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Modeling Of Brewery Effluent pH Value

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Abstract

The increased discharge of industrial effluents into the natural water bodies have led to the deterioration of their physio-chemical and technological characteristics and in particular caused a remarkable change in the pH value. Analyses have shown that the level of acidification is dependent on the extent of hydrolysis. This paper investigated the possibility of developing a model equation for assessing the overall brewery effluent's pH value via contributions of various pollutants and environmental condition, using the least square method. Parametric coefficients in the model equation obtained showed that the effect of some of the measured parameters on the overall pH value could be represented in the following order:

Temperature > Hardness > COD > Cl⁻ > TSS (pH) Mg²⁺ < Ca²⁺
Order of increasing acidification Order of increasing alkalization

Keywords

Effluents, least square method, pH, model equation.

1. Introduction

Water borne diseases such as typhoid, cholera, dysentery, malaria etc. are direct result of polluted water sources. Other less apparent disease in human may be the accumulation of toxic substances in the food chain and other natural cycles frequently used by man (Eckenfelder, 1989). The discharge of large amount of industrial effluent into natural bodies has led to the contamination of arable farmland and water bodies (Odigure 1998, Nikoladze 1989, Jenkins 1978). It may also cause serious reduction in the soil potency and productivity.

The law of active mass is applicable to dilute solutions of weak electrolyte and non-electrolytes. The ionization constant K of an electrolyte is dependent on the concentration of the ions in solution. That is: $K = f(C)$

The equivalent electroconductivity of strong electrolyte increases with dilution due to the reduction of the ion association phenomena. Molecules of acid, base and salt dissociate in water. However production of their dilute solutions with constant pH is practically impossible to obtain. This could be attributed to the facts that the presence of insignificant quantity of atmospheric CO_2 , the alkaline composition of the glassware and other impurities in solution can seriously affect the pH value (Karapetyant, 1981). It can be said that the concentration of a solution or its pH value is a reflection of prevailing conditions in which the solution exists.

For brewery effluent, the prevailing pH value is therefore the resultant of the dissociation of the organic and inorganic compounds and their subsequent hydrolysis. Commonly measured water quality parameters are in principle targeted at measuring characteristics that could evaluate the extent or possibility of dissociation of organic or inorganic compounds and their subsequent hydrolysis. In other words, measured water quality characteristics are inter-related but are not additive functions. Effluents from breweries can be characterized based on the relatively oxygen demand expressed as Biochemical Oxygen Demand (BOD) or Chemical Oxygen Demand (COD), suspended solids (SS), pH, temperature and flow parameter (Iyowun 2000, Imre 1984, Suess 1982, Lugben 1995).

The pH of a solution can be considered as a function of all measured characteristics;

$$pH = f(\text{Temperature, TSS, COD, hardness, } Ca^{2+}, Mg^{2+}, Cl)$$

The major objective of this work is to develop a model equation for the assessment of water quality.

2. Experiment

The samples were collected at the point of discharge from the factory. The sampling bottles were first rinsed with concentrated hydrochloric acid and then with distilled

waters and allowed to dry. The dried sampling bottles were again rinsed with the sample twice before being filled, corked and then placed in refrigerator at a temperature of 4°C for a maximum holding period of 6 hours. The samples were then analyzed for their physical and chemical characteristics such as temperature, total suspended solids (TSS), pH, total hardness, biochemical oxygen demand (BOD), COD, and the ions of Ca²⁺, Mg²⁺, Cl (Iyowun 2000, Kemmer 1988, Metcalf 1978). The results of the analyses are presented in Table 1.

2.1 Modeling For Water Quality Using pH As The Optimization Criteria

The pH of a solution is a reflection of the resultant effects of TSS, COD hardness and the various ions present. The pH is modeled using the empirical method of the least square method (Carnahan et al. 1969, Himmelblau 1987). Mathematically;

$$\text{pH} = f(\text{Temperature, TSS, COD, hardness, Ca}^{2+}, \text{Mg}^{2+}, \text{Cl}) \dots\dots\dots 1$$

Let Temperature = T, TSS = t, COD = C₁, hardness = H, calcium = C₂, Magnesium = M and chloride = C₃, then equation 1 becomes;

$$\text{pH} = f(aT + bt + cC_1 + dH + eC_2 + fM + gC_3) \dots\dots\dots 2$$

Where the pH is the dependent variable in the equation and a,b,c,d,e,f,g are the coefficients (constants) which need to be determined and T,t,C₁,H,C₂,M,C₃ are the independent variables for the desired pH.

