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Simple systems to characterize wastewaters - the case of biomethane potential

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Abstract:

When the design or operation of wastewater treatment plans is considered, it is important to measure the polluting loads to be treated. These loads are calculated as the product of a daily volume of liquid waste and the average concentration of the pollutant. Of course, to do this, the sample must correctly represent the liquid effluent. Extensive analytical equipment can be used to characterize the numerous compounds contained within wastewaters with high accuracy but cheap, simple, and even sometimes mobile equipment are mostly used for the daily operations of treatment plans. In this regard, we present the use of a pH-respirometer, based on manometric methods, to characterize wastewaters that will be treated by aerobic biological systems. Another type of biological treatment system is based on anaerobic processes when the effluents have a high content of biodegradable organic compounds. Anaerobic digestion is very attractive as it is possible to produce a valuable gas (biogas) out of the waste instead of consuming energy and oxygen to realize an aerobic treatment. In this paper, we will present the meaning of biochemical methane potential (BMP) curves and compare those curves to respirometric curves such as biological oxygen demand (BOD) tests.

Keywords: **anaerobic digestion, biogas, BMP, treatment, wastewater.**

Classification number: **2.2**

Introduction

Manometric methods, also called respirometers, have been used for decades to measure the main parameters defining the organic pollution of wastewaters, such as BOD (biochemical oxygen demand) or COD_b (biodegradable chemical oxygen demand). In fact, BOD (or COD_b) are not compounds but properties of wastewater. For known compounds, the theoretical COD_b can be calculated. For example, with an aerobic system and tertiary compounds (C, O, H):

$$C_nH_aO_b + \left(n + \frac{a}{4} - \frac{b}{2}\right)O_2 \longrightarrow nCO_2 + \frac{a}{2}H_2O \quad (1)$$

It results that COD_b will serve to evaluate the quantity of oxygen that is needed to totally oxidize the compound. This information is very important as it is estimated that 80% of the energy consumed in a wastewater treatment plant (WWTP) is related to the oxygen needed for the treatment. As oxidation is an electron transfer reaction, it is also possible to estimate the potential chemical energy associated with the compound. BOD aims at the quantification of the fraction of the COD that can be oxidized by biochemical processes, mainly as biological growth of aerobic bacteria.

If we combine oxidation and bacterial growth for a substrate such as glucose, one discovers a reaction as in Eq. (2):

$$24C_6H_{12}O_6 + (59+5x)O_2 + (17-x)NH_3 \longrightarrow (17-x)C_5H_7O_2 + (59+5x)CO_2 + (110+2x)H_2O \quad (2)$$

with a value for x between zero (growth) and 17 (full oxidation), the value $\frac{(17-x)\times M_{C_5H_7NO_2}}{24\times M_{C_6H_{12}O_6}}$ is known as the cell yield, Y, here expressed in g/g. From this equation, we see that even for a fully biodegradable compound such as glucose, the cell yield value depends on the degree of use/oxidation of the substrate. In a continuous system where the

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biomass is known (and high) there will be nearly no biomass production (x=17) and the substrate is oxidized to provide energy to the bacteria. In the present case, the concept of feed/microorganism ratio (F/M) expressed in energy (of equivalent O_2) is equal to $\frac{24\times 192}{160\times(17-x)}$.

When we measure BOD, we perform a batch test starting with a high F/M ratio and wait until the formed biomass is partly or totally degraded by the endogenous process under aerobic conditions. Those concepts can be associated with the classical growth curve of micro-organisms as shown in the following figure (Fig. 1).

mixing system, usually a magnet, is used to ensure that the liquid is mixed well and the equilibrium between gas and liquid phases is rapid.

