

Model Development for pH, Salinity and Conductivity Monitoring and Predicting the Diffusion Concentration in Stagnant Water

Ukpaka CP^{1*} and Douglas IE²

¹Department of Chemical/Petrochemical Engineering, Rivers State University of Science and Technology, Nkpolu PMB 5080, Port Harcourt, Nigeria

²Department of Marine Engineering, Rivers State University of Science and Technology, Nkpolu PMB 5080, Port Harcourt, Nigeria

Abstract

The research work presents the development of a mathematical model for predicting the diffusion of pH, salinity and conductivity in a stagnant water environment. The model was formulated from the basic principle of mass and momentum concept which was resolved to obtain an ordinary differential equation of $-\frac{\partial c}{\partial t} = \frac{\partial}{\partial y} \left(D \frac{\partial c}{\partial y} \right) - \frac{\partial}{\partial y} (VC) - k_p$. A mathematical tool known as the least square method was applied to resolve the differential equation to a quadratic equation of the form; $C = Dd^2 + Vd + k_p$. Five water samples were collected at a depth of ≤ 5 cm, 15 cm, 30 cm, 45 cm, and 60 cm, in the vicinity of the Asphalt plant Company, located at Enito 3, in Ahoada West L.G.A of River State. The samples were analyzed to determine their physiochemical parameters. 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 contaminants 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 contaminant diffusion in stagnant water.

Keywords: Model development; pH; Salinity; Conductivity; Monitoring; Predicting; Diffusion concentration; Stagnant water

Introduction

Water is used by humans for consumption and utility and we rely on access to clean, safe, water for almost all aspect of our societal functions. Throughout history, water has acted as a waste transport medium carrying away the byproduct of our settlement and dispersing them into our environment. As population and economic activities grow larger, more pollutants are generated. Many of these are water borne and may be deposited on surface (Stagnant) and subsurface water bodies thus degrading the water quality and the aquatic ecosystem at large [1]. Water quality is becoming an ever more important issue, as water of low quality causes many significant problems. In particular, there is a wide range of microbial and chemical constituents of surface stagnant water that can cause either acute or chronic detrimental health effects, and the detection of these constituents in treated water is often time-consuming, complex and expensive from economic perspective as resources have to be directed towards improving the water supply system every time problem occurs. For these reason, there is a growing need to improve water treatment and water quality management in order to enhance pollutant-free water for aesthetic and recreational purpose and also for consumption at a reasonable cost [2-5]. Systematic assessment of polluted water and operational monitoring techniques are needed to meet these challenges.

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 [3,6-10]. Pollutant deposition on surface and underground water has become one of the most critical environmental problems of the century.

Many drinking water supplies and aquatic ecosystem are contaminated with pesticides and other chemicals from widespread agricultural uses, crude oil and its derivatives used for fuel, lubrication; plastic manufacturing and many other purposes get into water mainly by means of accidental spills. Plant and animals require water that is moderately pure and they cannot survive if their water is loaded with toxic heavy chemicals or harmful microorganisms. If severe, water pollution can kill a large number of fish, birds, and other animals in some cases killing all members of specie in an affected area. Pollutant deposition makes streams, lakes and coastal waters unpleasant to look at, to smell and to swim in Ref. [11-14].

Fish and shellfish harvested from polluted water can become ill, and with prolong exposure may develop cancer or bears children with birth defects. The following points stated below highlights the aims and objectives of the research work. To develop a mathematical model that can monitor and predict the rate of diffusion pH, salinity and conductivity concentration diffusion in stagnant water. To investigate

***Corresponding author:** Ukpaka CP, Department of Chemical/Petrochemical Engineering, Rivers State University of Science and Technology, Nkpolu PMB 5080, Port Harcourt, Nigeria, E-mail: chukwuemeka24@yahoo.com

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the contribution of the Asphalt Company activity in environmental pollution as well as the migration of the pollutant generated in water body of the region where they are operating, to ascertain the impact of its effluent discharge within the operational zone on water environment, its effect on the aquatic ecosystem, interaction of the functional parameters and Identification of the nature of contaminants.

