Experimental Investigation on the Rate of Diffusion of Nitrate and Sulphate in Stagnant Water Environment

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Abstract

Mathematical model for predicting and monitoring the diffusion rate of nitrate and sulfate in a stagnant water environment was investigated as presented in this article. The model was formulated from the basic principle of mass and momentum concept which was resolved to obtain an ordinary differential equation. A mathematical techniques known as the least square method was applied to resolve the differential equation to obtain quadratic equation. The samples collected were analyzed to determine, predicting and monitoring the diffusion rate of nitrate and sulfate turbidity in a stagnant water environment. 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 and monitoring the diffusion rate of nitrate and sulfate in a stagnant water environment.

Keywords: Experimental, investigation, diffusion, nitrate, sulphate, stagnant water, environment.

Introduction

Though water pollution may occur from a variety of sources, there are two terms used to describe how the water became polluted. When water is polluted from a single source or from a discrete location, it is called POINT-SOURCE POLLUTION. This discrete location could be a factory, a sewer pipe or a runoff from a single farm. The BP oil spill in 2010 is an example of point-source pollution because the massive amount of oil leaked from a single point of origin.

When several points of contamination over a large area contribute to the pollution of water body, it is called a NON-POINT SOURCE POLLUTION. For example, one water body may be contaminated by multiple sources like agricultural runoff, city street runoff, construction site and residential lawns. The Mississippi river is at a great risk for non-point source because it is so large and is exposed to variety of possible pollution sources. Most types of water pollution only affect the immediate area but sometimes the pollution can travel hundreds or thousands of miles and then it is called trans-boundary pollution. There are many types of water pollution since water comes from many sources. These are; Surface water pollution, Ground water pollution, Oxygen pollution, Nutrient pollution, Microbial pollution, Suspended matter pollution and Chemical water pollution.

Surface water includes natural water found on the earth surface like rivers, lakes, lagoons and oceans. It is the most visible form of pollution and we can see it floating on water. Trash from human consumption such as water bottles, plastics and other waster products is most often evident on water surfaces. This type of pollution also comes from oil spills and gasoline waste, which float on the surface and affect the water and its inhabitants. Ground water pollution is caused by highly toxic chemicals and pesticides from farming that leak through the ground to contaminate the wells and aquifers below the surface. When humans apply pesticides and chemical to soil, they are washed deep into the ground by rainwater. This gets to the underground water, causing pollution underground. Water bodies have microorganisms. These include aerobic and anaerobic organisms. When there is an influx of biodegradable material from such things as waste or erosion from farming, the number of these microorganisms increases and utilizes the obtainable oxygen in the water. When these oxygen levels are depleted, harmful aerobic microorganism die and anaerobic microorganism thrive. Some of these microorganisms produce damaging toxins like sulphides and ammonia.

Nutrients such as phosphorus and nitrogen are essential to plant growth. Some wastewater, fertilizers and sewage contains high levels of nutrient. If they end up in water bodies, can cause excessive vegetation of algae and weeds. This will make the water undrinkable and even clog filters. Too much algae will also use up all the oxygen in the water and other organisms in the water will die out of oxygen starvation. Microbial pollution is the natural from of water pollution that is caused by microorganism in untreated water. They are water borne and most of these microorganisms such as bacteria, viruses and protozoa can cause serious diseases such as cholera and typhoid. They can also cause fish and other water life to die.

Some pollutant (Substances, particles and chemicals) do not dissolve in water. This kind of material is called particulate matter. Some suspended pollutants later settle under the water body. This is harmful to wildlife and cause long term problem due to imbalance in the natural infrastructure of the water. Many industries and farmers work with chemical that end up in water. These include chemicals that are used to control weeds, insects and pests. Metals and solvents also flow out of factories into water bodies, polluting the water. These are poisonous to many forms of aquatic life and may slow their development, causing them infertile and kill them.

