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Prediction of Chemical Oxygen Demand from Turbidity Measurement of Tannery Effluents: An Empirical Relation

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A linear relation form of chemical oxygen demand (COD) [COD = a * (Turbidity) + b] is being proposed to predict the values of chemical oxygen demand as a function of turbidity for the tannery effluents. By fitting this relation to the available data, the values of the empirical constants are found to be a as 5.96 and b as 670.23, when chemical oxygen demand and turbidity are expressed as mg L^{-1} of oxygen and nephelometric turbidity unit (NTU), respectively. The observed chemical oxygen demand of effluent samples collected from different tannery industries are compared statistically with predicted values and the proposed empirical relation shows fairly good agreement.

Key Words: Chemical oxygen demand, Turbidity, Tannery effluent, Empirical relation.

INTRODUCTION

One of the major objectives in the global clean-up action of WHO is to find out strategies and analytical tools for the rapid monitoring of water pollution. This has accelerated the research activities of environmental scientists to find out analytical tools, models and methods. It has been well established by number of researchers[1-9] in the application of regression technique in water chemistry such as, the prediction of binding capacity of Pb using the concentrations of OH^-, CO_3^{2-} and SO_4^{2-} and the binding capacity of Cu using OH^- and SO_4^{2-}, in northern European surface waters[1]; the existence of positive correlation-dissolved Cu and dissolved organic carbon (DOC) and Zn and DOC in south Francisco Bay[2]; the existence of significant correlations (water quality index and K^+, COD and phosphate ion, temporary hardness and permanent hardness) for the Match industry effluent of Sivakasi, India[3]; the linear relation to predict the values of COD as a function of TSS for the effluent of Modigram Cement Limestone Mines at Modi Nagar, India[4]; linear regression equation correlating trihalomethane and haloacetic acids of finishing drinking waters from heterogeneous sources[5], *etc.*

The chemical oxygen demand (COD) is the measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxident[10]. The measurement of COD is particularly important and most frequently used for the characterization of industrial and municipal effluents and their treatment[11]. Kumaresan *et al.*[12] published a review of various methods for the determining COD which covers-titrimetry, spectrophotometry, electro-analysis, flow injection analysis and empirical relations.

In present investigation, the possibility of determining COD, using empirical relations, from a typical set of data (120) including COD, total solids (TS), electrical conductivity (EC) and turbidity, in this case obtained from effluent treatment plant (ETP) of Sri Chamundi Leathers, Chennai (India), is a continuation of endeavor along the similar lines.

EXPERIMENTAL

Sri Chamundi Leathers (Chennai) discharges 42 m^3/day of raw effluent for 1000 kg of finished product. The effluent treatment plant comprises of primary clarifier, anaerobic lagoon, pH correction unit, chemoautotrophic activated carbon oxidation (CAACO) system (R3 reactor) and colour removal unit. The flow chart for the unit operations in the ETP of a typical leather industry is shown in the Fig. 1. The raw tannery effluents and effluents of all the stages of treatment were collected for 15 d, with a time gap of 3 d (hence the total number of samples are 30) during the year May 2002. After each and every collection, samples were analyzed for the determination of COD, TS (total solids), EC (electrical conductivity) and turbidity using standard procedures[6]. The measurements mentioned above were carried out in three replications and the results were given as mean value (Tables 1-6).

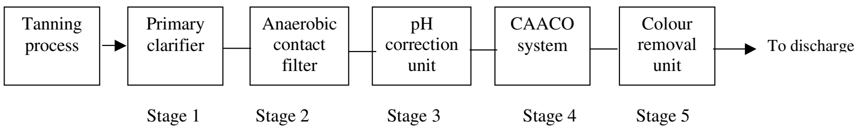

Fig. 1. Flow chart of the unit operations in effluent treatment plant (ETP) of tannery industry

The analytical data were subjected to substantial analysis and the correlation coefficient was found for (a) COD *vs.* EC, (b) COD *vs.* Turbidity, and (c) COD *vs.* TS.

Among the three relations, the best correlation was selected for the one with the r-value closer to 0.9. For the selected pair, a linear relation was proposed using the regression constants a & b. This proposed equation was applied for the determination of COD for different tannery effluents, raw or outlet of any stage of treatment and it is compared statistically with the standard method of analysis.

