

Metal Diffusion in Stagnant Water Environment in Niger Delta Area of Nigeria

C.P. Ukpaka

Department of Chemical/Petrochemical Engineering
Rivers State University of Science and Technology Nkpolu PMB 5080,
Port Harcourt, Nigeria
Email: chukwuemeka24@yahoo.com

Abstract – The diffusion of metals concentration in a stagnant water environment was monitored using experimental and theoretical approach. The model developed was 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. Experimental data obtained from the analysis were fitted into the model to obtain their diffusivities and velocities of the metals concentration upon the influence of contaminants diffusion in the stagnant water system. Metals concentrations of the contaminants in the stagnant water system 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 metals concentration in a stagnant water environment.

Keywords – Diffusion, Environment, Metal Niger Delta Area, Nigeria, Stagnant Water.

I. INTRODUCTION

Diffusion occurs when a contaminant is transported along a concentration gradient from a region of high concentration towards a region of lower concentration [1]-[14]. Diffusion transport occurs because of random mixing of motions in the water as well in this case 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 [6]- [12].

Study on modeling of water treatment processes using linear and nonlinear modeling methods to model residual aluminum and turbidity in treated water, using both laboratory and data as input variables [4]-[13]. At the first stage, variables were selected using multiple linear regressions and a sequential forward search. The data were divided into two subsets: a training subset comprising of the total number of samples, to be used for training the model, and a validation data set consisting of the remaining of the samples, to be used as an independent means of testing the model. The first eight variables that improved the performance of the model most were finally chosen, because in practice the models did not seem to improve beyond this point.

Next, variables were selected using multiple linear regression (MLR) network with a back-propagation algorithm and a sequential forward search. The data were divided into three subsets: a training subset, comprising of the total number of samples, to be used for training the

network, of which a test subset containing 20% of the training data was reserved for back-propagation error calculations and a validation data set, consisting of the remaining of the samples, to be used as an independent means of testing the model.

The artificial neural network consisted of the process parameters as inputs, one hidden layer with 5 neurons and the output neuron describing the predicted variable. The parameters of the neural network and the training algorithm were determined experimentally. The radial basis (radbas) transfer function was used for the hidden layer and the linear (purelin) transfer function for the output layer. The Bayesian regularization back-propagation (trainbr) algorithm was exploited in training, and the sum squared error (sse) as the error function in training. Matlab (version 7.11) software with the Neural Network Toolbox (version 7.0) was used for the data processing.

Research conducted revealed that in both cases (linear and nonlinear), the goodness of the nonlinear model was slightly better than that of the linear one, which would indicate that both problems have some nonlinear features. On the other hand, the improvement in the goodness of the model is not great, which seems to suggest that simpler computational methods may be applicable to these problems.

As for turbidity, the results showed that the linear model is able to predict the generic trend, whereas the majority of the peaks are modeled better by Multilayer perceptrons (MLPs). It seems, however, that the reasons for some of the sharp peaks remain obscure regardless of the method used. In particular, the F-test test did not show any significant difference between the linear and nonlinear model. Overall, it is reasonable to use the linear method if the objective is only to reveal generic trends and the

nonlinear one if the objective is to predict the extreme values as accurately as possible. In addition, multilinear regressions (MLR) is more suitable for applications which require explicit models or fast calculation, for example, in adaptive soft sensors. Conversely, slightly better models can be achieved for residual aluminum. In fact, the fit of the nonlinear model for aluminum (approximately 0.7-0.9) is very good. Besides producing more accurate estimates, multilayer perceptrons (MLPs) also seems to be superior to the linear method because it is able to predict both the generic trend and the concentration peaks, whereas the linear method cannot find the reasons for the peaks. In addition, the F-test showed a statistically significant difference between the models. Multilayer perceptrons (MLPs) may, therefore, be regarded as the preferable method for modeling residual aluminum [6]-[13].

Relevance of study includes 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.