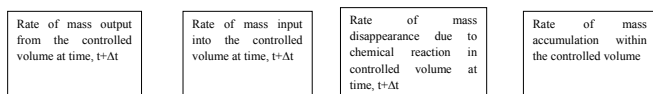
Materials and Methods

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 discrete 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,



$$+ M|_t = M|_{t+\Delta t} + \Delta t \left(\frac{\Delta M}{\Delta t} \right)_{Tr} + \Delta t \left(\frac{\Delta M}{\Delta t} \right)_P + \Delta t \left(\frac{\Delta M}{\Delta t} \right)_S \quad (1)$$

Where: $M|_t$ =Mass in volume element at the beginning of time t , $M|_{t+\Delta t}$ =Mass in volume element at the end of time $t+\Delta t$, $\left(\frac{\Delta M}{\Delta t} \right)_{Tr}$ =change in volume element by transport., $\left(\frac{\Delta M}{\Delta t} \right)_P$ =change in volume element by physical, (bio)chemical or biological process and $\left(\frac{\Delta M}{\Delta t} \right)_S$ =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;

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

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 x_0 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.

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

Dispersive transport: The dispersive transport, T_{y0}^D (M/T), across a surface area is assumed to be proportional to the concentration gradient $\frac{\partial C}{\partial y}|_{y=y_0}$ at site x_0 times the surface area A .

Letting Dy_0 (L^2/T), be the dispersion or diffusion coefficient at site y_0 .

$$T_{y0}^D = -D_{y0} \times A \times \frac{\partial C}{\partial y}|_{y=y_0} \quad (4)$$

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.

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

Mass transport by advection and dispersion

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

$$\left(\frac{\Delta M}{\Delta t} \right)_{Tr} = [V_{y0} C_{y0} - D_{y0} \times A \times \frac{\partial C}{\partial y}|_{y=y_0}] \times A \quad (6)$$

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

$$\left(\frac{\Delta M}{\Delta t} \right)_{Tr} = [V_{y0} C_{y0} - V_{y_0+\Delta y} C_{y_0+\Delta y} + D_{y_0+\Delta y} \frac{\partial C}{\partial y}|_{y_0+\Delta y} - D_{y_0} \frac{\partial C}{\partial y}|_{y_0}] \times A \quad (7)$$

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

$$\frac{M|_t - M|_{t+\Delta t}}{\Delta t} = A_{y_0} V_{y_0} C_{y_0} - A_{y_0+\Delta y} V_{y_0+\Delta y} C_{y_0+\Delta y} + D_{y_0+\Delta y} A_{y_0+\Delta y} \frac{\partial C}{\partial y}|_{y_0+\Delta y} - D_{y_0} A_{y_0} \frac{\partial C}{\partial y}|_{y_0} - \left(\frac{\Delta M}{\Delta t} \right)_P + \left(\frac{\Delta M}{\Delta t} \right)_S \quad (8)$$

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

$$\frac{M|_t - M|_{t+\Delta t}}{\Delta t} = A_{y_0} V_{y_0} C_{y_0} - A_{y_0+\Delta y} V_{y_0+\Delta y} C_{y_0+\Delta y} + D_{y_0+\Delta y} A_{y_0+\Delta y} \frac{\partial C}{\partial y}|_{y_0+\Delta y} - D_{y_0} A_{y_0} \frac{\partial C}{\partial y}|_{y_0} - k_p \quad (9)$$

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

$$\frac{C|_t - C|_{t+\Delta t}}{\Delta t} = \frac{D_{y_0+\Delta y}}{\Delta y} \frac{\partial C}{\partial y}|_{y_0+\Delta y} - \frac{V_{y_0} C_{y_0} - V_{y_0+\Delta y} C_{y_0+\Delta y}}{\Delta y} - k_p \quad (10)$$

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

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

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

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

Assuming steady state transport,

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

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

Equation (13) can be expressed as

$$-Dd + Vd + k = 0 \quad (14)$$

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.

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

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

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

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,

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

For conductivity,

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

For BOD concentration,

$$CBOD = Dd^2 + Vd + k \quad (19)$$

Experimental Methods and Procedures

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 65 metres 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 sample was 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

Digital pH meter, Conductivity/Salinity meter, Burette and Pipettes, Beaker 10 ml and 250 ml, volumetric flask 50, 100, 250 ml and 500 ml.

