



Measuring Biodegradability of Industrial Wastewater by A Low-Cost differential Respirometer

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Abstract

A low-cost differential manometric respirometer was fabricated to assess the biodegradability of industrial wastewater. Test samples were collected from four different industrial sources i.e. dairy, tannery, pharmaceutical and dyeing industry. In this study, various parameters such as ultimate oxygen uptake (OU_{∞}), reaction rate constant (k), seed dependent biodegradability (α_s) and relative oxygen uptake rate ($R\%$) were calculated to assess the overall biodegradation criteria of the wastewater samples. Respirograms were plotted to evaluate the oxygen uptake rate (OUR) profile. Rate of biodegradation was found maximum for dairy industrial source while sample from dyeing industry exhibited retardation effects on the microbial biodegradation process.

Keywords: Industrial wastewater, differential respirometer, biodegradability, respirogram.

Introduction

Global industrialization is a very important and critical issue in context of the present society. It is often extremely difficult, especially in developing countries, to handle the situation properly ensuring sustainable green environment in and around the state. Certain chemicals or organic matters have caused serious damage to the environment and to human health resulting in suffering and premature death. Many activities are known to cause contamination of soil, surface and groundwater¹. That is why, it is very important to possess the knowledge of the eco-toxicological properties of chemicals or organic matters to maintain environmental stability^{3,4}. 'Biodegradability' is an important parameter due to the simple fact that it allows to know the ecological behavior of substances and products. Information on the degradability of chemicals may be used for hazard and risk assessment⁵.

Being heterogeneous and composed of a wide variety of compounds, it is very difficult to select a unique direct method for estimating the biodegradability of organic contents and bio-kinetic parameters for a wastewater sample. For this purpose some indirect estimation such as determination of biochemical oxygen demand (BOD), chemical oxygen demand (COD) and total organic carbon (TOC) are applied as common laboratory investigations. Method like COD is quite accurate and takes relatively short time for estimating the organic contents. But it cannot differentiate biodegradable organic matter from non-biodegradable one. Due to this fact, BOD test is generally preferred over COD determination in the environmental engineering field⁶.

However, BOD method has some limitations which affect the effluent treatment plant's (ETP) efficiency and management activity. Selection of dilution factor and long experimental duration are very problematic in BOD determination. Due to these limitations, a comparatively efficient method known as 'Respirometry' is now being used widely in wastewater engineering field⁵. Respirometry is the measurement and interpretation of the rate at which a biological system consumes oxygen under well-defined experimental conditions. It can provide much information concerning treatment plant performance, wastewater characteristics, degradability of special concentrated streams as well as parameters needed for mathematical modeling⁷⁻⁹. The oxygen depleted during respirometric experiment is due to the fact that the microorganisms contained in the wastewater or biosolid materials consume oxygen for their own survival (endogenous respiration) and for the oxidation of the biodegradable materials (exogenous respiration). Under aerobic condition, the microorganisms consume oxygen in proportion to the organic matter and biomass present in the sample. In case of headspace gas respirometer, microorganisms in the wastewater sample take aerial oxygen to degrade (oxidize) the organic substances in it. As oxygen is consumed to oxidize the organic substances, carbon dioxide (CO_2) is evolved which is trapped by a special type of scrubber used in the system. As a result, headspace pressure is decreased which is indicated by the fluid movement in the manometer tube of a respirometric device⁵⁻⁹.

Present study comprises two major issues i.e. i. fabrication of a low-cost differential respirometer and other supporting accessories with local technology to encourage academic and industrial personnel of developing countries to build and arrange their own experimental methodologies with self finance and

available technologies and ii. Presenting a comparative parametric tools for making easy operation and reliable management decision on the treatment of different industrial effluents.

Material and Methods

Fabrication of respirometer, collection of samples and subsequent experimental investigations were conducted during February to June, 2012. In the study, wastewaters of four types of major industries were used. They are: i. Dairy Industry ii. Tannery Industry iii. Pharmaceutical Industry and iv. Dyeing Industry. After collection of the samples, floating materials and settled sludge were separated through standard procedure. Laboratory investigations were performed to determine COD and oxygen uptake profile of the samples according to standard laboratory methods¹⁰.



