MATHEMATICAL MODELLING OF PHYSIOCHEMICAL PROPERTIES OF A WASTEWATER TREATMENT PLANT

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ABSTRACT

The mathematical modelling and simulation of the physiochemical properties of a typical wastewater plant with the aim of increasing fundamental knowledge of the treatment system is the hallmark of this paper. To achieve this, a mathematical model was developed based on the theoretical relationship between the properties of the plant and the experimental data obtained over two-year period (2000 and 2001). The developed model is: TH=-0.033+347.738pH-1149.4/T+0.26221TAC-0.0086Cl$^-$. Correlation of the model obtained with that of the experiment gave 0.79. Comparing the operating parameter of the treatment plant with the Federal Environmental Protection Agency (FEPA) standards, it was discovered that the parameters were within the standard. Thus the developed model could be used as a tool for monitoring and controlling environmental pollution.

INTRODUCTION

Water is the most important natural resources It is a basic necessity to man, animals and plants without which life on earth would have been impossible and agricultural and industrial activities would not have been in existence, water may be said to be the single most dominant factor in settlement, civilization and growth of ancient empires and kingdoms (Perry and Green, 1997; McGhee, 1991; Stirlon, 1971). The dumping of domestic or industrial waste in them pollutes water bodies. Lack of planning for population growth in cities has led to severe violation of environmental law thereby causing pollution of the nearest water course.

Wastewaters from our homes and industries are collectively called sewage. Domestic waste water results from the use of water in dwelling of all types, and include both water after use and the various waste materials added. Industrial wastewater could be the contaminated water from an industry by industrial waste or the dumping of industrial toxic waste into a watercourse. Industries also use water for cooling of industrial plants, which they send into water bodies at high temperature thereby upsetting the ecological balance of the waterway to pose a threat to nature life forms (Rao, 1991; Eckenfelder, 1989; White, 1987; Kovac, 1985; Lohani, 1978). A wastewater treatment plant is a process plant established for the basic aim of treating the wastewater from houses (residential), office complexes and industries. A sewage treatment plant is established to reduce the danger posed by untreated sewage to our communities (Tochobanoglous and Burton, 1991; Horan, 1990; Metcalf and Eddy, 1972; Fair et-al, 1968). Thus the objectives of this paper are to propose a mathematical model which could be used to predict the total hardness of a given wastewater plant as functions of other parameters. This is to serve as a tool of monitoring and controlling environmental pollution.

EXPERIMENTAL METHODOLOGY

Measurement of pH

The electrode is placed in a buffer solution to maintain its pH at the neutral point. The electrode was washed with distilled water before dipping into the sample to be analysed. The values displayed on a digital display screen were allowed to stabilize at a constant value before the pH was taken.

Measurement of Total Hardness

The measuring cylinder was filled to the 50ml mark with the sample to be tested. The sample was then transferred to the conical flask. 20 drops of TH buffer solution was then added and the mixture stirred. 4 drops of erichrome' black T indicator was also added and was stirred to mix. The EDTA solution was then added drop by drop and the mixture stirred to mix continuously as the solution was added. The EDTA solution was added until the mixture changed from purple to blue. The result of the total hardness in (mg/l) was then calculated by multiplying the number of drops of EDTA used by MF where MF is the multiplication factor calculated using the concentration of the EDTA (Solomon, 1989; Nikolodze et-al, 1989).

Measurement of Total Alkalinity Content (TAC)

A measuring cylinder was filled to the 50ml mark with the sample to be tested. The measured sample was then transferred to a conical flask. 4 drops of phenolphthalein was added after which H_2SO_4 was added drop by drop while stirring until the colour changed from purple to colourless. The drops counts were recorded as phenolphthalein alkalinity. 4 drops of methyl orange was then added and stirred. H_2SO_4 was then added while stirring until the colour changed from yellow to orange. The drop count was recorded as methyl orange alkalinity.

Phenolphthalein alkalinity = drop counts of H_2SO_4 added x MF

Methyl orange alkalinity = drop counts of H_2SO_4 added x MF

TAC = Phenolphthalein alkalinity + methyl orange alkalinity

MF was found by standardizing H_2SO_4 using Na_2SO_4 and NaOH solution.