Experimental analysis

Determination of pH: The pH meter was used for the determination of the pH of the water samples. Before the measurement, the pH is standardized with two buffer solutions of different pH values, namely pH 4 and 9. The electrode is thoroughly rinsed and then dipped into the water samples and a steady pH is recorded as the pH of the water sample.

Determination of Salinity: The conductivity meter has a salinity position so that as the probe is dipped into the water body, the control

switch is turned to the salinity position and when a steady reading is obtained, it is recorded as the salinity of the water sample.

Determination of Conductivity (μScm^{-1}): Electrical conductivity of the water of the water sample was measured with the conductivity and salinity meter. The probe of the meter was inserted into the water sample and the central control switched to the conductivity position. A steady reading is recorded as the conductivity of the water in μScm^{-1} .

Results and Discussion

The results obtained from the analysis of the water samples are presented in Tables 1-4. The Figure 1 shows in terms of its physiochemical properties as well as pH, salinity and conductivity. The result in Figure 2 illustrates the experimental pH value of contaminated stagnant water plotted against depth. The pH was high at the surface and is observed to decrease with an increase in depth of water and then starts to increase sharply until it gets to a depth of 40 cm where the pH is 6.45 and again starts to decrease. The undulating nature of the pH value can be attributed to the dilution factor, the variation in depth, as well as the degree of deposition and diffusion of contaminant in the water environment. The polynomial of the curve is given as $C_{pH}(\text{exp}) = 6.294$ and the coefficient of determination is $R^2 = 2E-28$. The theoretical developed model is given as $C_{pH}(\text{theo}) = -0.0001d^2 + 0.0076d + 6.239$. In Figure 3 illustrate the relationship between the Experimental, Theoretical, and Validated pH value of contaminated stagnant water against the depth. A point of intersection can be seen at the depth of 28 cm and 58 cm indicating a good match of the theoretical and the experimental model.

In Figure 4 is a graph displaying the result obtained for the salinity of contaminated stagnant water plotted against the depth. A rise in salinity concentration was observed from the surface to the depth of 15 cm, a drop between 15 cm and 30 cm, and a corresponding rise below

Parameters	units	Depth (cm)					WHO Standard
		0	15	30	45	60	
pH		6.32	6.14	6.40	6.44	6.17	6.5 – 8.5
Salinity	mg/L	0.03	0.05	0.04	0.08	0.09	
Conductivity	$\mu\text{S/cm}$	168.00	250.00	243.00	285.00	279.00	

Table 1: Experimental Determination of Physiochemical Parameters with respect to depth.

Depth (cm)	pH (Experimental)	pH (Theoretical)	pH (Validated model)
0.00	6.32	6.24	6.29
15.00	6.14	6.33	6.29
30.00	6.40	6.37	6.29
45.00	6.44	6.38	6.29
60.00	6.17	6.33	6.29

Table 2: Comparison of Experimental, Theoretical, and Validated pH concentration.

Depth (cm)	Salinity (Experimented)	Salinity (Theoretical)	Salinity (Validated model)
0	0.03	0.03	0.028
15	0.05	0.04	0.043
30	0.04	0.05	0.058
45	0.08	0.07	0.073
60	0.09	0.09	0.088

Table 3: Comparison of Experimental, Theoretical, and Validated Salinity concentrations.

Depth (cm)	Conductivity (Experimental)	Conductivity (Theoretical)	Conductivity (Validated model)
0	168.00	175.46	193.60
15	250.00	228.38	219.30
30	243.00	263.16	244.99
45	285.00	279.81	270.69
60	279.00	278.32	296.38

Table 4: Comparison of Experimental, Theoretical, and Validated Conductivity concentrations.

30 cm depth. The polynomial of the curve is given as $Y=0.001x+0.028$ for the validated model with the coefficient of determination given as $R^2=0.839$. The above polynomial curve can also be written as $C_{sal(val)}=0.001d+0.028$. The theoretical developed model is given as $C_{sal(theo)}=0.000095d^2+0.0004d+0.0322$.