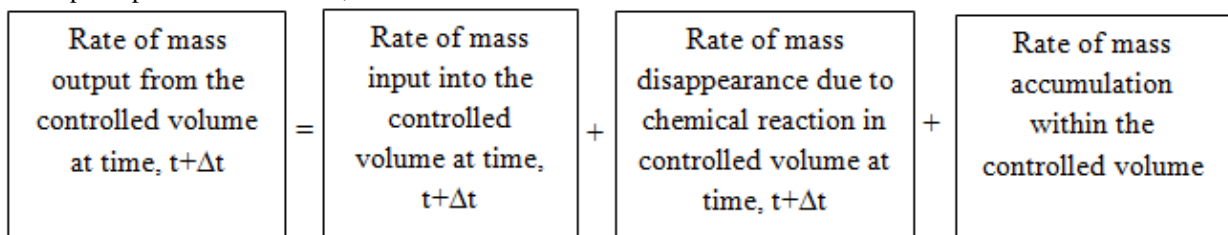
II. MATERIALS AND METHODS

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;

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

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, $T_{y_0}^A (M/T)$ of a constituent at site x_0 is the product of the average water velocity, $V_{y_0} (L/T)$, 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.

$$T_{y_0}^A = V_{y_0} \times A \times C_{y_0} \quad (3)$$

Dispersive Transport

The dispersive transport, $T_{y_0}^D (M/T)$, 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 $D_{y_0} (L^2/T)$, be the dispersion or diffusion coefficient at site y_0 .

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

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.

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

Mass Transport by Advection and Dispersion

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

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

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

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

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

$$\begin{aligned} \frac{[[M|]_t - M|]_{t+\Delta t}}{\Delta t} &= A_{y_0} V_{y_0} C_{y_0} - \\ &A_{y_0 + \Delta y} V_{y_0 + \Delta y} C_{y_0 + \Delta y} + D_{y_0 + \Delta y} A_{y_0 + \Delta y} \frac{\partial C}{\partial y} |_{y_0 + \Delta y} - D_{y_0} A_{y_0} \frac{\partial C}{\partial y} |_{y_0} \\ &- \left(\frac{\Delta M}{\Delta t} \right)_p + \left(\frac{\Delta M}{\Delta t} \right)_s \end{aligned} \quad (8)$$

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

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

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 $(V = A_y \Delta y)$, result in a one dimensional equation as shown below

$$\begin{aligned} \frac{[[C|]_t - C|]_{t+\Delta t}}{\Delta t} &= \frac{D_{y_0 + \Delta y} \left[\frac{\partial C}{\partial y} \right]_{y_0 + \Delta y}}{\Delta y} + \\ &\frac{V_{y_0} C_{y_0} - V_{y_0 + \Delta y} C_{y_0 + \Delta y}}{\Delta y} - k_p \end{aligned} \quad (10)$$

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,

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

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 metals concentration,

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

Experimental Procedures

Experimental Method

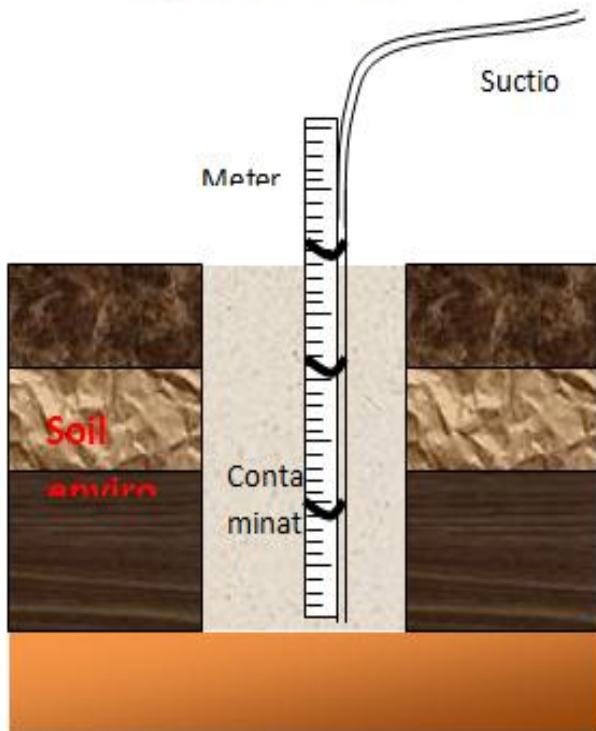


Fig.1. Experimental Set-up to investigate the diffusion process of effluent contaminant in water environment.

