CORRELATION BETWEEN BIOCHEMICAL OXYGEN DEMAND (BOD) AND CHEMICAL OXYGEN DEMAND (COD) FOR DIFFERENT INDUSTRIAL WASTE WATERS.

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Abstract: Biochemical oxygen demand (BOD) and chemical oxygen demand (COD) are two important parameters used in estimating the degree of organic pollution in waste waters. The determination of BOD is tedious and time consuming and depends on biochemical factors while COD is precise, time saving and completely chemical in nature. COD is not dependent on biochemical factors. Relationship between 3-day BOD (BOD3) and COD for three different food industrial waste waters was investigated. Synthetic samples of water with known composition having five different theoretical oxygen demands (ThOD) made from glucose and phthalate separately were analysed for relationship between BOD3 and COD. The correlation coefficient (r) determined by regression analysis of glucose was found to be 0.97 and that of phthalate 0.96. The correlation coefficients were also obtained for samples of effluents from three different food industries, viz. non alcoholic carbonated beverage and an ice cream factory (r = 0.87), fruit and vegetable processing factory (r = 0.93) and a dairy product factory (r = 0.89). As BOD3 and COD were found to be correlated, an estimate of BOD3 may be obtained in a few hours through the determination of COD with substantial reduction of time and cost.

Key words: Biochemical oxygen demand, chemical oxygen demand, industrial waste waters.

INTRODUCTION

The chemical and biological characteristics of industrial waste waters are highly variable. When waste water is discharged into a water body depletion of dissolved oxygen in water body occurs. There are interactions between certain types of chemicals and oxygen dissolved in the water body. The dissolved oxygen content in a water body gives information on the extent of the above interaction. The interactions can be best evaluated by measurements of the chemical oxygen demand (COD) and biochemical oxygen demand (BOD).1,2 As the qualitative and quantitative compositions of waste water are unknown, the theoretical oxygen demand (ThOD) can be approximated by the oxygen demand measured in terms of chemical oxygen demand.1-5 Attempts have been made to reduce the incubation period of the standard 5-day BOD (BOD5) measurements by introducing a 3-day BOD test (BOD3) for the tropics.6,7 Yet the reliability of this method has not been thoroughly evaluated in the Sri Lankan climate. Despite many drawbacks, the BOD
test persists as an important analytical measure of waste waters. This is because it measures the concentrations of different chemicals that, impose an oxygen demand, under the influence of microbial activity, without identifying the chemicals directly.\textsuperscript{1,2,8}

Long incubation time has made the BOD test difficult. On the other hand the COD test is advantageous because of its simplicity, speed, accuracy and the fact that oxidizes a very large percentage of the organic material present.\textsuperscript{1-3} However the COD test is not able to differentiate between the biodegradable and non biodegradable organic matter.\textsuperscript{2,4} An attempt was made to perform the BOD\textsubscript{3} test taking advantage of the ambient air temperature of 28\textdegree{}C in Sri Lanka. The main objective of this study was to investigate the relationship between COD and the introduced BOD\textsubscript{3} for three different effluents from food processing factories viz. (a) fruit and vegetable processing factory (b) dairy product industry (c) non-alcoholic carbonated beverage industry with an ice cream plant. Prior to analysis of waste water correlation of COD and BOD\textsubscript{3} was determined by developing a model of five different levels of ThOD (20, 40, 60, 80 & 100 mgdm\textsuperscript{-3}) with respect to glucose and phthalate separately.

As BOD\textsubscript{3} was measured instead of the standard BOD\textsubscript{5} for waste water samples, the validity of this was verified by studying the correlation of BOD\textsubscript{5} at 20\textdegree{}C and BOD\textsubscript{3} at room temperature separately for the synthetic samples containing glucose, phthalate and glucose/glutamic acid 1:1 mixture.