Figure-1
'BIOSUST' differential respirometer integrated with a water bath and peristaltic pump

Measurement of oxygen uptake in respirometer: Oxygen uptake measurement was done by a single reactor differential manometric respirometer (MODEL SRMR-BS103) as shown in figure 1 fabricated at Centre for Environmental Process Engineering Laboratory in SUST. Oxygen uptake values obtained from the apparatus was routinely checked by evaluating the biodegradation test results achieved for the standard Glucose-Glutamic acid (GGA) solution as calibrating substrate and corresponding machine correction factor was incorporated in the test results of various experimental samples⁸. In the respirometric operation, a special reactor vessel filled with 60 ml wastewater sample, 20 ml seed inoculums and 220 ml oxygen saturated distilled water (OSDW) was used to make a total feed volume of 300 ml. Another flask filled with 20 ml seed and 280 ml OSDW was used as compensating reactor. Magnetic stir bars were placed in both reactors for continuous

agitation. After completing the initial setup, the oxygen uptake data against time interval were tabulated on a data book.

Working formula: Referring to the figure 2, Let the initial pressure in both reactors is P_0 (in length of manometric index fluid), their volume up to the meniscus of the index fluid in the symmetrical position is $V_{\text{reaction unit}} = V_{\text{compensating unit}} = V_g$, α is the slope of the manometer legs, A is the cross section of the manometer tube and d is the distance travelled by both meniscus after an consumption of a gas volume V_{consumed} (here, concerned gas is oxygen) in reaction unit¹¹.

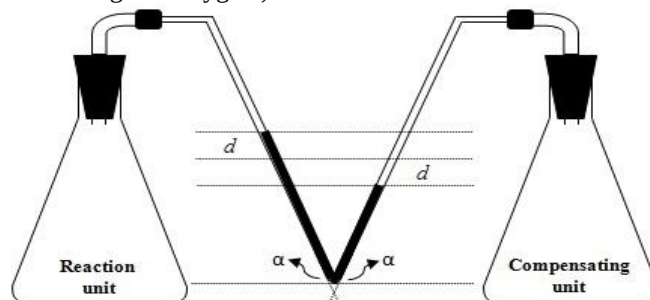


Figure-2
Schematic diagram of a differential respirometer

Then approximately (neglecting higher power of $\frac{Ad}{V_g}$)

$$V_{O_2 \text{ consumed}} = 2d \left(\frac{V_g}{P_0} \sin \alpha + A \right) \quad (1)$$

When choosing $\alpha = 90^\circ$ a "manometer" is obtained for which the equation becomes (provided as usual $A \leq \frac{V_0}{P_0}$)

$$V_{O_2 \text{ consumed}} = 2d \frac{V_g}{P_0} = \frac{2V_g}{P_0} \left[\frac{V_{\text{observed}}}{A} \right] = \frac{2V_g}{P_0 A} V_{\text{observed}} = K * V_{\text{observed}} \quad (2)$$

Now for the present differential pressure respirometer, the total mass of oxygen consumed (at STP) is,

$$V_{O_2 \text{ consumed}} = K * \left[\frac{P}{P_0} * \frac{273}{T} \right] * V_{\text{observed}} \quad (3)$$

Where, $K = \frac{2V_g}{P_0 A}$ = flask constant

Treatment of the experimental data: The data will be treated considering only the manometer reading under the following assumptions. i. The components of the gases in the headspace system follow ideal gas laws and the Dalton's law of partial pressure. ii. The partial pressure of water vapor in the headspace is equal to its saturated vapor pressure at the working temperature. iii. The oxygen concentration in the gas and the liquid phase is always in equilibrium and follows Henry law of gas solubility in liquid. iv. Carbon dioxide evolved in the process is totally absorbed by the scrubber. v. Unidentified anaerobic process is not taking place in any part of the sample.

