principles law of mass transfer on the diffusion concept, relating the developed mathematical model into the empirical model in terms of least square method and validation of the developed model.
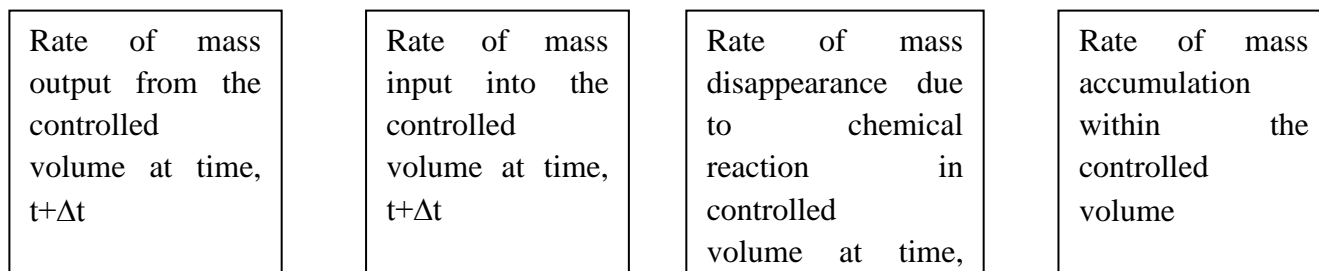
Materials and Methods
Mass-Balance Principle

The basic principle of water quality model is that of mass balance. The water system can be divided into different segments or volume elements. For each segment, there must be a mass balance for each water quality constituents over a time periods, Δt. Time is divided into discreet intervals t and the flow are assumed constant within each of those time period intervals. For each segment and each time period, the mass balance of substance in a segment can be defined. Component of the mass balance in a segment include:

- Change by transport (Tr) into and out of the volume element.

- Change by physical or chemical processes (P) occurring within the volume element.
- Change by sources \ discharges to or from the volume element (s).

  From the principle of mass balance,

Rate of mass output from the controlled volume at time, t+Δt	Rate of mass input into the controlled volume at time, t+Δt	Rate of mass disappearance due to chemical reaction in controlled volume at time,	Rate of mass accumulation within the controlled volume

$$M\big|_t = M\big|_{t+\Delta t} + \Delta t(\tfrac{\Delta M}{\Delta t})_{Tr} + \Delta t(\tfrac{\Delta M}{\Delta t})_P + \Delta t(\tfrac{\Delta M}{\Delta t})_S \qquad (1)$$

Where: $M\big|_t$ = Mass in volume element at the beginning of time t., $M\big|_{t+\Delta t}$ = Mass in volume element at the end of time t+Δt., $(\tfrac{\Delta M}{\Delta t})_{Tr}$= change in volume element by transport., $(\tfrac{\Delta M}{\Delta t})_P$= change in volume element by physical, (bio)chemical or biological process and $(\tfrac{\Delta M}{\Delta t})_S$= change in volume element by sources (e.g waste load, river discharges).

Changes by transport include both advective and dispersive transport.
Equation (1) can be rearranged as;

$$\frac{M|_t - M|_{t+\Delta t}}{\Delta t} = (\tfrac{\Delta M}{\Delta t})_{Tr} + (\tfrac{\Delta M}{\Delta t})_P + (\tfrac{\Delta M}{\Delta t})_S \qquad (2)$$

Model Formulation
Model for Transport of Contaminant
To model the transport of contaminant (pollutant) over a space, a water system is divided in small segment or volume elements. Each volume elements is defined by its volume and its dimensions in one, two or three directions (Δx, Δy, and Δz) depending on the nature of the schematization (1D, 2D, or 3D).

Advective Transport
The advective transport, $T_{y0}^A (M/T)$ of a constituent at site x0 is the product of the average water velocity, V_{y0} (L/T), at that site, the surface or cross sectional area A (L^2), through which advection takes place at the site and the average concentration (M/L^3) of the constituent.

$$T_{y0}^A = V_{y0} \times A \times C_{y0} \qquad (3)$$

Dispersive Transport
The dispersive transport, $T_{y0}^A (M/T)$, across a surface area is assumed to be proportional to the concentration gradient $\frac{\partial c}{\partial y}\big|_{y=y0}$ at site x0 times the surface area A.