TABLE-1
ANALYTICAL RESULTS OF PHYSICO-CHEMICAL PARAMETERS IN THE OUTLET OF TANNING PROCESS*

Parameters	1st collection	2nd collection	3rd collection	4th collection	5th collection	6th collection
pH	5.10 ± 0.08	4.90 ± 0.06	5.31 ± 0.09	4.80 ± 0.07	5.00 ± 0.06	NC
EC (mS/cm)	5.74 ± 0.06	5.70 ± 0.05	5.79 ± 0.09	5.70 ± 0.08	5.71 ± 0.06	NC
TS (mg L^{-1})	4952.23 ± 9.54	4796.67 ± 10.68	5100.63 ± 12.30	5095.71 ± 8.21	4950.43 ± 14.61	NC
Turbidity (NTU)	342.04 ± 1.64	340.77 ± 1.22	490.04 ± 1.13	375.63 ± 1.02	340.42 ± 1.92	397.00 ± 1.50
COD (mg $O_2 L^{-1}$)	2560.42 ± 35.61	2400.65 ± 29.28	3067.72 ± 34.14	2900.23 ± 32.64	2657.11 ± 31.66	2815.00 ± 32.65

*Number of replicates = 3; NC - Not calculated.

TABLE-2
ANALYTICAL RESULTS OF PHYSICO-CHEMICAL PARAMETERS IN THE OUTLET OF PRIMARY CLARIFIER (STAGE 1)*

Parameters	1st collection	2nd collection	3rd collection	4th collection	5th collection	6th collection
pH	7.10 ± 0.02	7.30 ± 0.06	7.46 ± 0.04	7.50 ± 0.04	7.30 ± 0.06	NC
EC (mS/cm)	5.60 ± 0.06	5.62 ± 0.09	5.59 ± 0.11	5.60 ± 0.10	5.69 ± 0.09	NC
TS (mg L^{-1})	4574.09 ± 11.90	4328.97 ± 12.62	4899.84 ± 9.86	4711.54 ± 12.67	4611.12 ± 14.08	NC
Turbidity (NTU)	114.54 ± 2.65	324.43 ± 2.98	245.43 ± 3.11	129.34 ± 2.64	120.21 ± 3.67	176.41 ± 2.34
COD (mg $O_2 L^{-1}$)	1960.76 ± 21.64	1855.44 ± 19.58	2562.45 ± 22.17	2000.32 ± 29.28	1989.21 ± 14.62	1537.33 ± 18.92

*Number of replicates = 3; NC - Not calculated.

TABLE-3
ANALYTICAL RESULTS OF PHYSICO-CHEMICAL PARAMETERS IN THE OUTLET OF ANAEROBIC LAGOON (STAGE 2)*

Parameters	1st collection	2nd collection	3rd collection	4th collection	5th collection	6th collection
pH	7.23 ± 0.03	7.310 ± 0.05	7.40 ± 0.07	7.20 ± 0.05	7.62 ± 0.02	NC
EC (mS/cm)	5.26 ± 0.09	5.590 ± 0.11	5.56 ± 0.06	5.00 ± 0.12	5.36 ± 0.08	NC
TS (mg L^{-1})	2600.78 ± 19.52	3614.670 ± 17.45	4001.05 ± 11.51	2590.76 ± 9.25	2609.43 ± 9.28	NC
Turbidity (NTU)	77.50 ± 2.11	116.065 ± 3.19	105.00 ± 3.11	71.50 ± 2.34	78.60 ± 3.04	96.00 ± 3.67
COD (mg $O_2 L^{-1}$)	1215.60 ± 28.68	1690.510 ± 29.61	2038.63 ± 32.66	1210.60 ± 29.62	1221.00 ± 31.68	1457.33 ± 30.69

*Number of replicates = 3; NC - Not calculated.

