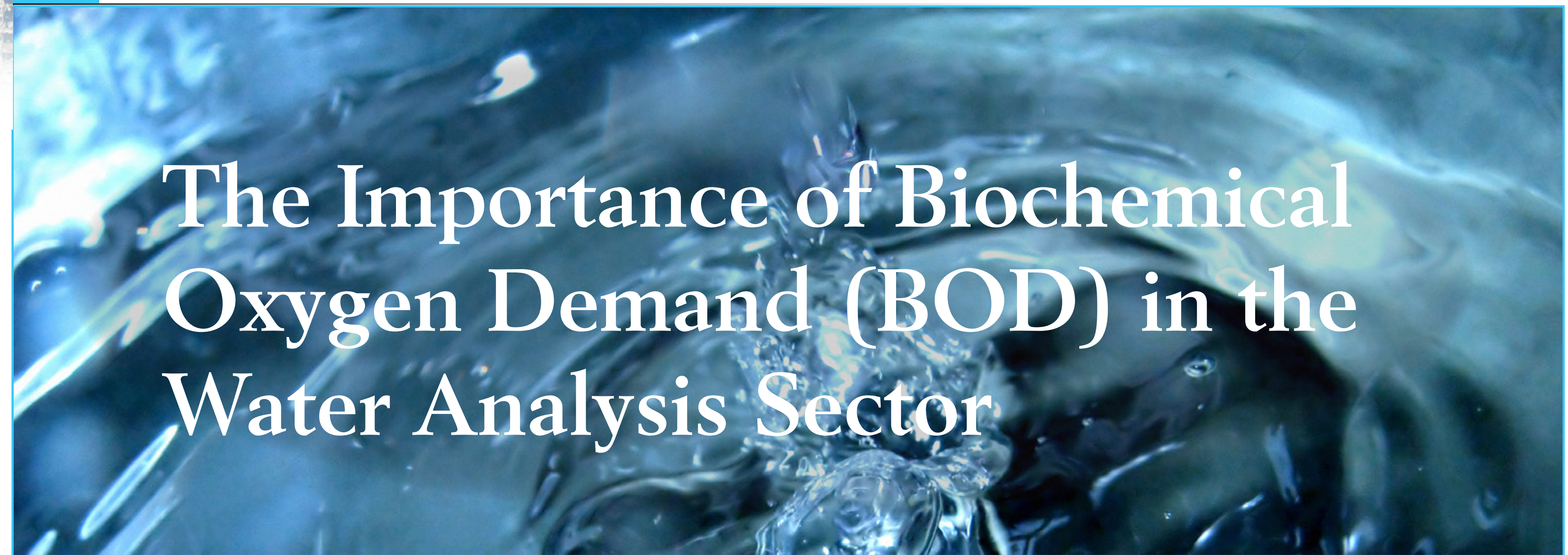

The Importance of Biochemical Oxygen Demand (BOD) in the Water Analysis Sector

A high standard of living involves a high demand for water and, at the same time, causes much greater pollution of this essential element for life. The resultant interference in the natural cycle can often overwhelm natural processes of recovery, so that, in addition to products arising from the decomposition of natural substances (e.g., proteins, greases, carbohydrates) there is a build-up of anthropogenous additives such as pesticides, effluents and garbage, which contaminate drinking water supplies with their toxic or hormonal effects. They may also consume such large quantities of oxygen that water resources become fouled.
To prevent the threat of possible danger to health, or the very existence of certain species, it is essential to determine the quality of a water source before water is drawn off for consumption.

"The conditions for determining BOD are so defined that the quantity alone of the organic materials contained in a sample limits the growth of microorganisms - i.e., the greater the number of organic nutrients present, the greater the material-exchange activity of the bacteria and, therefore, the resultant BOD."

Water Analysis

Water quality is dependent on its constituents, which can be divided into organic and inorganic substances. Given the wide range of natural and synthetic compounds which exist, an analysis of the individual constituents is not a practical proposition and, in any case, a complex affair. In practice, in order to arrive at significant milestones which will permit an evaluation of water quality, rapid methods of analysis are used which consider groups of parameters, rather than the individual parameters themselves. In this connection, BOD is employed to determine the aerobic destructibility of organic substances. As long ago as 1870, Frankland carried out the first BOD measurements, which were very similar to the dilution method in use today (see below).

Terms & Definitions

BOD_n (Biochemical Oxygen Demand after n days) is defined in detail in German Standard DIN 38 409-H51[1] and is associated with certain experimental conditions. It represents the quantity of oxygen which is consumed in the course of aerobic processes of decomposition of organic materials, caused by microorganisms. The BOD therefore provides information on the biologically-convertible proportion of the organic content of a sample of water. This leads to the consideration of these materials in terms of their susceptibility to oxidation by the use of oxygen. BOD is stated in mg/l of oxygen and is usually measured within a period of 5 days (BOD_5).