BMP tests are usually done in GSS type bioreactors. Instead of measuring the consumption of a reactive (O_2) gas as in the BOD tests, the product of the serial reactions (biogas) is quantified in the BMP tests. As the quantity of expected biogas is much higher than the quantity of oxygen consumed, a pressure increase in the gas phase could have a negative effect on the metabolic activities, i.e. part of the biogas can be evacuated out of the bottle. If the biogas flows out of the bottle, we have a flowing gas, static liquid (GFS)

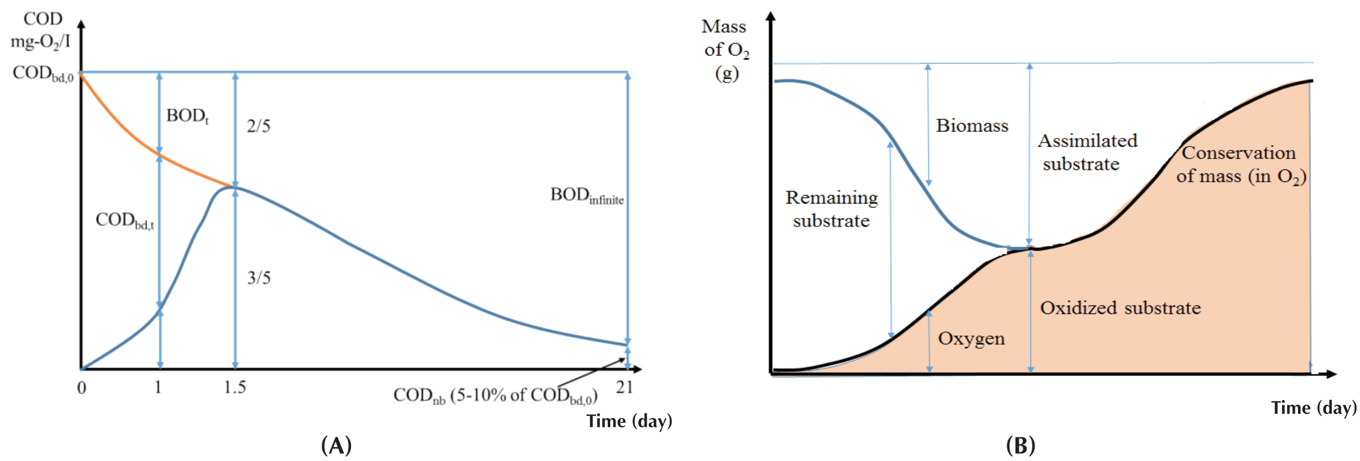

Fig. 1. The relation between the growth curve and BOD test in terms of (A) COD and (B) mass of oxygen.

In fact, when we perform a BOD test, we are measuring the cumulative oxygen consumption, which is the inverted part of the upper region of the graph. BMP tests have many similarities with BOD tests that will be described in the following paragraphs, but instead of a pressure decrease in the bottle due to the oxygen consumption, we observe a pressure increase due to biogas (CO_2 and CH_4) production. Holliger, et al. (2016) [1] recommend not to exceed 300 kPa in the bottle.

In this paper, the fundamental, as well as the applicability, of BMP tests in the characterization of wastewaters is presented.

Materials and methods

BOD is usually measured in closed respirometers operating in batch mode. More precisely, it is a static gas, static liquid (GSS) type respirometer, which means that measurements are done in the gas phase (G) by manometric methods and liquid and gas are static (closed system). A

system, which means that we need to measure the volume of collected gas (volumetric method) or the gas flow rate. Those methods must be combined with gas chromatography to measure the CO_2/CH_4 ratio, except if the CO_2 is adsorbed in a separate system and remaining CH_4 is measured subsequently.

Reliable and cheap sensors to measure gas flow rates over a very small range are not easy to find. For example, the measurement in the bioprocess control system is based on small volumetric equipment. Otherwise, storage can be done but the mass balance will be more complicated.

If the test is aiming at measuring the total production of methane (the energy-containing gas) a separation of CO_2 and CH_4 must be selected, most often using absorption of CO_2 in an alkaline solution. In the case of BOD, the quantity of CO_2 produced is small and can be neutralized in a small volume containing KOH directly integrated into the cap, which is not enough in the case of anaerobic systems.

Here, a simple concept of a BMP device that can simultaneously measure biogas and CH_4 is demonstrated (Fig. 2). This system contains two bottles: the first bottle [bottle (1)] is an anaerobic reactor, in which the bacteria use organic compounds as food and release biogas; and the second [bottle (2)] is a CO_2-absorbed part that contains an alkaline solution, e.g. NaOH or KOH.