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 AAcollection 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 10“ml” and 250“ml”, volumetric flask 50, 100, 250“ml” and 500“ml”

Atomic Absorption Spectrometry

The metal ions Cd , Zn , Pb , Cr , Fe , and “Mn” were analyzed using the Atomic Absorption Spectrometer. Samples were acid-digested in the fume hood (fume cupboard), diluted with dissolved water, filtered and sent to the central research laboratory for AAS analysis.

III. 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 metals concentration

Table I: Experimental determination of physiochemical parameters with respect to depth

Parameters	units	Depth (cm)					WHO Standard
		0	15	30	45	60	
Cadmium (Cd)	“mg/L”	0.002	0.02	0.01	0.002	0.02	0.003
Zinc (Zn)	“mg/L”	0.26	0.38	0.24	0.28	0.34	3.00
Chromium(Cr)	“mg/L”	0.028	0.034	0.030	0.024	0.032	0.05
Iron(Fe)	“mg/L”	3.30	3.85	3.20	3.38	3.46	
Manganese (“Mn”)	“mg/L”	0.032	0.036	0.034	0.031	0.035	0.50

Table II: Comparison of experimental, theoretical, and validated model for Cadmium (Cd) concentration.

Depth (“cm”)	Cd(Experimented)	Cd(Theoretical)	Cd(Validated)
0.00	0.00	0.01	0.01
15.00	0.02	0.01	0.01
30.00	0.01	0.01	0.01
45.00	0.00	0.01	0.01
60.00	0.02	0.01	0.01

Table III: Comparison of Experimental, Theoretical, and Validated Zinc concentration.

Depth (“cm”)	Zn(Experimented)	Zn(Theoretical)	Zn(Validated)
0.000	0.260	0.296	0.288
15.000	0.380	0.291	0.288
30.000	0.240	0.294	0.288
45.000	0.280	0.306	0.288
60.000	0.340	0.327	0.288

Table IV: Comparison of Experimental, Theoretical, and Validated Lead (Pb) concentration against depth.

Depth	Pb(Experimented)	Pb(Theoretical)	Pb(Validated)
0.000	0.001	0.001	0.001
15.000	0.002	0.001	0.001
30.000	0.002	0.001	0.001
45.000	0.000	0.001	0.001
60.000	0.002	0.001	0.001

Table V: Comparison of Experimental, Theoretical, and Validated Chromium (Cr) concentration against depth.

Depth ("cm")	Cr (Experimented)	Cr (Theoretical)	Cr (Validated)
0.000	0.028	0.030	0.030
15.000	0.034	0.030	0.030
30.000	0.030	0.029	0.030
45.000	0.024	0.029	0.030
60.000	0.032	0.029	0.031

Table VI: Comparison of Experimental, Theoretical, and Validated Iron (Fe) concentration against depth.

Depth ("cm")	Fe (Experimented)	Fe (Theoretical)	Fe (Validated)
0.000	3.300	3.441	3.468
15.000	3.850	3.458	3.483
30.000	3.200	3.474	3.498
45.000	3.380	3.491	3.513
60.000	3.460	3.507	3.528

Table VII: Comparison of Experimental, Theoretical, and Validated Manganese ("Mn") concentration against depth

Depth	Mn(Experimented)	Mn(Theoretical)	Mn(Validated)
0.000	0.320	0.288	0.206
15.000	0.036	0.111	0.161
30.000	0.034	0.024	0.116
45.000	0.031	0.027	0.071
60.000	0.035	0.120	0.026