Several mechanisms exist for the transformation and transport of contaminants in water

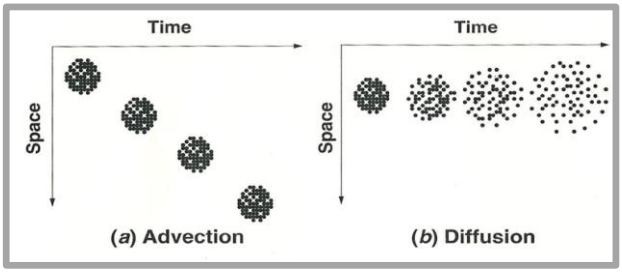

Figure .1: Transport of contaminant in water: (a) advection and (b) diffusion (Chapra, 1997).

Within the water body itself, the possible mode of transportation of contaminants include: advection, diffusion and dispersion

Advection occurs when contaminants moves as a result of fluid motion but the Contaminant concentration remains unchanged. Chapra, (1997) defines advection as a flow that is unidirectional and does not change the identity of the substances been transported. Basic example of advection is the downstream transport of a contaminant (1) In a river (2) Through conduit. Diffusion occurs when a contaminant is transported along a concentration gradient from a region of high concentration towards a region of lower concentration (Tchobanoglous and Schroeder, 1987). Diffusion transport occurs because of random mixing of motions in the water. Diffusion can be model by using Fick's First law

Fick's law shows that the mass flux is proportional to the rate of change of the concentration of the contaminants. The diffusion coefficient is used to quantify the rate of diffusion process. Therefore, if little or no mixing or turbulence occurs in a water body, the diffusion coefficient will be low. On the other hand, if mechanical mixers are present in water body the diffusion coefficient would be high (Chapra, 1997).

Dispersion is the third possible mode of transport within a water body. Dispersion is related to diffusion in that it will mix a contaminant in water body. However, whereas diffusion mixers contaminants in water is due to random motion in the water over time (i.e. wind, wave and turbulence), dispersion mixes contaminants due to velocity difference in a given space (Chapra, 1997). Figure 2 shows an example of dispersion in a pipe.

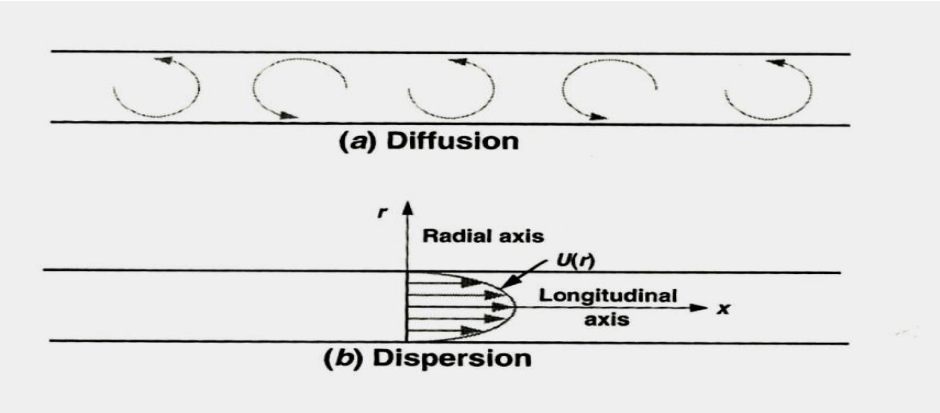

Figure.2: Contrast between (a) diffusion and (b)dispersion. Diffusion is caused by random motion over time; dispersion is caused by differential movement of water over a space (Chapra,1997*)*.

The velocity near the walls of the pipe is less than the velocities in the center of the pipe. The difference in these velocities results in a gradual mixing of water along the axis of the pipe. The figure also demonstrates diffusive mixing, which is completely random in nature.

The following points stated below highlights the aims and objectives of the research work such as: to develop a mathematical model that can monitor and predict the rate

of turbidity, total dissolved solid and total suspended solid diffusion in stagnant water, to investigate 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.

Relevance of study: 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.