Letting D_{y0} (L^2/T), be the dispersion or diffusion coefficient at site y0.

$$T_{y0}^D = -D_{y0} \times A \times \frac{\partial c}{\partial y}\big|_{y=y0} \qquad (4)$$

Dispersion is done according to Fick's law of diffusion. The minus sign originate from the fact that dispersion causes net transport from higher to lower concentrations and so in opposite direction of the concentration gradient. The concentration gradient is the difference of concentration per unit length over a very small distance across the cross section.

$$\frac{\partial C}{\partial X}\big|_x = \lim_{\Delta x \to 0}\left(\frac{Cx+\Delta x - Cx}{\Delta x}\right) \qquad (5)$$

Mass Transport by Advection and Dispersion

Adding the advective and dispersive terms in equation (3) and (4) result to the net change in transport.

$$\left(\frac{\Delta M}{\Delta t}\right)_{T\,r} = \left[\, V_{y0}C_{y0} \;-\; D_{y0} \times A \times \frac{\partial c}{\partial y}\Big|_{y\,=\,y0}\right] \times A \qquad (6)$$

Now including the terms at site $y_0 + \Delta y$, gives;

$$\left(\frac{\Delta M}{\Delta t}\right)_{Tr} = \left[\, V_{y0}C_{y0} \;-\; V_{y0+\Delta y}C_{y0+\Delta y} \;+\; D_{y0+\Delta y}\frac{\partial C}{\partial y}\Big|_{y0+\Delta y} - D_{y0}\frac{\partial C}{\partial y}\Big|_{y0}\right] \times A \qquad (7)$$

Substituting eqn. (7) into eqn. (2), we obtain;

$$\frac{M|_t - M|_{t+\Delta t}}{\Delta t} = A_{y0}V_{y0}C_{y0} - A_{y0+\Delta y}V_{y0+\Delta y}C_{y0+\Delta y} + D_{y0+\Delta y}A_{y0+\Delta y}\frac{\partial C}{\partial y}\Big|_{y0+\Delta y} - D_{y0}A_{y0}\frac{\partial C}{\partial y0}\Big|_{y0} - \left(\frac{\Delta M}{\Delta t}\right)_p + \left(\frac{\Delta M}{\Delta t}\right)_s \quad (8)$$

Assuming a zero order reaction for the rate of change of volume element by physical, biochemical or biological process, and also knocking out the term for the rate of change in volume element by sources, gives

$$\frac{M|_t - M|_{t+\Delta t}}{\Delta t} = A_{y0}V_{y0}C_{y0} - A_{y0+\Delta y}V_{y0+\Delta y}C_{y0+\Delta y} + D_{y0+\Delta y}A_{y0+\Delta y}\frac{\partial C}{\partial y}\Big|_{y0+\Delta y} - D_{y0}A_{y0}\frac{\partial C}{\partial y0}\Big|_{y0} - k_p \quad (9)$$

Where k_p is the rate constant due to chemical reaction.

Expressing eqn. (9) in terms of concentration and dividing throughout by the elemental volume (($V = Ay\Delta y$), result in a one dimensional equation as shown below

$$\frac{C|_t - C|_{t+\Delta t}}{\Delta t} = \frac{D_{y0+\Delta y}\frac{\partial C}{\partial y}\Big|_{y0+\Delta y}}{\Delta y} + \frac{V_{y0}C_{y0} - V_{y0+\Delta y}C_{y0+\Delta y}}{\Delta y} - k_p \qquad (10)$$

Taking asymptotic limit $\Delta t \to 0$ and $\Delta y \to 0$, the advection-diffusion equation for one dimension results:

$$-\frac{\partial C}{\partial t} = \frac{\partial}{\partial y}\left(D\frac{\partial C}{\partial y}\right) - \frac{\partial}{\partial y}(VC) - k_p \qquad (11)$$

Clearing the negative sign on the L.H.S and opening the bracket gives,

$$\frac{\partial C}{\partial t} = -D\frac{\partial^2 C}{\partial y^2} + V\frac{\partial C}{\partial y} + \frac{\partial C}{\partial y} + k_p \qquad (12)$$

Assuming steady state transport,

$$0 = -D\frac{d^2 C}{dy^2} + V\frac{dy}{dx} + k_p \qquad (13)$$

If we let $\frac{d^2 C}{dy^2} = d^2,\,and\,\frac{dy}{dx} = d,$

Equation (13) can be expressed as

$$-Dd^2 + Vd + k_p = 0 \qquad (14)$$

Where;

d is the depth of water from the surface to the subsurface.