**METHODS & MATERIALS**

**Synthetic samples:** Synthetic samples of water with known composition having five different ThOD (20, 40, 60, 80 and 100 mgdm\textsuperscript{-3}) were prepared with glucose and phthalate separately. As the synthetic samples do not contain a microbial population capable of degrading them, an aliquot of 'seed water' (settled domestic sewage containing bacteria) obtained from a drain was incorporated into each sample.\textsuperscript{1,9-11} An appropriate volume of each sample was diluted with aerated water to supply sufficient dissolved oxygen (DO) to bacteria. In order to obtain the 30\% of initial dissolved oxygen (DO 2mgl\textsuperscript{-1}) for the incubated sample, the two series of experiments were done: (a) with the same seed concentration but varying dilutions (b) varying seed concentration (1.0 cm\textsuperscript{3}, 2.0 cm\textsuperscript{3}).

**Dilution:** To obtain the appropriate depletion of DO in the incubated samples, the optional dilution of the synthetic samples of glucose and phthalate, was carried out.

**Seed:** Having shown that the majority of samples contained 30\% of initial DO for the samples incubated with 1.0 cm\textsuperscript{3} seed concentration at various levels of dilution of the sample, all the BOD experiments were done with 1.0 cm\textsuperscript{3} 'seed water' taken from the same drain thereafter.
Correlation Between BOD and COD

Samples were kept inside a cupboard to minimize fluctuations in temperature and light. To ensure that the BOD was due to carbonaceous demand and that there was no toxic material present in the sample three replicates with varying dilution factors were analysed.\textsuperscript{1,2,9-11}

Sampling of effluent: As averaging of COD and BOD values obtained for many samples could give misleading values, grab samples were used for measurements.\textsuperscript{12} Precautions were taken on site to minimize the deterioration of the sample between sampling and the analysis. As the pollution strength of waste waters was very high compared to the synthetic solutions, preliminary tests were done to estimate the range of dilutions which would give 30\% of DO for the incubated sample.\textsuperscript{10,11} As the strength varied with the products processed, three different dilutions were made with each sample of waste water for BOD\textsubscript{3} experiments.\textsuperscript{13} Since food industry waste waters contain their own biological population (bacteria), ‘seeding’ was not carried out. The pH value of the waste water samples was adjusted to 7 to reactivate the dormant bacteria in the measurement of BOD\textsubscript{3}.

Determination of biochemical oxygen demand: Oxygen content of samples was determined using azide modification of the Winkler method (before and after incubation). The BOD levels were computed using the initial and final concentration of dissolved oxygen.\textsuperscript{9-11}

Determination of chemical oxygen demand: A sample was refluxed with acid potassium dichromate solution and silver sulphate for two hours and excess dichromate was determined by titrating with ferrous ammonium sulphate solution with ferroin indicator.\textsuperscript{9-11,14}

RESULTS

A significant correlation between BOD\textsubscript{3} and BOD\textsubscript{5} was shown for glucose and phthalate separately (Table 1). The conversion factor for BOD\textsubscript{5} to BOD\textsubscript{3} for glucose and phthalate was found to be 1.06 and 1.07 respectively. According to our study 56-61 per cent of the theoretical oxygen demand for glucose and 64-71 per cent for phthalate had been exerted during 3-day BOD (Tables 2 & 3).

Table 1: The relationship between BOD\textsubscript{5} at 20\textdegree C and BOD\textsubscript{3} at room temperature (28\textdegree C) for different samples.

| Chemical                  | Regression equation         | N   | Correlation coefficient | 95\% Confidence limits for slopes | Significance level |
|---------------------------|-----------------------------|-----|-------------------------|----------------------------------|-------------------|
| Glucose                   | BOD\textsubscript{3} = 1.7621 + 1.0612 BOD\textsubscript{5} | 35  | 0.99                    | 0.99-1.23                       | 0.001             |
| Phthalate                 | BOD\textsubscript{3} = 2.6072 + 1.0672 BOD\textsubscript{5} | 55  | 0.98                    | 1.01-1.12                       | 0.001             |
| 1:1 glucose & glutamic acid | BOD\textsubscript{3} = 41.6965 + 0.9052 BOD\textsubscript{5} | 15  | 0.91                    | 0.66-1.15                       | 0.001             |
Table 2: COD, BOD\textsubscript{3} and coefficient of variations (c.v.) obtained for different levels of ThOD for glucose (15 samples were analysed for each level).