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 conveying the samples to the department of Pure and Applied Chemistry, Niger Delta University for examination and analysis. Experimental methods to be carried out includes: physiochemical analysis on reliability or 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, $t+\Delta t$		Rate of mass input into the controlled volume at time, $t+\Delta t$	+	Rate of mass disappearance due to chemical reaction in controlled	+	Rate of mass accumulation within the controlled volume

$M\big|_t = M\big|_{t+\Delta t} + \Delta t(\frac{\Delta M}{\Delta t})_{Tr} + \Delta t(\frac{\Delta M}{\Delta t})_P + \Delta t(\frac{\Delta M}{\Delta t})_S$ (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., $(\frac{\Delta M}{\Delta t})_{Tr}$= change in volume element by transport., $(\frac{\Delta M}{\Delta t})_P$= change in volume element by physical, (bio)chemical or biological process and $(\frac{\Delta M}{\Delta t})_S$= 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;

$\frac{M|_t - M|_{t+\Delta t}}{\Delta t} = (\frac{\Delta M}{\Delta t})_{Tr} + (\frac{\Delta M}{\Delta t})_p + (\frac{\Delta M}{\Delta t})_s$ (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.

$T_{y0}^A = V_{y0} \times A \times C_{y0}$ (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 $x_0$times the surface area A.

Letting D_{y0} $(^{L^2}/_T)$, be the dispersion or diffusion coefficient at site y_0.

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

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

$(\frac{\Delta M}{\Delta t})_{Tr} = [V_{y0}C_{y0} - D_{y0} \times A \times \frac{\partial c}{\partial y}\big|_{y=y0}] \times A$ (6)

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

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

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

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

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=AyΔy), result in a one dimensional equation as shown below

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

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

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

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

Equation (13) can be expressed as

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

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,

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

Experimental Procedures

Experimental Method

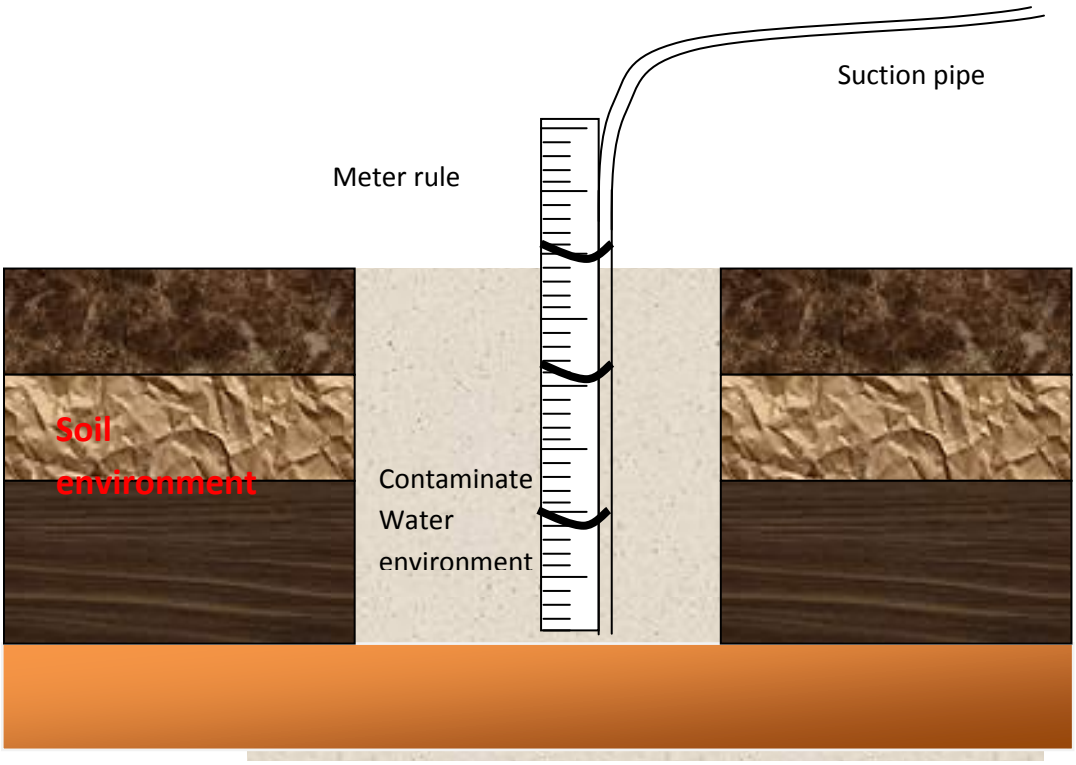

Fig.2a: Experimental Set-up to investigate the diffusion process of effluent contaminant in water environment.