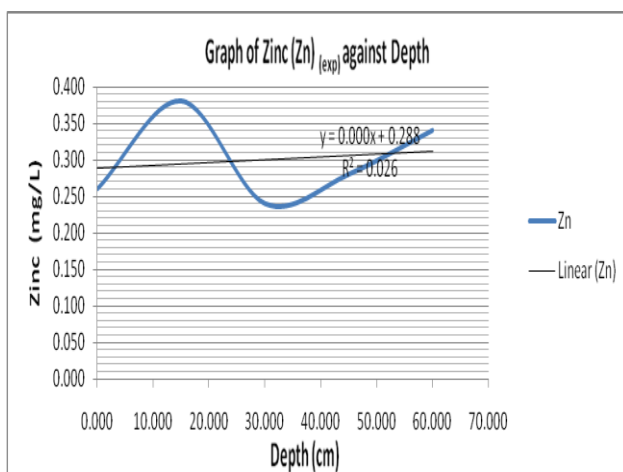


Fig.II. Graph of experimental Zinc concentration against the Depth of water.

The plot of the graph in Figure II describes the relationship of the experimental zinc concentration with respect to the depth of water. The undulating nature of the graph may be attributed to the increase and decrease in the concentration of zinc due to

dilution factor, the rate of contaminant deposition and diffusion at the various depth of water. The polynomial of the curve is given as $C_{Zn(val)} = 0.000D + 0.288$, the coefficient of determination is $R^2 = 0.026$. The developed model is expressed as $C_{Zn(theo)} = 0.0000D^2 - 0.00074D + 0.2966$

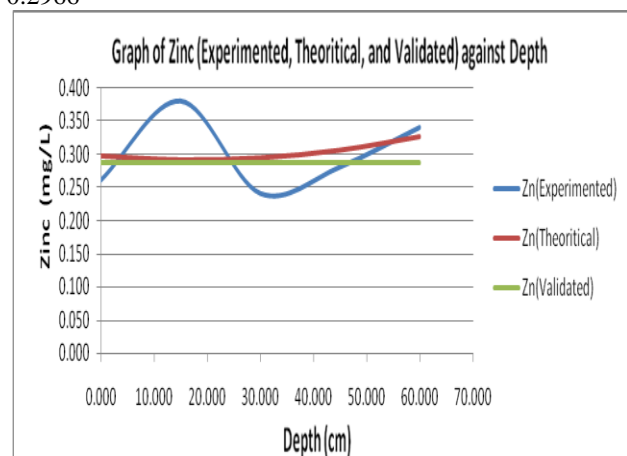


Fig.III. Graph of Experimental, Theoretical, and Validated Zinc concentration against Depth of water.

Figure III illustrate the relationship of the experimental, theoretical and validated model. The relationship shows a good match for the theoretical and validated model up to the depth of 30“cm” indicating that the model can be used to predict the zinc content in contaminated stagnant water.

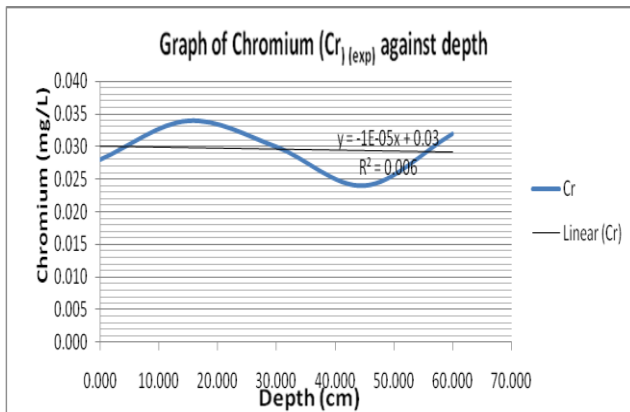


Fig.IV. Graph of experimental Chromium concentration against the Depth of water.

Figure IV above shows a rise and fall in Chromium concentration as the depth of water increases. This behavior may be due to dilution factor, variation in depth as well as the rate of deposition and diffusion. The polynomial of the curve is given as $Y = -1E-05X + 0.03$, which can also be expressed as $C_{Cr(val)} = -1E-05X + 0.03$, with a coefficient of determination of $R^2 = 2E-28$. The theoretical developed model is given as $C_{Cr(theo)} = 0.0000006D^2 - 0.00005D + 0.0303$.