Measurement of Chloride

The measuring cylinder was filled with the sample up to the 50ml mark. The content of the measuring cylinder was transferred to a conical flask. 1 to 2 drops of phenolphthalein was added and stirred and if there were colour changes, oxalic acid was added drop by drop until the colour disappeared. But in the case where there was no colour change $K_2Cr_7O_4$ was added straight without oxalic at first. The mixture was stirred; $AgNO_3$ was then added drop by drop while stirring until the colour changed from yellow to brick red.

Chloride (Cl^-, mg/l) = Number of drop of $AgNO_3$ added x MF

MF was found from $AgNO_3$ usng NaCl solute.

CONCEPTUALISATION OF MODELLING TECHNIQUES

Modelling for Total Hardness (TH)

Hardness is caused by divalent metallic cations of which calcium and magnesium are the principal ions. The cations are normally associated with some anions (Sawyer and McCarthy, 1989). The most important anions with which they are associated are HCO_3^-, SO_4^{2-}, Cl^-, NO_3^- and SiO_3^{2-}. The solubility of hardness causing compounds (mostly salts of Ca^{2+} and Mg^{2+}) in water depends on some physical and chemical parameters of the water, which include temperature, pH, and total alkalinity content (Odigure and Adeniyi, 2002; Karapetyant and Drakin, 1981). For a fixed set of condition, the total hardness of wastewater is a function of temperature, pH, total alkalinity content and concentration of the anion associated with hardness.

$$TH = \text{constant} = k$$

Where TH is the total hardness of the wastewater in mg/l. Assuming that the operating parameters (T, pH, TAC, Cl) have an independent and cumulative effect on k.

Influence of pH

According to American Society of Civil Engineers (1990), water softening and in particular high pH lime treatment has been shown to be effective in removing a number of heavy metals associated with hardness. The removal of these metals tends to increase with increasing pH. This means that the total hardness reduces with increasing pH (ASCE, 1990).

TH α 1/pH

TH = $\underline{k_1}$ / pH (1)

Influence of temperature

Two types of hardness are namely carbonate and bi-carbonate hardness (Sawyer and McCarthy, 1989). Carbonate hardness is the part of total hardness associated with carbonate and bicarbonate ions. This portion of hardness precipitates out at elevated temperature as obtained in boilers.

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + H_2O$$

This form of hardness Sawyer and McCarthy (1989) called temporary hardness can be removed at elevated temperature, then total hardness can be said to reduce with increasing temperature and given by:

TH α 1/T

TH=K_2/pH (2)

Where T = Temperature in °C, K_2 = constant

Influence of Total Alkalinity Content

Alkalinity in sewage is due to presence of hydroxides, carbonates and bicarbonate of metals such as magnesium, calcium, sodium, potassium and so on (Metcalf and eddy, 1972). Of these calcium and magnesium bicarbonate are most common. According to the American Society of Civil Engineer (1990), carbonate hardness is the portion of the total hardness which is present in the form of bicarbonate and carbonate salt of calcium, magnesium and some other metals. The higher the concentration of bicarbonates and carbonates salt in a water samples the higher the possibility of having a bicarbonate and carbonate salt of calcium and magnesium. This means that the higher the alkalinity the higher the hardness (Imre, 1996; James, 1973). With the above, it can be deduced that the total hardness is directly proportional to alkalinity. TH and alkalinity (TAC) introducing a constant of proportionality K gives

TH = K_3TAC (3)

Where TAC = Total Alkalinity Content (mg/l).

Influence of Chloride

The American Society of Civil Engineers (1990) suggested that total hardness can be differentiated into carbonate and non-carbonate hardness. Non-carbonate hardness is caused by anion other than carbonates and bicarbonate like Cl^-, NO_3^- and SO_4^{2-}. This implies that the more the concentration of chloride salt as Mg^{2-} and Ca^{2+} and other heavy metals associated with hardness, the higher the non carbonate hardness. Therefore it can be said that,

TH α Cl^-

Introducing a constant gives;

TH=K_4Cl^- (4)

Since the four parameters above are not the only parameters, which affect total hardness, a constant K_0 is introduced to account for the influence of the other parameters. Also assuming that the individual parameters have independent and cumulative influence on total hardness, the following model is thus proposed

$$TH = K_0 + K_1/pH + K_2/T + K_3TAC + K_4Cl^- \quad (5)$$

Where TH = total hardness in mg/l, pH = pH, T = Temperature, TAC = Total alkalinity content (mg/l).