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: TDS/Turbidity meter, Burette and Pipettes, Beaker 10ml and 250ml, volumetric flask 50, 100, 250ml and 500ml

Determination of Nitrate (NO_3^-)

The wagtech water kit was used to determine the anions namely NO_3 , NO_2^- , SO_4 and chlorides.

The appropriate tablet is grinded and dissolved in 10ml sample. Left to stand for ten minutes (10min) and read at the appropriate wavelength on the wagtech spectrophotometer 5000. The reading is read from a table supplied by the company.

Determination of Sulfate (SO_4)

100ml of sample was placed into a 250ml conical flask. 5ml of conditioning reagent was added and mixed properly. A spatula full of Barium Chloride was added and stirred with magnetic stirrer. The solution then poured in a measuring cell. The spectrophotometer was set 425nm. Absorbance values were taken and read off from the calibration curve which has been previously done using standard sulphate solutions.

Results and Discussions

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 nitrate and sulphate.

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

Parameters	**units**	**Depth (cm)**					**WHO Standard**
		0	**15**	**30**	**45**	**60**	
Nitrate (NO_3^-)	mg/L	0.218	0.289	0.236	0.307	0.226	10.0
Sulfate(SO_4^-)	mg/L	5.36	5.70	4.65	7.54	4.38	250

Table 2: Comparison of Experimental, Theoretical, and Validated Model for Nitrate (NO_3) Concentration.

Depth (cm)	NO_3^-(Experimented)	NO_3^-(Theoretical)	NO_3^-(Validated)
0.00	0.22	0.23	0.25
15.00	0.29	0.27	0.25
30.00	0.24	0.28	0.25
45.00	0.31	0.27	0.25
60.00	0.23	0.24	0.25

Table 3: Comparison of Experimental, Theoretical, and Validated Sulfate (SO_4^-) concentration

Depth (cm)	SO_4^-(Experimented)	SO_4^-(Theoretical)	SO_4^-(Validated)
0.00	5.36	5.11	5.55
15.00	5.70	5.76	5.55
30.00	4.65	5.96	5.55
45.00	7.54	5.74	5.55
60.00	4.38	5.07	5.55

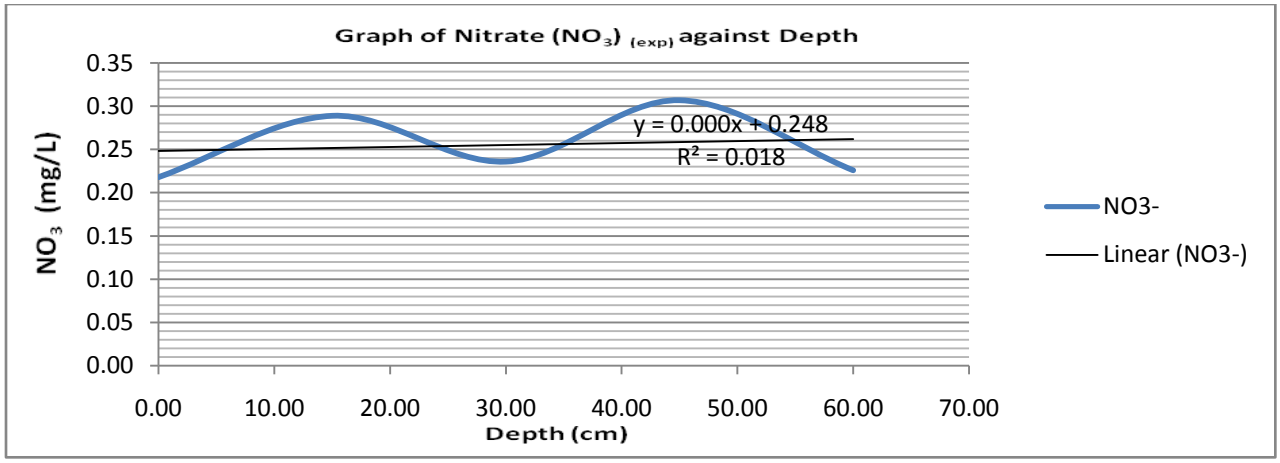

Figure 3: Graph of Experimental Nitrate concentration against Depth.