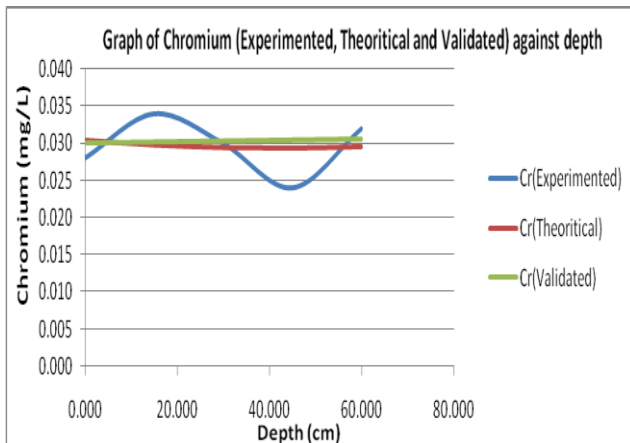


Fig.V. Graph of Experimental, Theoretical, and Validated Chromium concentration against Depth of water.

The Figure V above is a display of the experimental, theoretical, and validated chromium concentration with respect to the depth of water. Points of intersection are obtained at various points on the graph for the three models indicating a good match and reliability of the developed model.

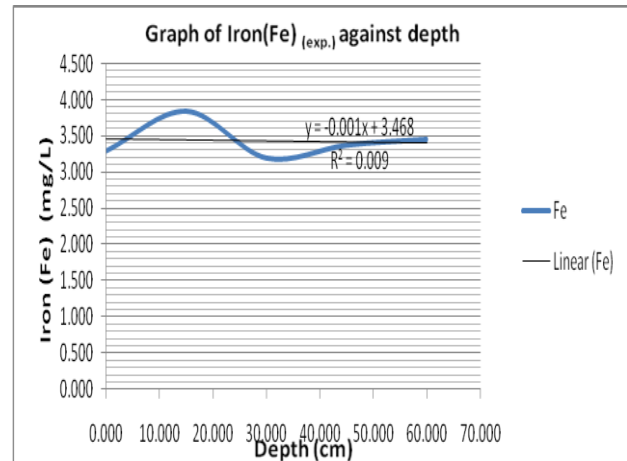


Fig.VI. Graph of experimental iron (Fe) concentration against the Depth of water.

The graph shows a rise in concentration of iron to a depth of 18cm and then starts to drop and again rises after attaining a depth of 30cm. the polynomial of the curve is $Y = 0.001D + 3.468$, with a coefficient of determination of $R^2 = 0.009$. the theoretical developed model is expressed as $C_{Fe(val)} = -0.00003D^2 + 0.0011D + 3.4523$.

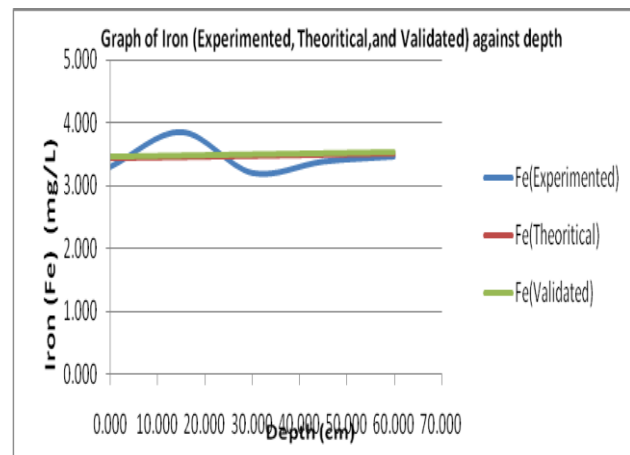


Fig.VII. Graph of Experimental, Theoretical, and Validated Iron (Fe) concentration against Depth of water.

The graph above illustrates the relationship of the experimental, theoretical, and validated model for Iron concentration with respect to the depth of water. The graph presents a good match of the theoretical and validated model which indicates the reliability of the model for predicting the diffusion of iron in contaminated in water environment.