Application of Empirical Model

Applying the least square concept to the above equation, the concentration can be expressed as a function of depth.

$$C = -Dd^2 + Vd + k \qquad (15)$$

Since diffusion is taking place, the above expression can be normalized by neglecting the negative sign.

$$C = Dd^2 + Vd + k \qquad (16)$$

The above equation gives the developed model, which may be expressed in terms of the physiochemical parameters of water analysis as follows:

For pH concentration,

$$C_{pH} = Dd^2 + Vd + k \qquad (17)$$

For conductivity,

$$C_{cond} = Dd^2 + Vd + k \qquad (18)$$

For BOD concentration,

$$C_{BOD} = Dd^2 + Vd + k \qquad (19)$$

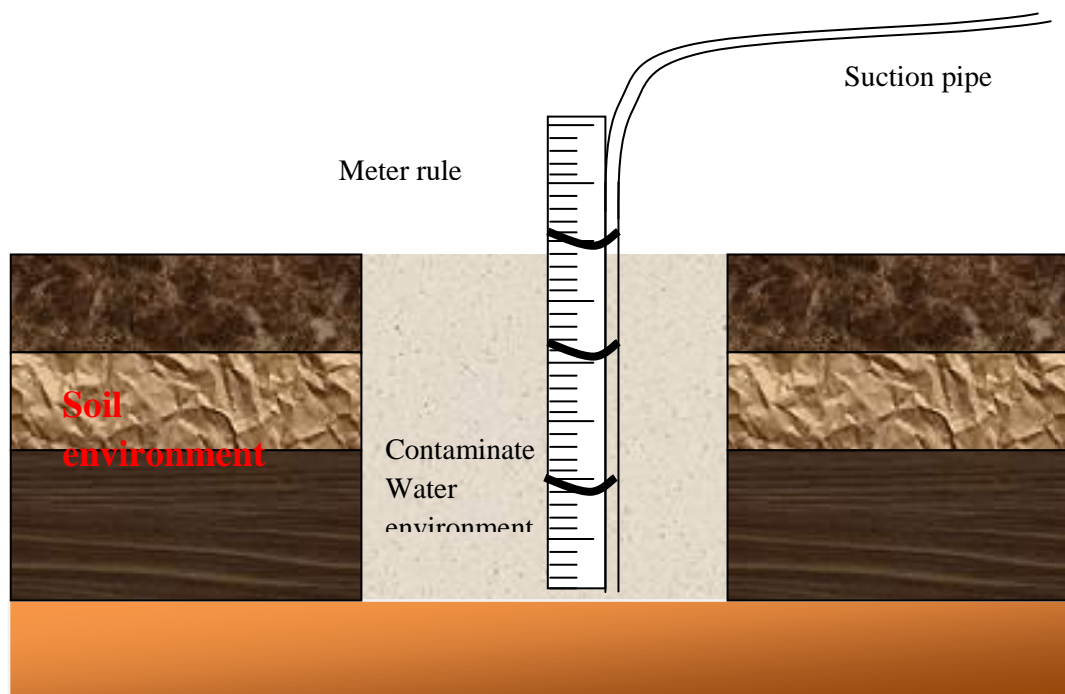**Experimental Procedures**
Experimental Method

Figure.1: Experimental Set-up to investigate the diffusion process of effluent contaminant in water   environment.

Sample Collection
Five water samples were collected from stagnant water in the neighborhood of the Asphalt Company Nigeria Limited located at Enito 3, a village located between Ahoada and Mbiama in Ahoada West Local Government Area of River State. The study distance is about 65metres from the company and samples were collected on a weekly basis. The analysis of the sample covers the following parameters: pH, Hardness and Conductivity. Samples were collected with the aid of a capillary tube and the depth at which each samples were collected is determined using a meter rule. Thereafter, samples were transported to the research laboratory of the department of chemical science, Niger Delta University for onward analysis.