| ThOD (mg dm\textsuperscript{-3}) | Mean COD ± s.e (mg dm\textsuperscript{-3}) | Mean BOD\textsubscript{3} ± s.e (mg dm\textsuperscript{-3}) | % of BOD\textsubscript{3} exerted at each ThOD | c.v. COD (%) | c.v. BOD\textsubscript{3} (%) |
|-------------------------------|---------------------------------|---------------------------------|--------------------------------|------------|----------------|
| 20                            | 18.93 ± 0.07                   | 11.13 ± 1.14                   | 56.5                            | 1.36      | 39.57         |
| 40                            | 37.53 ± 0.17                   | 23.07 ± 0.96                   | 57.68                           | 1.70      | 16.17         |
| 60                            | 57.87 ± 0.17                   | 33.73 ± 0.76                   | 56.23                           | 1.10      | 8.71          |
| 80                            | 77.27 ± 0.21                   | 49.40 ± 0.90                   | 61.75                           | 1.04      | 7.09          |
| 100                           | 98.67 ± 0.19                   | 58.73 ± 1.03                   | 58.73                           | 0.73      | 6.76          |

Table 3: COD, BOD\textsubscript{3} and coefficient of variation (c.v.) obtained for different levels of ThOD for phthalate (15 samples were analysed for each level).

| ThOD (mg dm\textsuperscript{-3}) | Mean COD ± s.e (mg dm\textsuperscript{-3}) | Mean BOD\textsubscript{3} ± s.e (mg dm\textsuperscript{-3}) | % of BOD\textsubscript{3} exerted at each ThOD | c.v. COD (%) | c.v. BOD\textsubscript{3} (%) |
|-------------------------------|---------------------------------|---------------------------------|--------------------------------|------------|----------------|
| 20                            | 18.93 ± 0.07                   | 12.80 ± 0.86                   | 64.00                           | 1.36      | 25.93         |
| 40                            | 38.0 ± 0.22                    | 28.53 ± 0.71                   | 71.33                           | 9.63      | 0.83          |
| 60                            | 58.67 ± 0.13                   | 39.8 ± 1.10                    | 66.33                           | 0.83      | 0.11          |
| 80                            | 79.2 ± 0.25                    | 54.33 ± 1.49                   | 67.91                           | 0.97      | 10.61         |
| 100                           | 99.67 ± 0.13                   | 65.60 ± 2.02                   | 65.60                           | 0.49      | 11.94         |

The correlation coefficients and regression equations obtained between COD and BOD\textsubscript{3} for glucose and phthalate separately are highly significant statistically (Table 4). There is a significant positive correlation between BOD\textsubscript{3} and COD values obtained for each of the three industrial waste waters (Tables 5 & 6).

Table 4: Separate analysis of linear regressions for 75 samples each for glucose and phthalate

|                   | Phthalate       | Glucose        |
|-------------------|-----------------|----------------|
| Correlation coefficient | 0.9647         | 0.9732         |
| Regression equation | BOD\textsubscript{3} = 2.0485 + 0.6480 COD | BOD\textsubscript{3} = -0.2975 + 0.6094 COD |
| 95% Confidence limits for slopes | 0.6066 & 0.6894 | 0.5757 & 0.6431 |
| Significance level  | P < 0.001       | P < 0.001      |
Table 5: BOD$_3$ and COD values for different food industrial waste waters

| Source                      | No. of Samples | Mean BOD$_3$ ± s.e (mg dm$^{-3}$) | Values of BOD$_3$ (mg dm$^{-3}$) | Mean COD ± s.e (mg dm$^{-3}$) | Values of COD (mg dm$^{-3}$) |
|-----------------------------|----------------|-----------------------------------|----------------------------------|-------------------------------|-------------------------------|
| Non alcoholic carbonated beverage + Ice cream factories | 40             | 138 ± 13                          | 28 - 410                         | 195 ± 17                      | 37 - 434                      |
| Fruit & vegetable processing factory | 35             | 1609 ± 272                        | 290 - 6300                       | 3761 ± 716                    | 610 - 18550                   |
| Dairy product industry      | 35             | 767 ± 73                          | 320 - 1400                       | 1294 ± 132                    | 540 - 3494                    |