Let I represent the square of the error between the observed pH and its predicted value (P), using the experimentally obtained data of T, t, C₁, H, C₂, M, C₃.

$$I = P - (aT + bt + cC_1 + dH + eC_2 + fM + gC_3)^2 \dots\dots\dots 3$$

For n experimental values of P and T, t, C₁, H, M, C₂, C₃

$$nI = \sum (P_i - aT_i - bt_i - cC_{1i} - dH_i - eC_{2i} - fM_i - gC_{3i})^2 \dots\dots\dots 4$$

To minimize nI with respect to the coefficients a, b, c, d, e, f and g using the first partial derivatives of nI with respect to these constant and equating these to zero we obtain the necessary condition for a minimum, so from equation (4);

$$\delta(nI)/\delta a = -2 \sum T_i (P_i - aT_i - bt_i - cC_{1i} - dH_i - eC_{2i} - fM_i - gC_{3i}) = 0 \dots\dots\dots 5$$

$$\delta(nl)/\delta b = -2\sum ti (Pi - aTi - bti - cCi_i - dHi - eC_{2i} - fMi - gC_{3i}) = 0 \dots\dots\dots 6$$

$$\delta(nl)/\delta c = -2\sum C_{1i} (Pi - aTi - bti - cCi_i - dHi - eC_{2i} - fMi - gC_{3i}) = 0 \dots\dots\dots 7$$

$$\delta(nl)/\delta d = -2\sum Hi (Pi - aTi - bti - cCi_i - dHi - eC_{2i} - fMi - gC_{3i}) = 0 \dots\dots\dots 8$$

$$\delta(nl)/\delta e = -2\sum C_{2i} (Pi - aTi - bti - cCi_i - dHi - eC_{2i} - fMi - gC_{3i}) = 0 \dots\dots\dots 9$$

$$\delta(nl)/\delta f = -2\sum Mi (Pi - aTi - bti - cCi_i - dHi - eC_{2i} - fMi - gC_{3i}) = 0 \dots\dots\dots 10$$

$$\delta(nl)/\delta g = -2\sum C_{3i} (Pi - aTi - bti - cCi_i - dHi - eC_{2i} - fMi - gC_{3i}) = 0 \dots\dots\dots 11$$

When rearranged, these sets of linear equations become;

$$\sum TiPi = a\sum(Ti)^2 + b\sum tiTi + c\sum Ti C_{1i} + d\sum HiTi + e\sum C_{2i}Ti + f\sum MiTi + g\sum TiC_{3i} \dots(12)$$

$$\sum tiPi = a\sum tiTi + b\sum(ti)^2 + c\sum Ti C_{1i} + d\sum tiHi + e\sum C_{2i}ti + f\sum Mit_i + g\sum tiC_{3i} \dots(13)$$

$$\sum C_{1i}Pi = a\sum C_{1i}Ti + b\sum C_{1i}ti + c\sum(C_{1i})^2 + d\sum C_{1i}Hi + e\sum C_{1i}C_{2i} + f\sum Mi C_{1i} + g\sum C_{1i} C_{3i} \dots(14)$$

$$\sum HiPi = a\sum HiTi + b\sum tiHi + c\sum Hi C_{1i} + d\sum(Hi)^2 + e\sum C_{2i}Hi + f\sum MiHi + g\sum HiC_{3i} \dots(15)$$

$$\sum C_{2i}Pi = a\sum TiC_{2i} + b\sum tiC_{2i} + c\sum C_{2i}C_{1i} + d\sum HiC_{2i} + e\sum(C_{2i})^2 + f\sum MiC_{2i} + g\sum C_{2i}C_{3i} \dots(16)$$

$$\sum MiPi = a\sum MiTi + b\sum MiHi + c\sum Mi C_{1i} + d\sum MiHi + e\sum C_{2i}Mi + f\sum(Mi)^2 + g\sum MiC_{3i} \dots(17)$$

$$\sum C_{3i}Pi = a\sum TiC_{3i} + b\sum tiC_{3i} + c\sum C_{3i}C_{1i} + d\sum HiC_{3i} + e\sum C_{2i}C_{3i} + f\sum MiC_{3i} + g\sum(C_{3i})^2 \dots(18)$$

where $\sum = \sum_{i=1}^n$ and $n = 12$ and the sum is obtained from the experimental data using basic program. The output of summation is as;

$$\sum(Ti)^2 = 7819.6 \quad \sum(ti)^2 = 128426.28 \quad \sum(C_{1i})^2 = 82613.3032 \quad \sum(Hi)^2 = 14312.08$$

$$\sum(C_{2i})^2 = 65789.4109 \quad \sum(Mi)^2 = 15239.48 \quad \sum(C_{3i})^2 = 171752.77 \quad \sum TiPi = 2825.74$$