Materials: Burette and Pipettes, Beaker 10ml and 250ml, volumetric flask 50, 100, 250ml and 500ml
Determination of Biochemical Oxygen Demand (BOD)
BOD is define as the amount of oxygen required by bacteria for breaking down to simpler substances, the decomposable organic matter present in water, waste water or treated effluent. BOD can be taken as a measure of the concentration of organic matter present in that kind of water. The greater the decomposable organic matter present, the greater the oxygen demand the greater the BOD value.
BOD test are usually carried out by measuring the amount of dissolved oxygen (DO) present in the water sample before and after the incubation in the dark for 5 days at $25^{o}C$.
Procedures:
Preparation of dilution water
    I.   Phosphate Buffer Solutions: this consist of the following-
        8.5g potassium dihydrogen phosphate (KH_2PO_4).
        21.75g dipotassium hydrogen phosphate (K_2HPO_4).
        33.40g disodium hydrogen phosphate ($Na_2HPO_4.7H_2O$)

1.70g Ammonium Chloride (NH_4Cl) in a litre of solution. This is preserved in a stock bottle.

II. Magnesium Sulphate ($MgSO_4$) Solution:

22.5g magnesium sulphate ($MgSO_4.7H_2O$ in 1 litre of solution.

III. Calcium Chloride ($CaCl_2$) Solution.

27.5g of Calcium Chloride ($CaCl_2$) in 1 litre of solution.

IV. Ferric Chloride ($FeCl_3.6H_2O$) Solution

0.25g $FeCl_3.6H_2O$ in 1litre of solution.

Item (I) to (IV) constitute the dilute water. the water samples were diluted by 2% into the 125ml BOD bottles,100ml of the 2%diluted water samples were placed by means of a long tipped 50ml pipette. This was followed by the addition of 25ml of the dilution water, so that the bottle was filled to the brim. The initial DO was taken from one the duplicate bottle and then the stopper was inserted into the mouths of the bottle leaving no air bubbles.

The samples were then incubated including the blank for 5 days in the dark at 25^oC in a cooled incubator. On the fifth (5th) day, the dissolved oxygen (DO) was measured in the incubated bottles including the blank.

Determination of Chemical Oxygen Demand (COD)

Chemical Oxygen Demand (COD) is rapidly measured parameter used to determine the pollution strength of domestic and industrial waste waters. This determination is achieved by using a strong oxidizing agent under acidic conditions. Excess amount of the oxidizing agent is used, oxygen is released, some is used to oxidize an equivalent amount of the waste to carbon dioxide (CO_2) and the unused is determine by titration with reducing agent of known strength. The amount used for the oxidation of the waste is known by difference.

PROCEDURE: 0.4g MERCURY (II) sulphate ($HgSO_4$) was weigh into a refluxing flask and 20ml sample added. 10ml of potassium dichromate ($K_2Cr_2O_7$) were also added by means of a pipette. Slowly and with gentle swirling, 30ml of Silver Sulphate (Ag_2SO_4) in concentrated H_2SO_4 was added. The refluxing condenser was connected.

The mixture was then reflux for 2hrs.the system was cooled and the condenser washed into a conical flask plus the mixture and allowed to attain room temperature with the aid of a 0.05M ferrous Ammonium sulphate (FAS) solution, the excess dichromate solution was titrated using ferrous (0.025M) as indicator. A blank was also prepared without the sample in the solution, which was also titrated.

Mg (COD) = $\frac{(Vb-Vs)\times M \times 16,000}{Volume\ of\ sample}$,

Where: Vb = ml of FAS for blank titration; Vs = ml of FAS for sample titration

M = Molarity of FAS, 16,000 = molar mass of oxygen in

Results and Discussion

The results obtained from the analysis of the water samples are presented in tables and figures in terms of its physiochemical properties as well as BOD and COD.

Table 1: Experimental Determination of Physiochemical Parameters with Respect to Depth

Parameters	units	Depth (cm)				
		0	15	30	45	60
BOD	mg/L	28.80	34.50	30.42	27.60	32.50
COD	mg/L	70.50	76.80	75.30	70.10	77.80

Table 2: Comparison of Experimental, Theoretical, and Validated BOD concentration against depth.

Depth (cm)	BOD(Experimental)	BOD(Theoritical)	BOD(Validated)
0.000	28.800	30.024	31.640
15.000	34.500	31.644	30.830
30.000	30.420	31.644	30.020
45.000	28.800	30.024	29.210
60.000	27.600	26.784	28.400

Table 3: Comparison of Experimental, Theoretical, and Validated Chemical Oxygen Demand (COD) concentration against depth.