Figure 3 shows the result obtained for the plot of experimental Nitrate concentration of contaminated stagnant water against the depth. The graph is sinusoidal with a polynomial equation presented as Y= 0.000X+0.248, with a coefficient of determination of R^2= 0.018. The polynomial equation can also be presented as $C_{N03(val)}$=0.000X+0.248. The developed model is given as $C_{N03(theo)}$= -0.0000546D^2+0.00345D+0.2262.

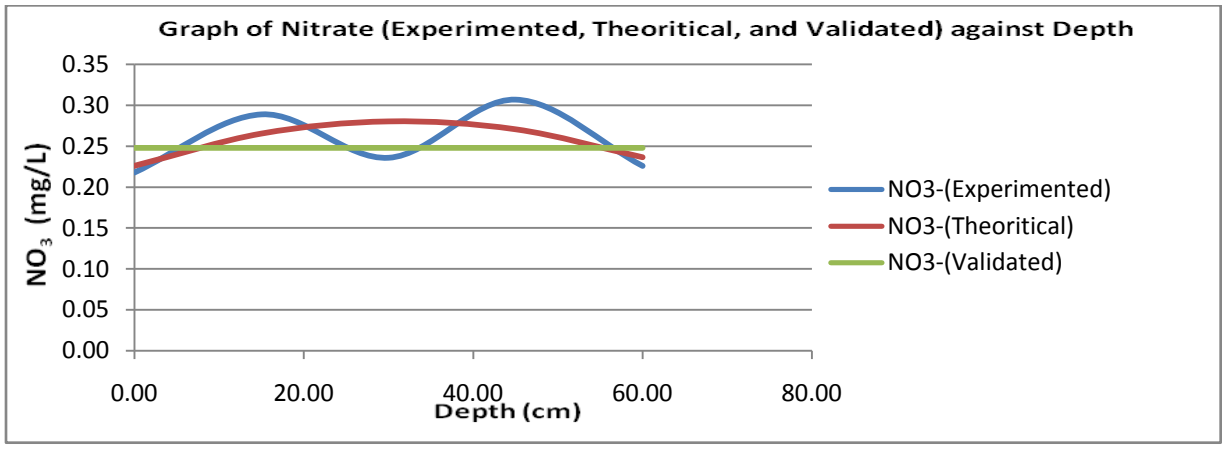

Figure 4: Graph of Experimental, Theoretical, and Validated Nitrate (NO_3^-) concentration against Depth.

Figure 4 is the relationship obtained for the experimental, theoretical, and validated model. The relationship presents a good match which indicates the reliability of the developed model when compared with the experimental model. Points of intersection were obtained for the three models at various concentrations such as 0.25mg/l.