In Figure 5 is a display of the relationship between the theoretical, experimental, and validated salinity concentration against depth. A point of intersection is observed at the following region between the theoretical and experimental data, the theoretical and validated data, and between the experimental and validated data. Firstly at the depth of 4 cm, 8 cm, and 18 cm corresponding to concentration of 0.032, 0.035, and 0.048, and secondly at a depth of 38 cm, 55 cm, and 42 cm corresponding to concentration of 0.051, 0.081, and 0.068 respectively. The theoretical developed model shows a good relationship than the experimental model. The point of intersection between these models is an indication of its reliability in predicting the contaminant diffusion in stagnant water environment. The result in Figure 6 shows the experimental conductivity concentration plotted against the depth of water. The conductivity is seen to increase with an increase in the depth of water. The polynomial of the curve was established as $Y=1.713x+193.6$ with a coefficient of determination given as $R^2=0.758$. The expression can be written as $C_{con(val)}=1.713D+193.6$ for the validated model while the theoretical model developed is established as $C_{con(theo)}=-0.040D^2+4.132D+175.457$.

In Figure 7 shows the result of the relationship for the three models. Points of intersections are obtained at different regions of the graph for the three models. A perfect intersection point is obtained for the experimental and validated model between the depth of 25 cm and 35 cm, and at a depth of 60 cm for the experimental and theoretical model. The theoretical model provides a better relationship than the experimental model. The relationship shows a good match indicating

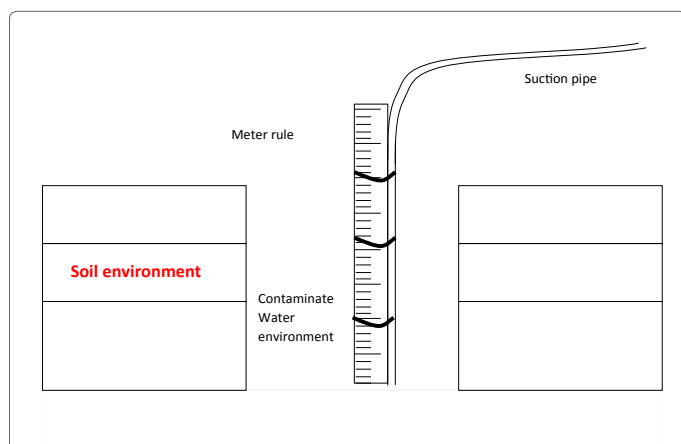


Figure 1: Experimental Set-up to investigate the diffusion process of effluent contaminant in water environment.

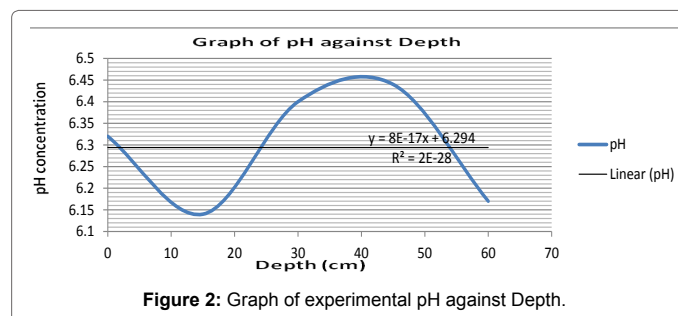


Figure 2: Graph of experimental pH against Depth.

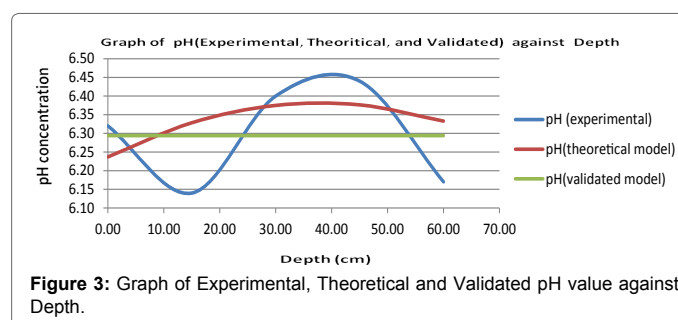


Figure 3: Graph of Experimental, Theoretical and Validated pH value against Depth.