$$\sum C_{1i}Pi = 9190.052 \quad \sum tiPi = 11420.82 \quad \sum HiPi = 12095.4 \quad \sum C_{2i}Pi = 8198.894$$

$$\sum MiPi = 3896.8 \quad \sum C_{3i}Pi = 13227.18 \quad \sum C_{1i}Hi = 108479.67 \quad \sum C_{1i}C_{2i} = 73655.6349$$

$$\sum Mi C_{1i} = 34826.41 \quad \sum C_{1i} C_{3i} = 118686.076 \quad \sum tiTi = 31538.74 \quad \sum TiC_{1i} = 25341.526$$

$$\sum HiTi = 33360.41 \quad \sum C_{2i}Ti = 22619.443 \quad \sum MiTi = 10741.7 \quad \sum TiC_{3i} = 36489$$

$$\begin{aligned} \Sigma C_{2i}H_i &= 96832.25, \Sigma MiH_i = 46283.28, \Sigma HiC_{3i} = 156579.5, \Sigma MiC_{2i} = 31045.045 \\ \Sigma C_{2i}C_{3i} &= 105790, \Sigma C_{1i}Ti = 102803.662, \Sigma HiTi = 134745.4, \Sigma C_{2i}Ti = 91614.376 \\ \Sigma MiTi &= 43134, \Sigma TiC_{3i} = 147645.7, \Sigma MiC_{3i} = 50813.25 \end{aligned}$$

Substituting these into 12 to 18 yields:

$$7819.6a + 31538.74b + 25341.526c + 33360.4d + 22619.543e + 10741.7f + 36489g = 2825.74 \dots\dots\dots(19)$$

$$315338.74a + 128426.28b + 102803.662c + 134745.4d + 91614.376e + 43134f + 147645.7g = 1142.82 \dots\dots\dots(20)$$

$$25341.526a + 102803.662b + 82613.3032c + 108479.62d + 73655.6349e + 34826.41f + 1188686.076g = 9190.052 \dots\dots\dots(21)$$

$$33360.4a + 134745.4b + 108497.62c + 143112.08d + 96832.25e + 46283.28f + 156579.5g = 12095.4 \dots\dots\dots(22)$$

$$22619.543a + 91614.376b + 73655.6349c + 96832.25d + 65789.4101e + 31045.045f + 105790g = 8198.894 \dots\dots\dots(23)$$

$$10741.7a + 43134b + 34826.41c + 46282.28d + 31045.045e + 15239.48f + 50813.25g = 3896.8 \dots\dots\dots(24)$$

$$36489a + 147645.7b + 118686.076c + 156579.5d + 105790e + 50813.25f + 171752.77g = 13227.18 \dots\dots\dots(25)$$

Equations 19 to 25 form a 7x7 symmetric matrix. A computer program using the Gauss-Jordan elimination method to obtain the constant coefficients also solved this:

$$\begin{aligned} a &= 0.11379493991, b = 0.0220990051, c = 0.083265244986, d = 0.0932383375, \\ e &= -0.080762128, f = -0.0735273196, g = 0.00034813083356 \end{aligned}$$

And the model obtained can be represented as:

$$\begin{aligned} pH &= 0.11379493991T + 0.02209920511 + 0.083265244986C_1 + 0.09372383375H \\ &\quad - 0.080762186C_2 - 0.073521273196M + 0.0034813083C_3 \dots\dots\dots 26 \end{aligned}$$

3. Result

The comparative values of the experimental results and the modeled pH values are presented in Table 2.

Table 1: Experimental effluent characteristics for Jan - Dec 1999

	PH	T (°C)	TSS (mg/l)	C ₁ (mg/l)	H (mg/l)	C ₂ (mg/l)	M (mg/l)	C ₃ (mg/l)
Jan	9.50	25.50	97.0	84.17	121.00	75.00	46.00	135.00
Feb	9.20	26.20	98.0	83.00	105.00	72.50	32.50	112.50
Mar	9.00	25.50	115.0	85.13	103.00	72.50	32.50	122.50
Apr	8.90	23.00	98.5	81.63	109.80	78.00	31.80	120.00
May	9.00	26.30	111.5	83.00	115.00	73.50	41.50	125.00
Jun	9.80	28.10	99.2	80.83	115.00	73.50	41.50	125.00
Jul	9.50	23.50	97.0	54.17	121.00	75.00	46.00	135.00
Aug	9.20	26.20	98.0	83.00	105.00	72.50	32.50	112.00
Sep	9.00	23.50	115.0	85.13	103.00	70.00	33.00	122.50
Oct	8.90	23.00	98.5	81.63	100.00	75.00	25.00	100.10
Nov	9.00	28.10	99.2	80.83	115.00	73.53	41.50	125.00
Dec	9.80	28.10	99.2	80.93	115.00	73.53	41.50	125.00
FEPA*	5.40	21.00	53.00	42.00	58.00	34.00	20.00	130.00
Ave/yr.	9.23	26.13	103.20	82.96	108.97	74.00	34.97	119.10