Principle

The self-cleansing ability of water is based on the activity of microorganisms[2] which are present in practically every area of life as a mixed population3. They feed on salts and organic compounds such as sugar, cellulose and convertible synthetic substances, which they consume in the presence of oxygen (O^2) - that is, biochemical oxidation occurs and the products are partially or completely broken down.

The expression "total decomposition of organic materials" ($C_{org.}$) is taken to mean their oxidation to carbon dioxide (CO_2) and inorganic salts (mineralisation), as covered by expression (1):

$$(1)\ C_{org} + O_2 \xrightarrow{\text{microorganisms}} CO_2 + \text{salts}$$

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The measured consumption of O_2 is the result of microbic conversion. In extremely anaerobic water sources, oxidation processes can also be detected in inorganic materials (e.g., $Fe^{2+} \longrightarrow Fe^{3+}$).

BOD5 and BOD Graph

Determining BOD values after five days (BOD_5) has been adopted as a compromise between a short test-period and the detection of a practically complete biological breakdown of organic materials. With domestic effluents, at 20 °C a complete degradation (= 100 % BOD) is achieved only after 20 days (BOD_{20}); however, after only 5 days, 70 % of the biologically convertible substances are broken down (Hütter, 1994).

Between the BOD_5 and BOD_{20} values, the following pattern applies: for a given interval of time, the same proportion of residual BOD by volume is broken down. At 20°C, the daily degradation capacity is 20,6 % of the relevant residual BOD (Habeck-Tropfke, 1992) which means that, in ideal conditions and with a total BOD (BOD_{20}) of 100 mg/l, after one day there would be a BOD value of 20,6 mg/l. This kinetic represents a first-order reaction. From this relationship it is possible to use the BOD_5 reading to estimate values from BOD_1 to BOD_{20} for domestic effluents. Further, it is possible to establish a relationship with BOD values taken at other temperatures (Pöppinghaus & Fresenius, 1994). The advantages of taking measurements after five days are, therefore, on the one hand, the short amount of time required for the analysis and, on the other, the fact that extrapolation can be carried out.

However, in some countries a testing period of 7 days is performed. A so-called BOD-Graph can be drawn up, in which BOD values are shown in graphical form over a given period of time. A slight deviation from the kinetic described above occurs, caused by fluctuations in the rate of breakdown. In their natural state, the microorganisms first consume the most easily disintegrated material completely, before they attack the

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next C-source. The transfer to the subsequent substratum is linked to an adaptation-phase and this causes a (generally short-term) reversal of material conversion activity (diauxia). Further considerations are based on the possibility that, under given standard conditions, adaptations4 of the inoculated microorganisms, caused by their environment, are cancelled out within the 5-day test period, so that comparable BOD values can nevertheless be obtained (Habeck-Tropfke, 1992).

Interpretation

On the basis of the BOD_n value, assertions may be made both with regard to the characteristics of a water-source and the biological activity of the incubated microflora. For example, where a heavy load is placed on a water source, the water may become anaerobic as a result of a lack of oxygen when effluent with a high oxygen demand (consuming a great deal of oxygen) is introduced, and may "tip over". In another case, the biological capacity of a sewage treatment plant can be tested by comparing the BOD value of a known, control solution with the BOD derived from a microbiosphere being present in the treatment plant.

In general, the following assertions may be made:

• a high BOD indicates a high content of easily degradable, organic material in the sample

• a low BOD indicates a low volume of organic materials, substances which are difficult to break down or other measuring problems (see below)

• the shape of the BOD graph (see above) shows what further information may be gained from the measurements (conformance with the measurement range; problems; pattern of decomposition)

BOD values are generally determined and evaluated in association with other parameters (e.g., COD, DOC, POC, TOC) and this makes them more useful in formulating predictions. For example, if we consider a comparison of the measured BOD value with the COD value:

• a small difference indicates that a large proportion of the organic materials can easily be degraded • a large difference indicates either that the organic loading cannot be easily broken down, or that a problem is present (see below)

BOD detects only the destructible proportion of organic substances and as a general principle is therefore lower than the COD value, which also includes inorganic materials and those materials which cannot be biologically oxidised.

Problems

Biodegradation of materials present in water occurs in two phases. The breakdown of carbons begins practically immediately. In the second phase, nitrification occurs, which also involves the consumption of oxygen. There are two groups of nitrifying bacteria, which catalyse the synthesis in a close relationship. As shown in expression (2) the first group oxidises ammonium (NH_4^+) to nitrite (NO_2), which represents the substratum for the second group, which creates nitrate (NO_3):

$$(2)\ NH_4^+ \xrightarrow{+1\ 1/2\ O^2} NO_2^- \xrightarrow{+1\ 1/2\ O^2} NO_3^-$$

This conversion requires 4.57 mg/l of oxygen per mg of NH_4^+ and has a significant effect on the BOD, which is intended only to detect the consumption of oxygen for carbon oxidation (CBOD). Generally speaking, nitrification sets in after 10 days but may occur within 5 days in samples which are not heavily loaded5 (Habeck-Tropfke, 1992; Hütter, 1994). To repress this undesirable occurrence, nitrification inhibitors, such as NAllylthiourea (ATH) or 2-chloro-6-(trichloro methyl) pyridine (CTMP) can be added. If it is desired to analyse oxygen consumption of the nitrification in itself (N-BOD) a comparison can be made of samples both with and without nitrification inhibitors.