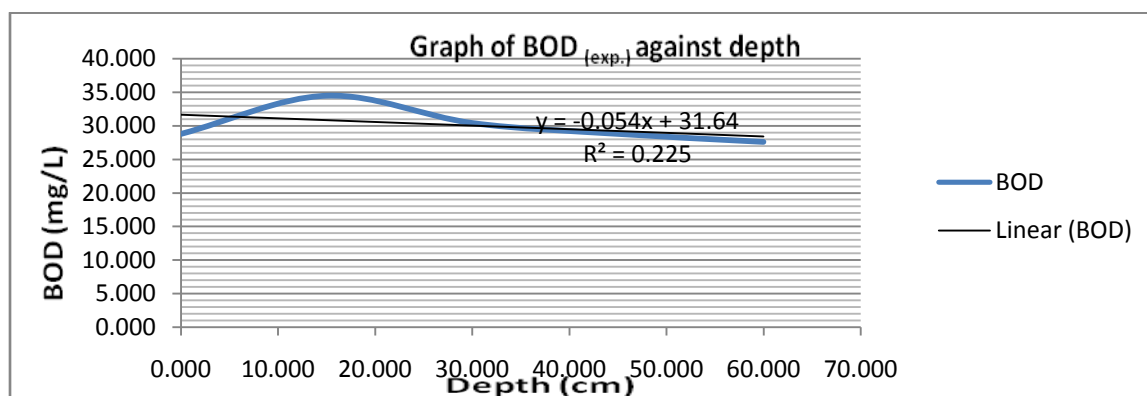| Depth (cm)	COD (Experimental)	COD (Theoretical)	COD (Validated)
0.000	70.500	72.391	72.520
15.000	76.800	73.373	73.300
30.000	75.300	74.224	74.080
45.000	70.100	74.945	74.860
60.000	77.800	75.535	75.640

Figure 2: Graph of experimental BOD concentration against the Depth of water.

Figure 2 is a display of the experimental BOD values plotted against the depth of water. The BOD concentration increases from the surface down to a depth of 18cm and starts to decrease gradually. The polynomial of the curve is $Y = 0.054X + 31.64$, which can be expressed also as $C_{BOD(val)} = 0.054D + 31.64$ the coefficient of determination is $R^2 = 0.225$, the expression for the developed model is given as $C_{BOD(theo)} = -0.0036D^2 + 0.162D + 30\ 024$.
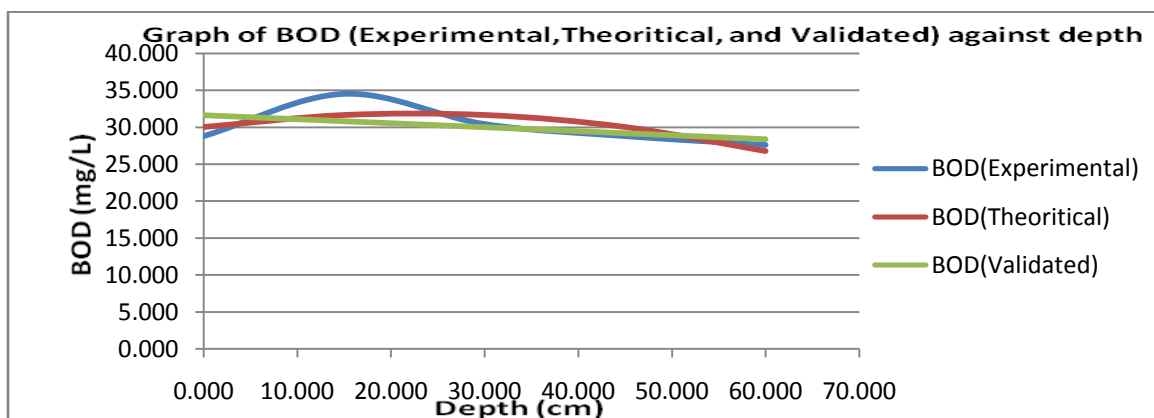

Figure 3: Graph of Experimental, Theoretical, and Validated BOD concentration against Depth of water.