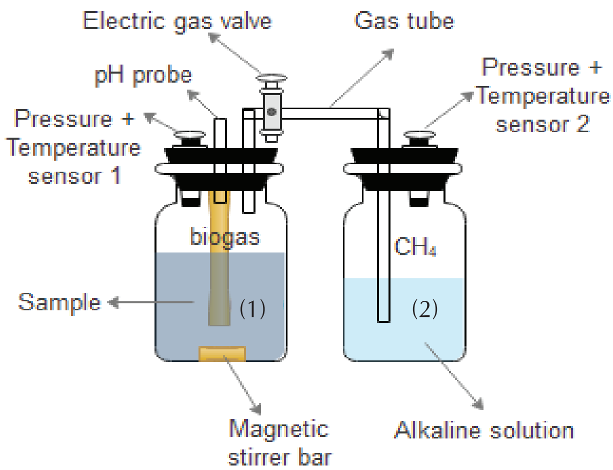

Fig. 2. A simple concept of a BMP device. Bottle (1) is the anaerobic reactor, and bottle (2) is the CO_2 absorbed part.

These bottles are connected by a gas tube. The movement of the gases between the two bottles is controlled by an electronic valve that is only opened when the pressure in bottle (1) is higher than a pre-set value, e.g. 1.2 bar. Then, the biogas will move through the gas pipe and be purged into the NaOH solution in bottle (2) to absorb all CO_2. The amount of gases could be calculated from the pressure and temperature data between valve opening times. To do that, each bottle is equipped with one pressure sensor and one temperature sensor.

Regarding the F/M ratio, it is quite different for aerobic and anaerobic measuring systems. In aerobic systems, we start with very high F/M ratios, but the kinetics are rapid and the O_2 consumption is fast. Usually, we consider that at the end of the test the final oxidation state is reached, including the oxidation of the synthetized biomass. The anaerobic metabolism is much slower and to reach a final stage within approximately the same period, it is necessary to start with a much lower F/M ratio. Often the inverse ratio, so-called ISR for inoculum-substrate ratio (expressed in g VS/g VS) is used in the BMP literature. Usually, tests are performed with an ISR in the range of 2 to 4. The BMP tests are performed at a loading rate of 20 to 60 g of total VS/l. If we take an average ISR ratio of 3, this will lead to a substrate loading rate of 5 to 15 g VS (substrate) per litre. If we compare with BOD tests, loading is less than 8 mg BOD/l in the case of the dilution method and in any case less than 2 g BOD/l for the manometric method.

In a closed anaerobic system, the electron quantity remains unchanged. Thus, the electrons (COD) contained in the substrate will be partly contained in the formed biomass and mostly in CH_4. As the yield factor, Y, is small in anaerobic systems, especially at a very small F/M ratio, we can assume that the final yield factor for CH_4 is close to 0.35 Nm^3 kg COD^{-1} (degraded). Taking into account a usual F/M ratio of g COD/l, we should observe a biodegradable compound production of litres of methane at the end of the test. This means that the average volume of biogas should be around 500 ml at 35°C. Himanshu-Teagasc, et al. (2017) [2] compared manometric methods and automatic volumetric methods to measure the BMP.

Several norms, aimed at standardization of BMP tests, exist such as DIN 38414 TL8 (1985), ASTM D 5210 (1992), ASTM D 5511 (1994), ISO 11734 (1995), and ISO 15985 (2004) have been developed but various international efforts are still being made to harmonize the standards and to improve the accuracy of the method.

More details about the test methodology, including sample preparation, inoculum, number of replicates, blank assays, expression of the results and standard deviation, and criteria for the rejection of results can be found in Holliger, et al. [1].

Results and discussion

Applications of BMP tests

We present some usual applications of BMP tests.

Measurement of total quantity of biogas (methane) that can be produced from an effluent: the BMP experimental curve has a pattern quite similar to a BOD curve (Fig. 3).