TABLE-4

ANALYTICAL RESULTS OF PHYSICO-CHEMICAL PARAMETERS IN THE OUTLET OF PH CORRECTION UNIT (STAGE 3)*

Parameters	1st collection	2nd collection	3rd collection	4th collection	5th collection	6th collection
pH	9.10 ± 0.08	9.40 ± 0.10	9.32 ± 0.03	9.50 ± 0.07	9.70 ± 0.06	NC
EC (mS/cm)	4.48 ± 0.07	4.45 ± 0.10	5.00 ± 0.11	4.19 ± 0.09	4.28 ± 0.10	NC
TS (mg L^{-1})	3185.00 ± 15.13	2848.78 ± 14.53	2889.00 ± 20.21	3081.00 ± 15.33	3099.00 ± 12.2	NC
Turbidity (NTU)	60.00 ± 1.54	53.00 ± 1.06	40.00 ± 1.15	50.00 ± 1.54	49.00 ± 1.12	48.00 ± 3.67
COD (mg O_2 L^{-1})	862.70 ± 24.34	1099.52 ± 29.65	1359.12 ± 28.22	800.70 ± 24.61	810.10 ± 21.81	1139.66 ± 26.23

*Number of replicates = 3; NC - Not calculated.

TABLE-5

ANALYTICAL RESULTS OF PHYSICO-CHEMICAL PARAMETERS IN THE OUTLET OF CAACO SYSTEM (STAGE 4)*

Parameters	1st collection	2nd collection	3rd collection	4th collection	5th collection	6th collection
pH	9.72 ± 0.10	9.50 ± 0.09	9.31 ± 0.07	9.46 ± 0.07	9.86 ± 0.08	NC
EC (mS/cm)	4.33 ± 0.12	3.71 ± 0.11	4.30 ± 0.09	4.60 ± 0.11	4.19 ± 0.08	NC
TS (mg L^{-1})	3198.00 ± 18.11	2477.25 ± 19.51	2599.00 ± 21.10	3190.00 ± 17.95	3180.00 ± 17.34	NC
Turbidity (NTU)	13.00 ± 1.54	18.00 ± 1.61	17.00 ± 1.15	11.00 ± 1.01	14.00 ± 1.14	15.00 ± 3.67
COD (mg O_2 L^{-1})	627.40 ± 21.58	525.70 ± 21.23	906.07 ± 33.44	631.00 ± 24.63	629.00 ± 24.82	916.33 ± 27.09

*Number of replicates = 3; NC - Not calculated.

TABLE-6

ANALYTICAL RESULTS OF PHYSICO-CHEMICAL PARAMETERS IN THE OUTLET OF COLOUR REMOVAL UNIT (STAGE 5)*

Parameters	1st collection	2nd collection	3rd collection	4th collection	5th collection	6th collection
pH	7.72 ± 0.04	7.60 ± 0.03	7.55 ± 0.04	7.47 ± 0.06	7.90 ± 0.05	NC
EC (mS/cm)	2.93 ± 0.07	2.30 ± 0.10	3.40 ± 0.09	2.83 ± 0.09	2.50 ± 0.11	NC
TS (mg L^{-1})	2597.00 ± 18.12	2097.13 ± 19.67	2500.00 ± 24.88	2397.00 ± 17.42	2190.00 ± 16.91	NC
Turbidity (NTU)	5.00 ± 0.05	4.00 ± 0.07	8.00 ± 0.11	6.00 ± 0.07	5.80 ± 0.08	4.00 ± 3.67
COD (mg O_2 L^{-1})	431.00 ± 11.11	350.47 ± 9.31	485.40 ± 17.69	400.00 ± 15.87	390.00 ± 14.71	466.00 ± 12.28

*Number of replicates = 3; NC - Not calculated.

RESULTS AND DISCUSSION

The correlation co-efficient for the pairs COD *vs.* TS, COD *vs.* turbidity and COD *vs.* EC are calculated using the eqn. 1.

$$r = \frac{\sum_{1}[(x_i - \bar{x})(y_i - \bar{y})]}{\left\{\left(\sum_{1}(x_i - \bar{x})^2\right)\left(\sum_{1}(y_i - \bar{y})^2\right)\right\}^{1/2}} \quad (1)$$

where the points on the graph are (x_1, y_1), (x_2, y_2), …. (x_i, y_i), …. (x_n, y_n). x and y are the mean values of x_i and y_i, respectively. The calculated values for the pairs COD *vs.* TS, COD *vs.* turbidity and COD *vs.* EC are 0.959, 0.961 and 0.885, respectively. Among the three, COD *vs.* Turbidity correlation co-efficient value was intimately correlated and thus a linear relation has been proposed for COD and turbidity, which is

$$\text{COD} = a \times (\text{Turbidity}) + b \quad (2)$$

The values of the empirical parameters a and b were calculated with help of the eqns. 3 and 4.