Figure 3 shows the relationship between the experimental, theoretical, and validated model for BOD concentration plotted against the depth of water. the graph shows a good match for the three models. Points of intersections are obtained for the experimental and theoretical model at a region of 30cm depth, and for the three models around 50cm depth of water. The theoretical model shows a better relationship compared with the experimental model.
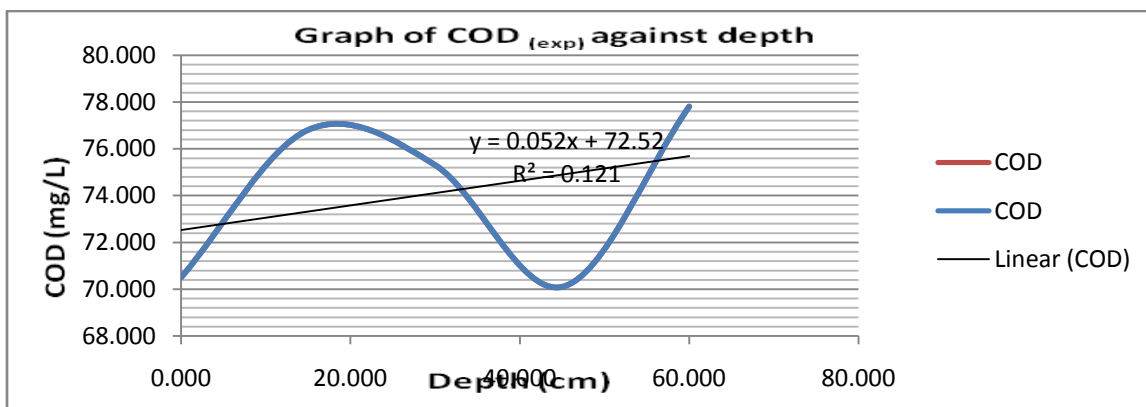
Figure 4: Graph of experimental COD concentration against the Depth of water.

Figure 4 present a sinusoidal curve when the COD concentrations were plotted against the depth of water. The polynomial of the curve is $C_{COD(val)} = 0.052D + 72.52$, the coefficient of determination is given as $R^2 = 0.121$. The theoretical developed model is given as $C_{COD(theo)} = -0.00029D^2 + 0.0698D + 72.391$.
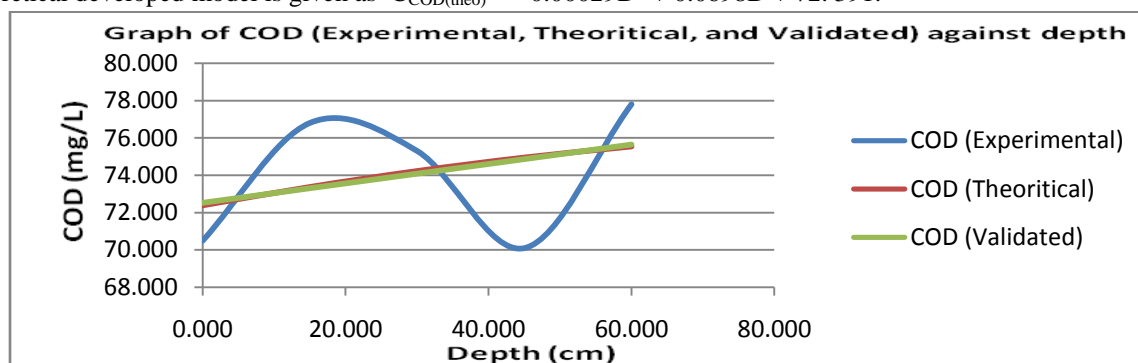

Figure 5: Graph of Experimental, Theoretical, and Validated COD concentration against Depth of water.

The Figure above presents a very good match for the theoretical and validated model.

Points of intersections are obtained for the three models at various depths such as 8cm, 35cm, and 58cm indicating the reliability of the developed model.

Conclusion

The following conclusion can be drawn from the research work: BOD concentration increases and later decreases. This is due to dilution factor, which also imply that no significant diffusion takes place. The COD concentration shows a sinusoidal nature of curve. This is attributed to the dilution factor, the degree of deposition and diffusion. The relationship between the theoretical and validated model present a perfect match which implies the reliability of the developed model. The study provides an efficient tool for analyzing specific problems associated with the discharge of effluents into surrounding water bodies. Amongst other potential applications, the model is recommended to be used by environmental impact agencies, as a real-time prediction tool for determining\ estimating water quality parameters. In addition, the predicted model can be used for proactive management of the process and for forecasting and evaluating water quality and the risk related to it. It can also serve as an effective tool for providing data assistance.

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