Parameters to measure: T , A , P , V_g (before respirometric experiment) and V_{observed} (during respirometric experiment)

Literature data to collect: P_0

Brief description of the apparatus: This is a specially designed device based on the principle of headspace gas respirometry. The body structure of the respirometer is organized in two sections: i. Reaction section (situated on the left side of the apparatus) containing two reactors with other accessories and ii. Measuring section (situated on the right side of the apparatus) containing a U tube manometer. The reaction and compensating unit with other control accessories, connected through a U tube manometer, is placed in a water tank associated with a magnetic stirrer. A locally fabricated water bath is incorporated with the reactors by a peristaltic pump which continually circulates the water within the system for maintaining constant thermal background.

Endogenous oxygen uptake measurement of seed: To prepare natural seed inoculums, wastewater was collected from a local food processing industry and cultured it with nutrients under continuous agitation and aeration for specific period of time. Endogenous oxygen uptake of the natural seed was measured in the laboratory with the same respirometer and total five day oxygen consumption was found as 100 mg/L.

Biokinetic parameters: Relative oxygen uptake rate: The relative oxygen uptake rate could be used as an important numerical parameter to compare the degree of biodegradability of different samples for a defined experimental period. The parameter was calculated according to the following equation⁵.

$$R\% = \frac{X_a - X_e}{X_e} \times 100\% \quad (4)$$

Where: X_a = 5 day oxygen uptake of biochemical respiration, X_e = 5 day oxygen uptake of endogenous respiration

Ultimate oxygen uptake and rate constant: Kinetic parameters such as reaction rate constant and ultimate oxygen uptake are calculated from the following first order single exponential relation¹².

$$OU_t = OU_{\infty}(1 - e^{-kt}) \quad (5)$$

Biodegradability: Biodegradability (α_0), of an effluent could be defined as follows:

$$\alpha_0 = COD_{SB,0}/COD_0 = (COD_0 - COD_{\infty})/COD_0 \quad (6)$$

Where the subscript 0 stands for at the time $t=0$ and ∞ stands for the parameter at the time $t \rightarrow \infty$. In a biodegradation process, COD_{SB} (soluble COD) is assumed zero at the time $t \rightarrow \infty$. Conventionally a $BOD-COD$ ratio is taken as a measure for the

biodegradability of an effluent. The BOD of an effluent is defined as the oxygen uptake, OU (amount of oxygen consumed by 1L of the solution), in a biodegradation process in a given time t . The BOD value increases with the biodegradation time, and conventionally, the criterion for the effluent quality is accepted to be BOD_5 (with biodegradation time $t = 5$ days) and the biodegradability is defined as

$$\alpha_s = BOD_u/COD_0 = OU_{\infty}/COD_0 \quad (7)$$

Where BOD_u known as 'ultimate BOD ' is the oxygen uptake for $t \rightarrow \infty$.

From the way of definition of the biodegradability, it becomes evident that α_0 is a seed-independent and α_s is a seed-dependent parameter. But if the oxygen uptake is measured for the biodegradation with naturally grown or adapted microorganism, the biodegradability, α_s , defined by the equation (7) is quite sound for practical purposes. The biodegradability, α_0 , defined by the equation (6) is of theoretical interest and could also be used for practical purposes.

Results and Discussion

Results of the oxygen consumption of the test samples as expressed on a cumulative basis over a 120 hours period are illustrated in figure 3. Calculated values of different biokinetic parameters along with initial COD concentration are shown in table 1.