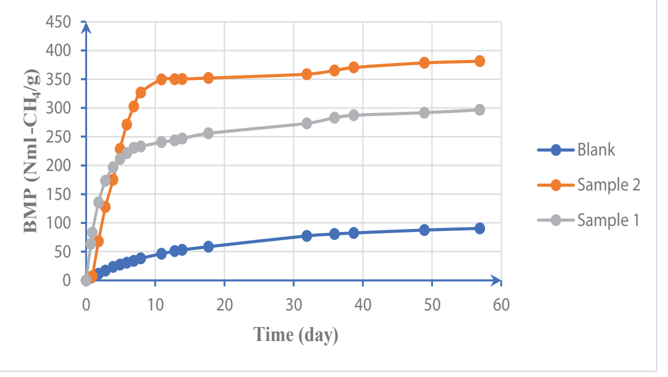

Fig. 3. Example of the BMP curves in a set of BMP measurements with a sample of municipal solid waste (Sample 1) and cellulose (Sample 2).

Consequently, similar equations can be used to describe the curve. One of those models may be written as:

$$BMP_t = BMP_{infinite}\left(1 - e^{-Kt}\right) \quad (3)$$

for which various fitting methods can be used. Such fittings will yield $BMP_{infinite}$ (which is the asymptote of the curve) and *K,* which is an apparent first-order kinetic coefficient; both useful information. Of course, the BMP of the blank (the seeming) must be deducted from the initial curve. More detailed methodology to fit these types of models, including sensitivity analysis, can be found in Da Silva, et al. (2018) [3].

If the elemental composition of the substrate is known, for example assuming the formula $C_nH_aO_bN_c$, the anaerobic degradation can be written as:

$$C_nH_aO_bN_c + \left(n-\frac{a}{4}-\frac{b}{2}+\frac{3c}{4}\right)H_2O \longrightarrow \left(\frac{n}{2}+\frac{a}{8}-\frac{b}{4}-\frac{3c}{8}\right)CH_4 + \left(\frac{n}{2}-\frac{a}{8}+\frac{b}{4}+\frac{3c}{8}\right)CO_2 + cNH_3 \quad (4)$$

If we consider the BMP as the volume of dry methane (at 273.15 K and 1 atm) per g of VS substrate, then the BMP value can be calculated as:

$$BMP = 22400 \times \frac{\left(\frac{n}{2}+\frac{a}{8}-\frac{b}{4}-\frac{3c}{8}\right)}{(12n+a+16b+14c)} \quad (5)$$

For an anaerobic system, the same tertiary compound as in Eq. 1 will be transformed into biogas as:

$$C_nH_aO_b + \left(n-\frac{a}{4}-\frac{b}{2}\right)H_2O \longrightarrow \left(\frac{n}{2}+\frac{a}{8}-\frac{b}{4}\right)CH_4 + \left(\frac{n}{2}-\frac{a}{8}+\frac{b}{4}\right)CO_2 \quad (6)$$

The molar ratio can be deducted from Eq. (6):

$$\frac{n_{CH_4}}{n_{CO_2}} = \frac{\left(\frac{n}{2}+\frac{a}{8}-\frac{b}{4}\right)}{\left(\frac{n}{2}-\frac{a}{8}+\frac{b}{4}\right)} = \frac{4n+a-2b}{4n-a+2b} \quad (7)$$

Thus, the CH_4/CO_2 ratio depends on *n*, *a*, and *b* values. For carbon (*n*=1), the ratio is equal to $\frac{4+\frac{a}{n}-\frac{2b}{n}}{4-\frac{a}{n}+\frac{2b}{n}}$. Moreover if we compare equation (6) to equation (1) we have $n_{CH_4} = \left(\frac{n}{2}+\frac{a}{8}-\frac{b}{4}\right) = \frac{n_{O_2}}{2} = COD$ (expressed in $\frac{1}{2}$ mol-O_2/l). The combination of both ratios yields *a* and *b* values.

In fact, biogas also contains some water. The BMP is defined as the quantity of dry methane that is produced by the degradation of 1 g of VS substrate. If the water vapor is not removed before analysis, then a correction can be made to calculate the contribution of water vapor in the biogas. Strömberg, et al. (2014) [4] suggested the following equation to calculate this contribution:

$$P_w = 10^{8.1962-\frac{1730.63}{T-39.724}} \quad (8)$$

with P_w being the vapor pressure (mbar) and T in Kelvin.