$$b = \frac{\sum_{1}[x_i - \bar{x})(y_i - \bar{y})]}{\sum_{1}(x_i - \bar{x})^2} \quad (3)$$

$$a = \bar{y} - b\bar{x} \quad (4)$$

The empirical parameters a and b determined were 5.96 and 670.23, respectively. The proposed empirical relation, COD = 5.96 × (turbidity) + 670.23 was applied for the 6th collection. The predicted and observed COD for raw effluent are 3028.66 and 2815.0. Similarly for the stages 1, 2, 3, 4 and 5 the predicted and observed COD are 1720.0 and 1537.33, 1242.66 and 1457.33, 956.00 and 1139.66, 757.00 and 916.33, 694.00 and 466.00, respectively. The correlation coefficient (r) and the paired t-test have been employed and the comparative results (Table-7) revealed that the correlation coefficient of the two results approaches the significant value (r = 0.971). The paired t-test of the analytical results further concluded that there is no significant difference between the two methods. The analytical results of observed and predicted COD of effluent samples collected from different tannery industries, having the said stages of treatment also show fairly good agreement (Table-8).

TABLE-7
OBSERVED AND PREDICTED COD ($mgO_2 L^{-1}$) OF EFFLUENTS OF VARIOUS STAGES OF ETP*

Sample type	Standard (Cr) method	From empirical relation
Raw effluent	2815.00 ± 95.60	3028.66 ± 6.5400
Primary clarifier	1537.33 ± 48.32	1720.00 ± 3.740
Anaerobic filter	1457.33 ± 69.77	1242.66 ± 4.920
pH correction Unit	1139.66 ± 76.84	956.00 ± 4.080
CAACO system	916.33 ± 54.80	757.00 ± 5.099
Colour removal Unit	466.00 ± 12.28	694.00 ± 4.080

*Number of replicates = 3; r (correlation coefficient) = 0.971
t (paired t-test) = -0.126; $t_{critical}$ = 2.45(P = 0.05).

TABLE-8
OBSERVED AND PREDICTED COD ($mgO_2 L^{-1}$) OF EFFLUENTS OF VARIOUS STAGES COLLECTED FROM DIFFERENT TANNERY INDUSTRIES*

Sample type	Standard (Cr) method	From empirical relation
Untreated	2978.00 ± 116.2	3102.00 ± 1.63
Outlet	492.33 ± 8.17	675.33 ± 4.49
Anaerobic lagoon	1507.33 ± 69.13	1278.33 ± 5.43
pH correction unit	1120.00 ± 46.91	951.66 ± 7.03
Primary clarifier	1545.33 ± 47.41	1748.66 ± 8.95
Untreated	3201.00 ± 75.37	2894.00 ± 9.93
Primary clarifier	1795.00 ± 68.64	2007.00 ± 4.32

*Number of replicates = 3; r (correlation coefficient) = 0.974
t (paired t-test) = -0.283; $t_{critical}$ = 2.45(P = 0.05)

Conclusion

A linear relation of the form COD = a × (turbidity) + b has been proposed to predict the COD as a function of turbidity for the tannery effluent. The values of the empirical constants are found to be a as 5.96 and b as 670.23. This empirical relationship shows fairly good agreement with the available data. The prediction of COD using this relation is based on the following aspects: (a) The outlet of the effluents from the various process carried out in the tannery industry should have same characteristics. (b) The various type of treatment adopted in the ETP should have the process similar to the effluents studied in the present investigation.

The most of the tannery industries of India are having similar tanning process and the said ETP system. Instead of CAACO system, aeration system has also been applied to treat the outlet effluent of pH correction unit and the observed reduction of COD is 25 % lower in the case of later compared with the former. So irrespective of the treatment adopted, the turbidity of tannery effluent is varied proportionally from stage to stage and hence the proposed relation is applicable. Also during the rainy season effluent is diluted. Based on the intensity of rainfall, COD as well as turbidity varied proportionally. So the mentioned empirical relation is applicable for all seasons.

The conventional method of determination of COD takes 3 h, whereas measurement of turbidity and calculating COD using empirical relation takes few minutes.

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