Using the least square method of multiple regression (Stroud, 1995), the predicted value of total hardness is given as;

$$TH = K_0 + K_1/pH + K_2/T + K_3TAC + K_4Cl^- \qquad (6)$$

Assuming the errors between the observed and predicted total hardness is e, then;

$$e = (TH - K_0 - K_1/pH - K_2/T - K_3TAC - K_4Cl^-) \qquad (7)$$

Finding the square of the error gives;

$$e^2 = \Sigma(TH - K_0 - K_1/pH - K_2/T - K_3TAC - K_4Cl^-)^2 \qquad (8)$$

For an experimental values of the physiochemical parameters (pH, T, TAC, Cl^-), then

$$ne^2 = \Sigma[(TH - (K_0 + K_1/pH + K_2/T + K_3TAC + K_4Cl^-)]^2 \qquad (9)$$

To minimize the square of the error (ne^2), this is partially differentiated with respect to the constants K_0, K_1, K_2, K_3 and K_4. The differentials are then equated to zero to obtain the following set of equations after rearrangement. We obtain

$$\Sigma TH = K_0 + K_1\Sigma 1/pH + K_2\Sigma 1/T + K_3\Sigma TAC + k_4\Sigma Cl^- \qquad (10$$

$$\Sigma TH/pH = K_0\Sigma 1/pH + K_1\Sigma 1/(pH)^2 + K_2\Sigma 1/TpH + K_3\Sigma TAC/pH + k_4\Sigma Cl^-/pH \qquad (11)$$

$$\Sigma TH/T = K_0\Sigma 1/T + K_1\Sigma 1/TpH + K_2\Sigma 1/(T)^2 + K_3\Sigma TAC/T + k_4\Sigma Cl^-/T \qquad (12)$$

$$\Sigma THTAC = K_0\Sigma TAC + K_1\Sigma TAC/pH + K_2\Sigma TAC/(T)^2 + K_3\Sigma(TAC)^2 + k_4\Sigma TACCl^- \qquad (13)$$

$$\Sigma THCl^- = K_0\Sigma Cl^- + K_1\Sigma Cl^-/pH + K_2\Sigma Cl^-/T + K_3\Sigma TACCl^- + k_4\Sigma(Cl^-)^2 \qquad (14)$$

A visual basic program was developed to calculate the summation and solve the matrix to obtain the constants K_0, K_1, K_2, K_3 and K_4 based on data for treated effluent. The constants were obtained and the proposed model is given as;

$$TH = -0.033 + 347.768/pH - 149.4/T + 0.2622TAC - 0.0036Cl^- \qquad (15)$$

RESULTS AND DISCUSSION

The results of experimental analysis for the two years under review (2000 and 2001) are presented in Table 1 and 2 while the comparative pH values for the experimental and the developed model are presented in Table 3.

Table 1: Physiochemical properties of wastewater for the year 2000

TH (mg/l)	Temp (°C)	pH	TAC (mg/l)	Cl^- (mg/l)
45	30	7.4	132	23
43	30	7.7	130	18
43	31	6.8	144	21
41	30	7.3	128	21
49	31	7.0	123	18
38	32	7.6	117	18
43	32	7.0	147	18
58	31	7.3	138	18
41	31	7.1	144	18
48	31	7.3	124	18
53	32	7.2	138	16
37	32	6.9	104	14
46	33	7.1	101	24
46	33	7.7	110	16
53	32	7.3	135	23

Table 2: Physiochemical properties of wastewater for the year 2001

TH (mg/l)	Temp (°C)	pH	TAC (mg/l)	Cl^- (mg/l)
34	30	7.4	86	27
31	27	7.3	100	21
24	25	7.6	95	29
48	27	7.1	147	21
38	25	7.0	147	26
34	25	7.2	138	23
34	24	7.3	149	23
35	24	7.4	150	23
35	24	7.0	141	24
32	25	7.0	119	19
41	29	7.2	116	26
43	27	7.3	156	26
41	32	7.3	105	18
32	29	6.9	93	26
32	26	6.9	112	29

Table 3: Comparative pH values for experimental and developed TH (mg/l)

Total hardness for the year 2000 (mg/l)		Total hardness for the year 2001 (mg/l)	
Experimental	Simulated	Experimental	Simulated
45	48.3	34	30.9
43	40.7	31	31.07
43	51.6	24	24.40
41	42.6	48	44.70
49	44.6	38	41.90
38	40.3	34	38.27
43	52.1	34	38.58
58	46.5	35	38.20
41	49.4	35	38.50
48	42.8	32	34.70
53	48.3	41	38.80
37	41.5	43	44.07
46	40.3	41	39.05
46	39.0	32	34.89
53	46.8	32	35.27