Distinguishing some fractions of the substrate (fractionation) in the conditions of the test: Pearse, et al. [5] suggested some changes to the methodology to apply BMP tests to landfilled municipal solid wastes. To quantify the kinetic (and parameters) of the main processes, of course, the *K* value of Eq. (3) already provides an evaluation of an apparent first-order kinetic equation. But more sophisticated models can be used, as will be presented.

Rapid evaluation of the effects of some operating parameters (pH, temperature, F/M ratio…) of substrates and co-substrates: for example, Biswanath Sahaa, et al. (2018) [6] found an optimal F/M ratio of 2, which is rather high, to degrade Ageratum conyzoides. Hobbs, et al. (2018) [7] also tested the optimal ratio of inoculum and substrate for various food wastes using BMP tests and obtained an optimal F/M ratio of 1.42 g COD (substrate)/g VS (inoculum). Tan, et al. (2018) [8], using BMP tests, studied the inhibitory effect of ammonia and/or sulphide on the methane yield with acetate and propionate as a carbon source. Krause, et al. (2016) [9], studied the optimal ratio between waste and seeming and obtained, in this case, an optimum of 3 g COD/g VS. We can observe that those tests were performed at ISR values much lower than the recommended values for BMP tests. To test the optimal proportion of various substrates on the efficiency of a digester, BMP tests were performed by Grosser (2018) [10] that studied the optimal ratio between sewage sludge, organic fraction of municipal solid waste, and grease trap sludge, to increase methane production. Rodrigues, et al. (2019) [11] evaluated the effect of temperature and municipal waste particle size also using BMP tests.

Possible combinations of BMP tests with other tools

Other developments can be considered as Fuzzy logic utilization to get more rapidly the results of the tests. Fuzzy logic is an interesting tool to predict the final values of BOD or BMP test using the time evolution of some parameters, without using sophisticated metabolic models.

Using of databases to collect the results of BMP tests in order to provide preliminary estimates of biogas potential for many substrates, co-substrates, and their mixtures: Holliger, et al. (2016) [1] recommend proceeding regularly at positive controls on the substrate whose BMP are well known, such as micro-crystalline cellulose or tributyrin, to check the equipment and quality of the seeming. Rodrigues, et al. (2019) [11] compared methods to estimate BMP results from some preliminary analyses (elemental analysis, organic fraction, COD or IR spectrum). Suitable results could be obtained with multivariable regressions, especially if biodegradability (particularly lignin content) is taken into account. Edwiges, et al. (2018) [12] studied the BMP of various fruit and vegetable wastes and predicted the result using multiregressions. That work suggested that HCV (high calorific value) could be one interesting regression factor. To facilitate the development of such databases, such preliminary analyses should be done systematically.

Combination of BMP test with dynamic mathematical models in order to fit some parameters of those models: aerobic treatment processes have been described by mathematical models including stoichiometry and kinetics of the various biological processes. For example, the ASM (activated sludge models) of IWA can also be used to describe respirometers as aerobic bioreactors and use the models to quantify some characteristics of the substrate such as rapidly or slowly biodegradable fractions of a complex substrate. This is called fractionation of the substrates and this tool is now very useful in the field of modelling and control of bioreactors.

Similarly, mathematical models such as ADM1 (Anaerobic Digestion Model 1) have been developed to describe anaerobic bioreactors, but it seems that, so far, the link to describe the operation of BMP reactors has not been developed. In this case, the BMP system would be seen as a smart sensor system.

Conclusions

BOD tests have been developed more than a century ago and used across many applications. The development of dynamic mathematical models to describe the behaviour of aerobic bioreactors yielded the development of various types of respirometers, including GSS-type ones such as BOD meters. Using these in combination with mathematical models to characterize some fractions of substrates and to fit parameters of the models, these respirometers can be called a smart sensor.

BMP tests were developed more recently, but the rapid development of anaerobic digesters to produce green energy should pave the way to the development of smart BMP sensors.

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