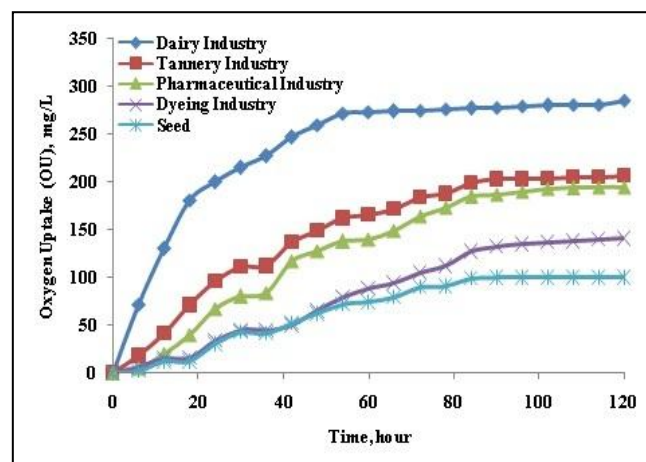


Figure-3
Respirograms for four different industrial wastewater samples with seed inoculums

Table-1
Different biokinetic parameters calculated from respirograms and laboratory investigations

Sample	COD_0 , mg/L	K , hr^{-1}	OU_{∞}	α_s	R%
Dairy Industry	450	0.052	280	0.62	180
Tannery Industry	390	0.021	231	0.59	107
Pharmaceutical Industry	410	0.021	200	0.49	95
Dyeing Industry	520	0.018	200	0.38	40

Ultimate oxygen uptake were found maximum for dairy industry wastewater with a value of 280 mg/L and corresponding reaction rate constant was calculated as 0.052 hr^{-1} which is indicating that high biomass as well as readily biodegradable substances were present in the sample. Both the reaction rate and R% for dyeing industry was found lowest with a value of 0.018 hr^{-1} and 40% respectively. Presence of inhibitory chemicals in dyeing sample may retard the overall microbial degradation process. However, the oxygen uptake rate profiles of the samples as shown in figure 4 illustrate a clear picture of the biodegradation phenomena of the test samples.

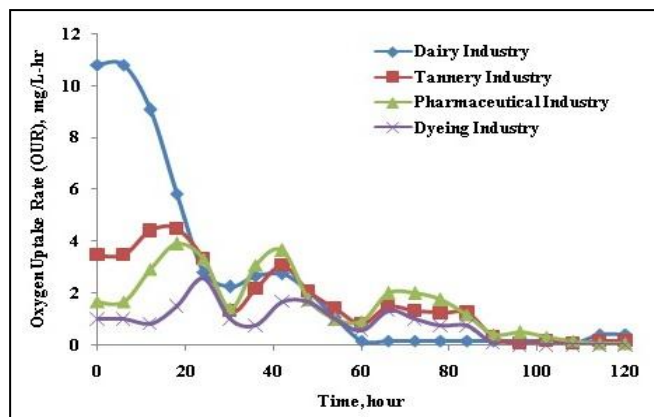


Figure-4
OUR profile for four different industrial wastewater samples

The OUR fingerprint of dairy wastewater shows two major peaks of which the first one occurs within the 10 hours of contact with a value of 11 mg/L-hr representing the oxidation of highly-biodegradable organic constituents. A second group of biodegradable constituents caused a second high OUR peak between thirty and fifty hours followed by a long tail of endogenous respiration profile.

The OUR fingerprints of tannery, dyeing and pharmaceutical industry represent varieties of biodegradable constituents. In these three cases, oxygen uptake between sixty and ninety hours correspond to the biodegradation of a final group of constituents before the OUR returns to endogenous rates. The fact that the OUR returned to endogenous rates indicates that essentially all the organic constituents of the wastewater were degraded.

Conclusion

Respirometry can be a simple cost effective tool for assessing biodegradation criteria of industrial samples as well as other materials. Wastewater with a higher value of R% is easily biodegradable in compare to others. So treatment decision can be taken on the basis of relative oxygen uptake rate (R%). Due to higher biodegradation rate, biological process can be an effective method to treat the effluent of dairy industry. However, in some cases pretreatment is required for removing

special fouling agents. Trend of the biodegradation parameters reveals that wastewater from dyeing industry is quite difficult to biodegrade. For this case, chemical process could be recommended as suitable treatment option.

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