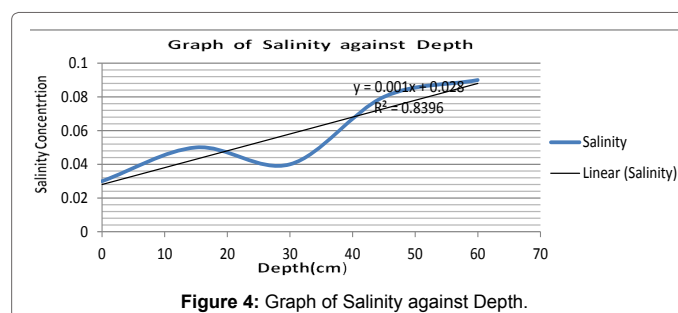


Figure 4: Graph of Salinity against Depth.

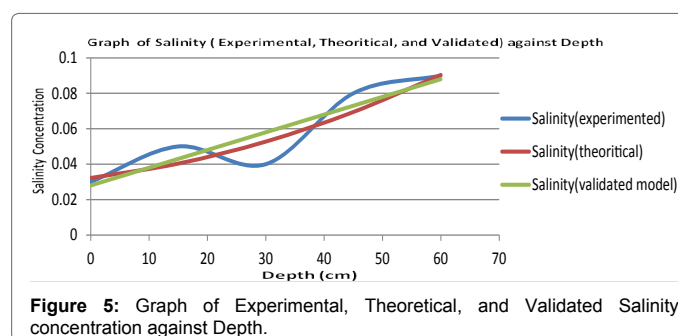


Figure 5: Graph of Experimental, Theoretical, and Validated Salinity concentration against Depth.

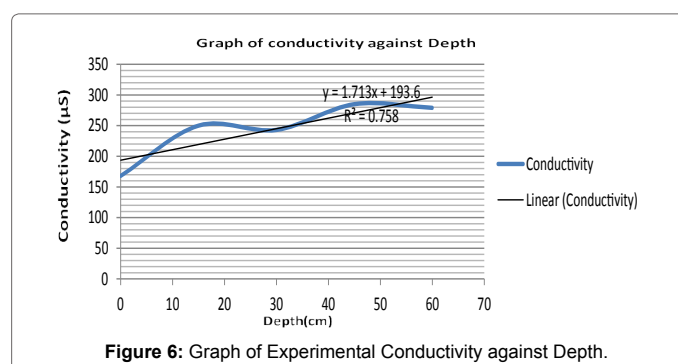
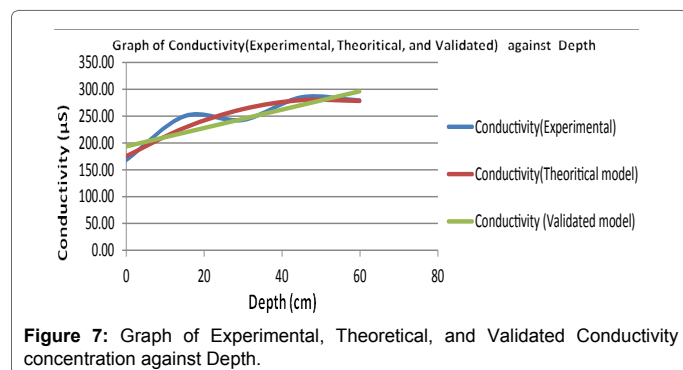


Figure 6: Graph of Experimental Conductivity against Depth.



the reliability of the developed model for predicting the conductivity of contaminated water.

Conclusion

The following conclusion can be drawn from the research work:

1. The undulating nature (rise and fall) of the pH concentration can be attributed to the dilution factor (i.e., the amount of contaminant in a given volume of water), and the degree of contaminant deposition and diffusion.

2. The salinity at the surface is low and increases as the depth of water increases. This is attributed to the high rate of contaminant diffusion from the surface to the subsurface. There may also be tendency of contaminant diffusion to the soil.

3. The conductivity increases with increase in the depth of water which indicate a high rate of diffusion of contaminant from the surface to the subsurface

4. 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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