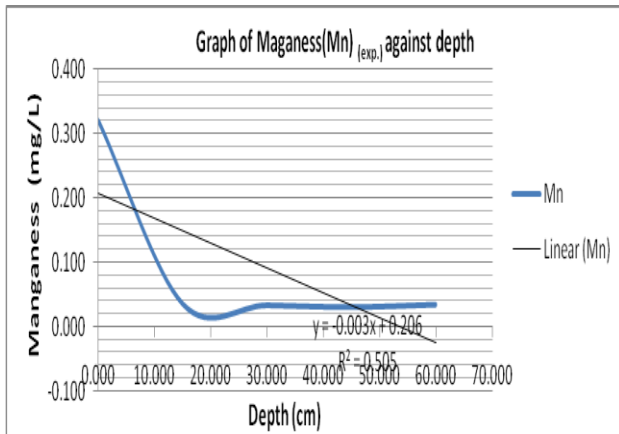


Fig.VIII. Graph of experimental Manganese (“Mn”) concentration against the Depth of water.5

Figure VIII above shows that the experimental Manganese concentration value is higher at the surface and gradually reduces as the depth of water increases. The polynomial of the curve is displayed as $C_{Mn(val)} = -0.003D + 0.206$ and the coefficient of determination is given as $R^2 = 0.505$. The theoretical developed model for manganese is given as $C_{Mn(theo)} = 0.0002D^2 - 0.0148D + 0.2883$.

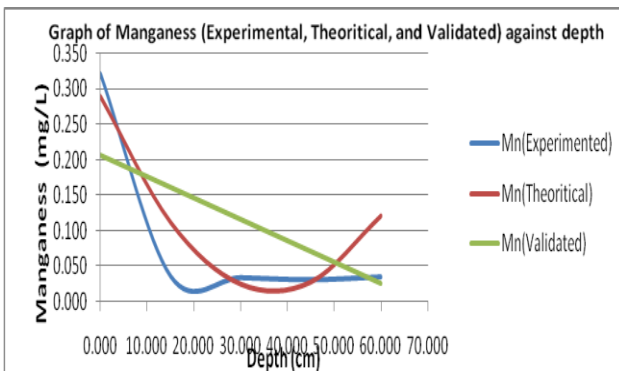


Fig.IX. Graph of Experimental, Theoretical, and Validated Manganese (“Mn”) concentration against Depth of water.

Figure IX illustrate the relationship between the Experimental, Theoretical, and Validated model for Manganese concentration plotted against Depth of water. It is seen that there is a good match up to a depth of 50“cm”. The theoretical model values show a good relationship compared with the experimental values. Increase in Manganese concentration was observed latter on for both experimental and the theoretical model.

IV. CONCLUSION

The following conclusion can be drawn from the research work:

a) The rise in zinc concentration can be attributed to movement of contaminant from the surface to the subsurface water body. The drop in concentration may be due to variation in depth.

b) The sinusoidal nature of chromium concentration can be attributed to the dilution factor as well as the degree of deposition and diffusion. The relationship displayed by the three models is an indication of the reliability of the developed model.

c) The increase and decrease in experimental iron concentration is due to dilution factor and the degree of migration of contaminant.

d) The concentration of manganese was high at the surface and decreases gradually as the depth of water increases. This implies that there was no significant diffusion of contaminant taking place. 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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AUTHOR'S PROFILE



Dr. C.P. Ukpaka

I am Emgr. Dr. C.P. Ukpaka, I was born on 24th December 1969 from the family of Ukpaka in Obite town of Ogba/Egbema/Ndoni Local Government Area of Rivers State of Nigeria. I attended Obite Community Primary School and obtained FSLC and further attended

Government Secondary School Emelego in Abua/Odual Local Government Area of Rivers State where I obtained my WASC in 1991. I attended Rivers State University of Science and Technology Nkpolu Port Harcourt where I obtained my B.Tech (2000), M.Tech (2004) and Ph.D (2009).

I am current a Senior Lecturer in the Department of Chemical/Petrochemical Engineering in the Faculty of Engineering, Rivers State University of Science and Technology Nkpolu, Port Harcourt. I have published more than 230 articles both local and foreign (majority of the articles are online. He is also a member of some professional bodies such member of Nigerian Society of Engineers (MNSE), Member of Nigeria Society of (MNSChE), member of COREN, Fellow of SINDRH etc and he has also held several positions in the professional bodies as well in the University.