Temperature = T, TSS = t, COD = C₁, hardness = H, calcium = C₂, Magnesium = M and chloride = C₃

*FEPA - FEDERAL ENVIRONMENTAL PROTECTION AGENCY

Table 2: Comparative pH values for experiments and developed model

Month	Observed pH value	Model pH value	Percentage Error (%)
Jan	9.50	9.52	0.21
Feb	9.20	9.25	0.54
Mar	9.00	9.00	0.00
Apr	8.90	8.70	2.25
May	9.00	9.08	0.88
Jun	9.80	9.53	2.76
Jul	9.50	9.52	0.21
Aug	9.20	9.25	0.54
Sep	9.00	9.00	0.00
Oct	8.90	8.70	0.25
Nov	9.00	9.07	0.77
Dec	9.80	9.50	3.06

Verification Of Result

In order to verify the correctness of the modeled equation, the percentage error was calculated for each of the months and compared with the corresponding experimental values. The percentage deviation ranged from 0 to 3.02%.

4. Discussion Of Result

Water is the most effective solvent. In principle all compounds – salts, hydrocarbon, protein, ester, fats, etc., can be hydrolyzed by water. That is the ions of these compounds can be exchanged with water molecules. This exchange reaction often results in shift of the water dissociation equilibrium constant. The extent or possibility of hydrolysis of the compound cation K^{n+} and anion A^{n-} is dependent on the electropositivity or negativity and atomic (molecular) radius. It is now established that hydrolysis of various compounds could take place in solution according to the following types (Karapetyant, 1981):

Type 1. Cation K^{n+} and anion A^{n-} with small charge and large atomic radius are insignificantly polarized by water molecules. In other word cation of strong base such as K^+ , Ca^{2+} and anion of strong acid Cl^- , NO_3^- are not hydrolyzed by water. Consequently the pH of the solution is relatively neutral ($pH \cong 7$).

Type 2. Salts, whose cations are from strong base and anion from weak acid, can hydrolyze only to produce alkaline solution. The reverse is also true strong acid and weak base will produce acidic solution.

Type 3. Salt with both cation and anion from weak acid and base will hydrolyze to produce weak acidic or weak alkaline solution.

Consequently, pollutants present in water can seriously affect the resultant pH. The extent of acidification or alkalization of the solution by pollutants is dependent, not only on the chemical nature of the compounds present, but also the prevailing technological conditions. From the calculated coefficients, it can be seen that the pH is most affected by

the temperature of the wastewater and least Cl⁻ content. Cations of base metals – Mg²⁺ and Ca²⁺ possess negative sign. This might be attributed to possibility of their being precipitated from the solution or the basicity nature. In principle they contribute little to the overall pH value because they cannot be hydrolyzed. However the effect of the presence of Ca²⁺ is higher than that of Mg²⁺ due to its high electropositivity. The effect of the presence of dissolvable solids predominantly of organic origin on the solution's pH, can be associated with a type 3 hydrolysis. Complex organic compounds are converted to less complex soluble ones by enzymatic hydrolysis. Most organic compounds such as carbohydrate and protein, on hydrolysis produce organic weak acid or weak base. The extents of these reactions depend on the prevailing environmental condition.

Analysis of the obtained coefficients for the various optimized variable show that the obtained values and signs to a great extent is a reflection of the chemical nature of the pollutants constituents. The effect of the measured parameters on the overall pH can be represented in the following order:

Temperature > Hardness > COD > Cl⁻ > TSS (pH) Mg²⁺ < Ca²⁺
 Order of increasing acidification Order of increasing alkalization

The results obtained from the model equation show that the pH of the effluent is much more higher than the standard stipulated by the Federal Environmental Protection Agency (FEPA). The average yearly pH was found to be 9.1 where as the maximum limit by FEPA is 5.6, this suggests that the effluent was not well treated.

5. Conclusion

The developed model showed that the pH value of industrial effluent is a reflection of the prevailing physio-chemical and technological parameters. Parametric coefficients in the model equation obtained showed that the effect of some of the measured parameters on the overall pH value could be represented in the following order:

Temperature > Hardness > COD > Cl⁻ > TSS (pH) Mg²⁺ < Ca²⁺
 Order of increasing acidification Order of increasing alkalization

This is a reflection of the influence of the prevailing parameters.

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