The pH values for the effluent ranges from 6.9-8.1 with an average of 7.0 at 25°C. all the pH values of the treated effluent are in conformity with the set standard of 6.5-8.5 set by FEPA. The total alkalinity content (TAC) values for the treated effluent range between 81-194 mg/l with an average yearly value of 121mg/l. It is a known fact that high alkalinity values favour the growth of algae. Algae used up carbon dioxide converting carbonate and bicarbonate to hydroxides and carbonates respectively (Sawyer and McCarthy, 1989; Nikoladze et-al, 1989). This conversion causes an increase in the pH of the water. This implies that high alkalinity values are not good for waste effluent. TAC values between 100-150 are moderately high value which when exceeded will lead to high pH of wastewater. The highest values obtained for treated effluent was 194 mg/l, which exceed the acceptable limit. The average of TAC of 121mg/L is within the acceptable limit.

Wastewater with total hardness (TH) between 0-75mg/l is described as soft while water with TH between 75-150 mg/l is moderately hard (Sawyer and McCarthy, 1989; Karapetyant and Drakin, 1981). The highest TH recorded for treated effluent in year 2000 was 70mg/L. This implies that the treated effluent was soft throughout the year. There are no conventional methods for removing chloride from wastewater. This is because the concentration of chloride ions rarely get out of hard except for places closes to the sea. The concentration of chloride ion was insignificant.

The accuracy of the experimental analysis depends on many factors. These factors include the method of analysis and type of equipment used. Temperature and pH were measured using more reliable equipment such as thermometer and pH meter respectively while TH, TAC and Cl^- were measured using drop count method of analysis, which is not very reliable. Human error is also another factor that could affect the accuracy of the data. The efficiency of the treatment plants depends on how close the parameters of the treated effluent are to the standards temperature, pH, Cl^-, TH and TAC data for the treated effluent are presented in Table 1 and 2. The average yearly temperature for 2001 was 29°C, which conforms to the standard of 30°C set by Federal Environmental Protection Agency (FEPA). Although some individual temperature data exceeded 30°C, they were still within good limits.

The results of the model show that it agrees with the experimental value for some weeks and differ greatly for some other weeks (Fig. 1 and 2). For week 34, an experimental TH of 36 mg/l differs from the model TH by 0.1mg/l while for week 17, an experimental TH of 70 mg/l differs by 15.6 mg/l from the model TH. The correlation of model and experimental was calculated to be 0.791. The accuracy level could have been due to data availability and discrepancy between data. For several weeks data for the independent parameter (pH, T, TAC, Cl^-) were quite close but the TH for these weeks varied greatly. For instance, for weeks 8 and 9, the difference between their total hardness was as high as 17 while pH, T, TAC and Cl^- were the same. These discrepancies could have been due to human error during the experiments. From the model obtained, it was observed that temperature and pH have the greatest influence on the TH of the effluent. Simulation of data for 2001 gave a correlation of 0.746.

CONCLUSION

A model for the prediction of the total hardness as a function of four different parameters of pH, temperature, total alkaline content and chloride has been developed. Parametric coefficients in the model equation obtained showed that the effect of pH and temperature are higher than the others. Results of analysis reveal that the wastewater treatment plant was operating efficiently during the period of study. Simulation results on the TH show various degrees of variations form experimental; the reason attributed to this was human error during experimentation and the constrains imposed during model development. The developed model could be used as a tool for monitoring and controlling environmental pollutions.