In contrast to this, inhibitors or toxic substances can reduce biological activity in water, or even kill off the organisms completely. Even so, it may be of interest to determine the BOD of a sample of this kind. This can be achieved with a dilute solution, in which substances such as metabolic poisons are below the concentration at which they would have an effect on aerobic decomposition.

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Procedures

There are two standard procedures, which are equivalent to each other under given conditions: the first is the dilution method to DIN 38409-H51 and gives the so-called dilution BOD_n over a period of n days. This is in most cases an officially-approved procedure. It is cumbersome and includes an optimization for test conditions required for the decomposition process at 20 °C. The oxygen content is measured directly in the water itself.

The more simple procedure is to measure oxygen depletion $Z_{S(n)}$ during a period of n days (as DIN 38409-H52), and this method is used for internal monitoring purposes. The respirometric method (manometer) is based on the fact that the oxygen converted to carbon dioxide is removed from the gaseous spectrum via the sample by means of a CO_2 adsorbent, usually potassium hydroxide (KOH). The resultant pressure drop can be measured in the closed system and is proportional to the volume of the consumed oxygen. The so called oxygen depletion value ($Z_{S(n)}$) can be interpreted as a BOD_n value where:

1. only the concentration of organic substances limits oxygen consumption in the samples and

2. the investigation takes place at 20 ± 1 °C.

In the past, pressure measurements were usually carried out with a mercury manometer. However, this can be done more simply and reliably, using an electronic BOD-OxiDirect from Lovibond.

Following measurement, the results are stored and can be called up to the display at any time in mg/l BOD. In particular, this eliminates the use of mercury, which can be dangerous to health (see Paras. 16 and 19 of the German Dangerous Substances Act).

Further Applications for the BOD Method

BOD is a criterion for aerobic, biological decomposition. A special application is found in water analysis as the BOD_n value. Variations of the method can lead to other possible applications, such as the following:

• checks on the aerobic decomposition of environmental chemicals (e.g., biodegradability to OECD 301) within 28 days

• determining the respiration of soils, sludge, sediment, garbage and liquids

• toxicity tests in soils, sludge, sediment, garbage and liquids

• bio-activity determination in various environ mental compartments

• performance checks in a sewage treatment plant

• determining the respiration rates of living beings (e.g., R/Q-value (respiration quotient), investigations of stress)

• oxygen consumption of cell cultures under the influence of various tests in the medicinal & pharmaceutical industry

Typical Values

Examples of typical BOD_5 values for natural and anthropogenous water sources shown in Table 1 are given for purposes of general guidance:

*Table 1: Typical BOD_5 values (taken from: *Pöppinghaus & Fresenius, 1994; Hütter, 1994; =LAW-RPL, 1997; SP: municipal sewage treatment plant; GKl.: saprobity (water quality classification))*

WATER	BOD_5 [mg/l]	EFFLUENT/ OUTFALL	BOD_5 [mg/l]
GKl. IV	>15	Blood*	160.000 - 210.000
GKl. IV/III	20-10	Liquid manure	7.000- 18.000
GKl. III	13-7	Whey*	45
GKl. III/II	10-5	Mosel River (D)	1,0 - 5,1
GKl. II	6-2	Nahe River (D)	<1,0 -5,1
GKl. II/I	2-1	Rhein River (D)	<1,0 - 1,9
GKl. I	≤1	SP-inlet	300-350
Drinking water	<1	S-outflow	<25

Bibliography

DIN: [German Standards] Deutsches Institut für Normung e.V., Beuth-Verlag GmbH, Berlin, Germany.

Habeck-Tropfke, 1992: Abwasserbiologie [The Biology of Effluents], 2nd edition, Werner-Verlag.

Hütter, 1994: Wasser und Wasseruntersuchung [Water & Water Investigations], 6th edition, Otto Salle Verlag Frankfurt am Main, Germany.

LAW-RPL, 1997: Data Record of German Rivers in 1995, offprint from Landesamt für Wasserwirtschaft Rheinland-Pfalz, Germany.

Pöppinghaus & Fresenius, 1994: Abwassertechnologie [Effluent Technology], editors: Institut Pöppinghaus GmbH und Institut Fresenius GmbH, 2nd edition, Springer-Verlag, Berlin, Germany.

Footnotes

[1] conforms in factual content with ISO 5815 (1983), German Standard DEV and Austrian Standard ÖNORM ISO 5815 (Hütter, 1994)

[2] bacteria, fungus, archaea, algae and protozoa

[3] groups of microorganisms exist alongside each other and are subject to mutual interaction

[4] adaptation of micro-organisms to individual environmental conditions (e.g., seasonal temperatures; various xenobiotics, etc.)

[5] e.g., at the outflow from a sewage treatment plant