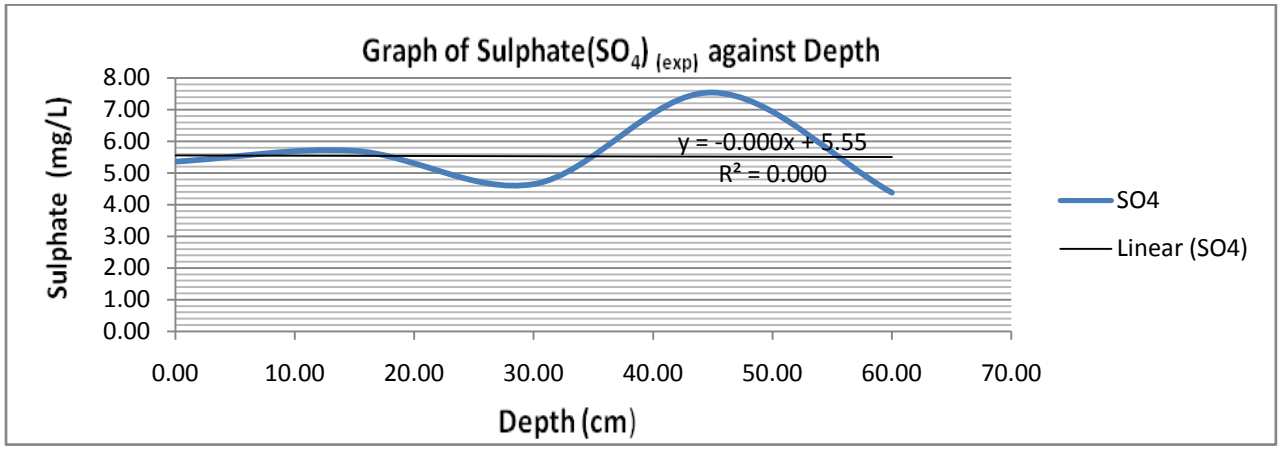

Figure 5: Graph of experimental Sulphate concentration against the Depth of water.

Figure 5 describe the relationship of the experimental sulphate concentration of contaminated stagnant water with the depth. The result shows a rise and fall in sulphate concentration as the depth of water increases. The polynomial of the curve is expressed as $C_{sul(val)}$ = 0.000D + 5.55, while the expression for the developed model is

$C_{sul(theo)}$= - 0.00097D^2 + 0.0575D +5.1129.

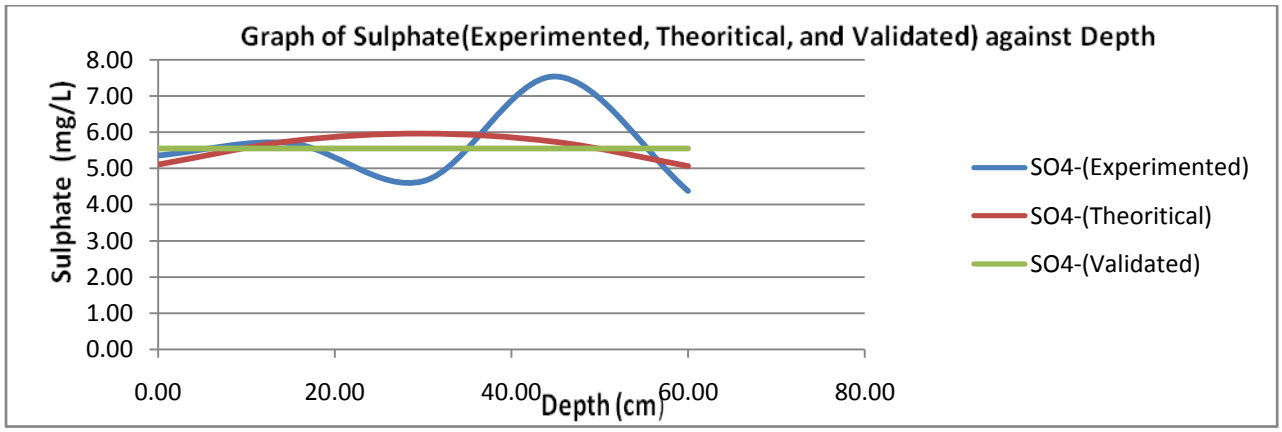

Figure 6: Graph of Experimental, Theoretical, and Validated sulphate (SO_4) concentration against Depth.

Figure 6 is a display of the relationship of the experimental, theoretical, and validated sulphate concentration of contaminated stagnant water with the depth. The theoretical model value shows a good relationship when compared with the experimental value. Point of intersection can be seen for the theoretical and validated model at the depth of 12cm and 52cm where the concentration is 55mg/l.

Conclusion

The following conclusion can be drawn from the research work:

a) The nitrate concentrations present an undulating behavior with increase in the depth of water, which can be accounted for by the dilution factor as well as the degree of deposition and diffusion of contaminant. The point of intersection obtained for the three models present a good relationship which indicates the reliability of the developed model.
b) The sulphate concentration was low at the surface and the increases and thereafter decreases. This implies no significant diffusion takes place.
c) Increase in bicarbonate concentration down the depth of water is as a result of the diffusion of contaminant from the surface to the subsurface.

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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