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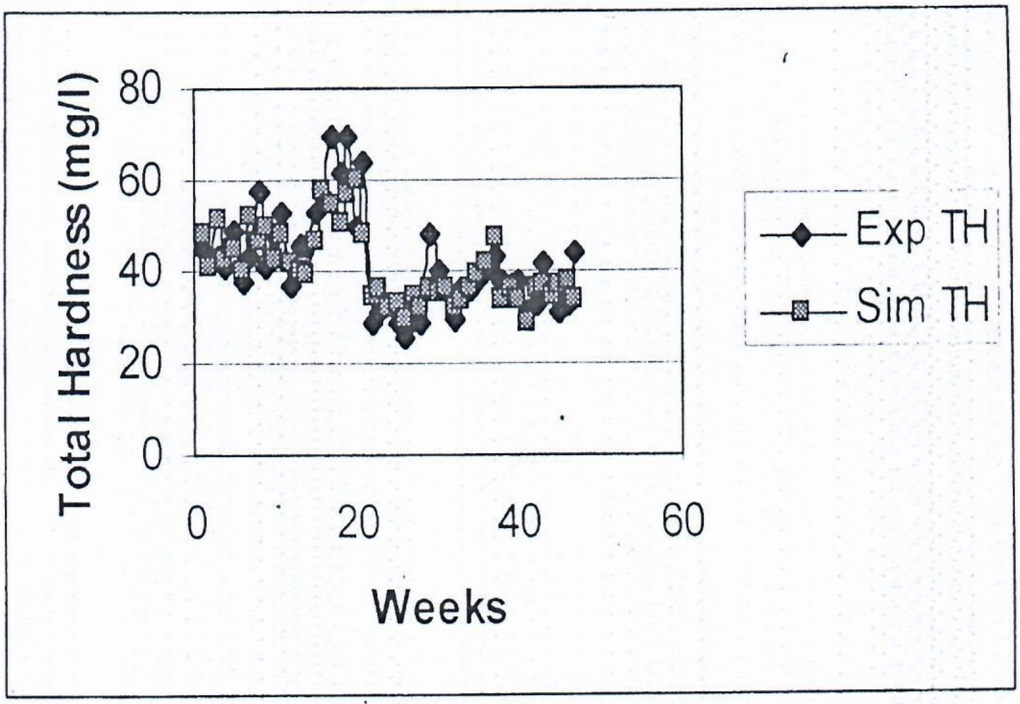

Fig 1: Total hardness versus weeks for experimental and simulation (2000)

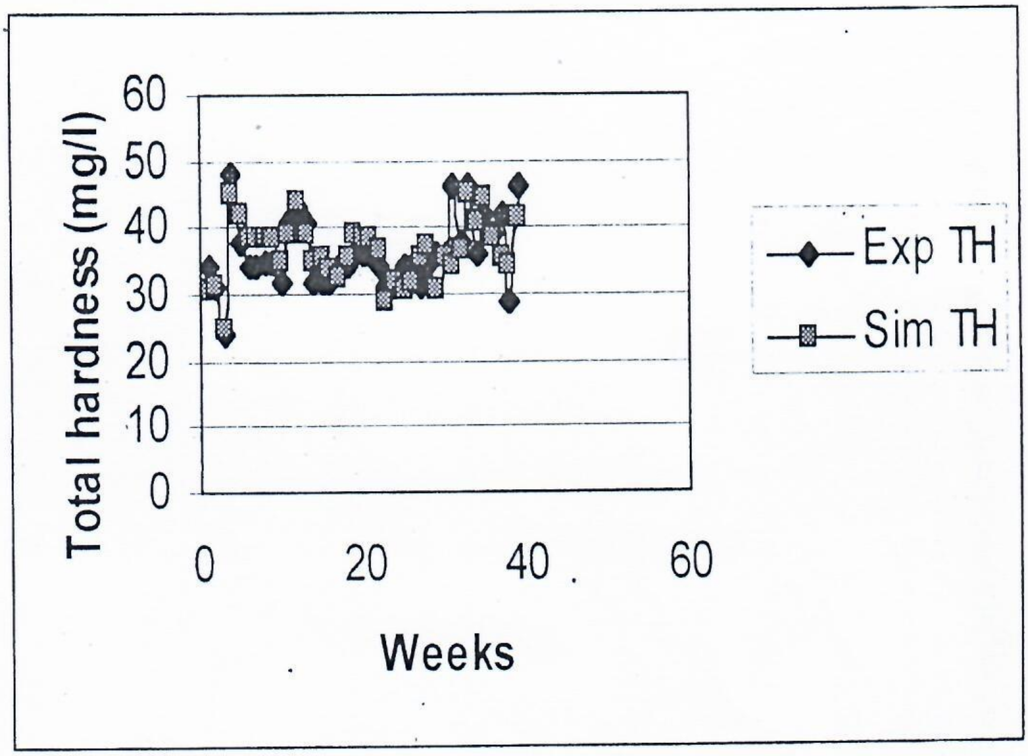

Fig 2: Total hardness versus weeks for experimental and simulation (2001)