Table 6: Correlation between BOD$_3$ & COD for three different industrial waste water

| Source of waste water | Correlation coefficient for BOD$_3$ & COD | Regression equation | Confidence limits of the gradient | Significance level | Average BOD$_3$ as a % of average COD | BOD$_3$/COD |
|-----------------------|------------------------------------------|---------------------|----------------------------------|--------------------|----------------------------------------|------------|
| Non alcoholic carbonate beverage + Ice cream factories | 0.87 | BOD$_3$ = 8.37 + 0.67COD | | | 71 | 0.67 |
| Fruit & vegetable processing factory | 0.93 | BOD$_3$ = 284.54 + 0.35COD | | | 43 | 0.35 |
| Dairy product industry | 0.89 | BOD$_3$ = 120.15 + 0.5COD | | | 59 | 0.5 |

DISCUSSION

It confirmed that synthetic water samples and the waste waters from three different food industries are amenable to biological oxidation. Potassium hydrogen phthalate could be degraded by heterogenous microbial populations in the BOD$_3$ experiments. Significant biodegradation with rapid acclimatization of microbes is possible even if it has an aromatic ring.

Pure synthetic compounds require an addition of a suitable source of micro-organisms (seeding) for their degradation by biochemical means. The pure compounds become mixtures of solutions when 'seed material' is added. The duration required by the bacteria for acclimatization (lag period) for different samples and different seed materials present in the seed inoculum will have an effect on BOD$_3$. 
As the rates of biochemical oxidation increase with temperature, oxygen demand is also increased. The reduction in time to three days is hence compensated by increasing temperature to around 28°C. The standard 5-day BOD at 20°C correlates with the BOD₃ value for 28°C for glucose and phthalate synthetic water samples with concentrations varying from 20-100 mgdm⁻³. The effect of higher temperatures (room temperature) is thus seen to compared with lower duration of the incubation period.

The gradient of BOD₃/BOD₅ for 1:1 glucose/glutamic acid is in agreement with 1.03 obtained by Chaudri. The regression equations under the conditions studied could be of immense use for the verification of analytical results; either for BOD or COD under similar experimental conditions maintained in the study. Correlation coefficients between COD and BOD₃ values for synthetic as well as waste waters are high. It is also desirable to determine whether the correlation of BOD₃ and COD exists for a wide variety of seed materials and substrates.

The composition of food processing waste is determined by the products and manufacturing processes involved. They differ from domestic sewage in general characteristics in particular by their higher concentration of organic matter. It is evident that none of the COD and BOD₃ values of the three industries satisfies the waste water quality requirements for such industrial effluents to be discharged into inland surface waters. Hence it is evident that all the factories studied were polluting the environment.

Separate analyses of COD and BOD₃ for different food industries indicated that it is possible to develop linear regression equations if the waste waters are of constant compositions and contain no toxic materials. An operator of an effluent treatment plant will have to wait for minimum of 3 days to obtain the BOD value for the effluent. The above correlation deduced by us will assist him to obtain BOD₃ value through the determination of COD which can be done within a short period of time. If there is an extensive data base for each of industrial waste waters covering a large range of BOD₃ and COD values regression equations under the conditions studied could be of immense use to obtain maximum information in shorter time with less costs incurred either for chemicals and manpower. An occasional determination of BOD₃ with regular COD determinations may be used for waste water treatment. If a correlation between COD and BOD₃ holds for an industry, BOD₃/COD value and the information regarding treatability can be predicted. The results will greatly simplify environmental monitoring procedures.

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