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► **To cite this version:**

P. Namour, N. Jaffrezic. Sensors for measuring biodegradable and total organic matter in water. Trends in Analytical Chemistry, 2010, 29 (8), p. 848 - p. 857. 10.1016/j.trac.2010.04.013. hal-00547575

HAL Id: hal-00547575

<https://hal.science/hal-00547575>

Submitted on 16 Dec 2010

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1 **Sensors for measuring biodegradable and total organic matter in water**

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7 **Abstract:** This critical review spans the past two decades and outlines sensors developed for
8 measuring total (TOM) and biodegradable organic matter (BOM) in water. We report the state
9 of the art of the most significant technologies. Although the focus is on *in situ* devices, we
10 also mention on-line techniques able to lead to sensors *sensu stricto* and discuss them as
11 possible emerging technologies. We divide the review into sections: (1) TOM; and (2) BOM.
12 We first briefly outline each technique then analyze the published literature. We conclude
13 with recommendations on the technological choices geared to specific research topics.

14 **Keywords:** biodegradable organic matter, Biochemical Oxygen Demand, Chemical Oxygen
15 Demand, Emerging technology, In situ device, On-line technique, sensor, water, river, BOD,
16 COD.

17 Abbreviations:

18 **ANN:** Artificial Neural Network; **BDD:** Boron Doped Diamond; **BOC:** Biodegradable
19 Organic Carbon; **BOD:** Biochemical Oxygen Demand; **COD:** Chemical Oxygen Demand;
20 **DOM:** Dissolved Organic Matter; **DON:** Dissolved Organic Nitrogen; **MFC:** Microbial Fuel
21 Cell; **OM:** Organic Matter; **PCA:** Principal Component Analysis; **PLS:** Partial Least Square
22 (regression method); **TOC:** Total Organic Carbon; **TOM:** Total Organic Matter; **TON:** Total
23 Organic Nitrogen; **WWTP:** Wastewater Treatment Plant.

1 Although 'Organic Matter' (OM) is a term that appears easy to decipher, paradoxically it
2 resists all attempts at formal chemical definition. Thus, since the beginnings of organic
3 chemistry, OM has been defined by its oxidizability, originally by calcination (volatile
4 suspended solid) and then, early in the twentieth century, by wet oxidation methods: chemical
5 oxygen demand (COD_{Cr}) to determine total OM (TOM) and five-day biochemical oxygen
6 demand (BOD_5) to determine biodegradable OM (BOM). The COD_{Cr} method uses a two-hour
7 reflux reaction in hot sulfuric acid and two highly toxic ions: Cr(VI) as oxidant reagent, and
8 Hg(II) as masking agent camouflaging the interference from the chloride. These two toxic
9 substances condemn this method. Furthermore, running a back titration of the excess
10 dichromate is too insensitive for measuring TOM in river samples [with limit of Detection
11 (LoD) = 30 mg/L]. The BOD_5 method is based on aerobic microbial consumption of BOM at
12 a temperature of 20°C, in the dark and over an elapsed period of five days. It is cheap, but
13 time-consuming (five-day incubation period) and labor-intensive, requiring skill to get
14 reproducible results. Its precision is around 15% - 20%. Moreover, BOM is highly unstable
15 and is partly destroyed during sampling, transport, storage, and test preparation. Even when
16 using a refrigerated sampler, up to 20% of BOM in raw sewage can be lost within the space of
17 24 hours. In the second half of the twentieth century, these limitations prompted the
18 development of instrumental methods based on elemental analysis of OM [e.g. total or
19 dissolved organic carbon (TOC or DOC) or nitrogen (TON or DON)]. These analyses do
20 offer alternatives to COD, but unfortunately there is no elemental method for BOD_5 . The
21 major drawbacks of these methods are acquisition and operation costs, and the need for
22 sampling and sample handling before laboratory analysis.

23 All current conceptual river models focus on daily and seasonal quantitative and qualitative
24 OM variations. The growing focus on the protection, remediation and restoration of aquatic
25 environments has generated an urgent need for advanced monitoring technology, especially in

1 response to new legislation. However, instrumental techniques cannot affordably deliver the
2 large datasets demanded by these new legislations. The urgent need for continuous, *in situ*
3 monitoring techniques has driven the search for simple, continuous and in-situ measurement
4 of OM content and time-course evolution. Sensors meet these needs.

5 This article focuses on sensors for TOM (section 2, Table1) and BOM (section 3). Table 2
6 recaps sensors that use Clark electrodes while Table 3 recaps the other techniques. Note that
7 there is confusing overlap in some publications between COD_{Cr} and the permanganate method
8 (COD_{Mn}). COD_{Mn} has 40-50% lower oxidation power, and therefore sometimes gives lower
9 results than BOD_5 . Another source of confusion is the use of various organic compounds as
10 standards, from glucose through to phthalic acid, which skews conclusions on the oxidizing
11 power of the methods proposed.

12 **1. Total Organic Matter**

13 **1.1. Photocatalytic Sensors**

14 These sensors use light to oxidize OM (Fig. 1). TiO_2 is used either alone [1-7] or mixed with
15 other oxides [8, 9]. ZnO alone gives good results [9]. Photocatalysis presents the low LoDs
16 ($COD > 1$ mg/L) needed for river monitoring, with satisfactory reproducibility, but lacks
17 oxidizing power compared to COD_{Cr} . An Australian team [10] coined the acronym “PECOD”
18 for “photoelectrochemical oxygen demand”, a technique based on a photoelectrocatalytic
19 degradation process in a thin-layer photoelectrochemical cell. The method is rapid, at around
20 2 min for phthalic acid, and concurs well with COD_{Cr} . $Ti/TiO_2/PbO_2$ electrodes gives good
21 results compared with COD_{Cr} , and the relative bias is below 6.0% [11]. Some authors have
22 compared their results with COD_{Mn} values or used readily-oxidizable standards (e.g. glucose
23 or glutamic acid).

1 Finally, photocatalysis requires close contact between sample and catalyst, and an injection
2 device has to push the sample through these sensors. However photocatalysis has found
3 industrial applications as a pretreatment for toxic industrial wastewater {chemical reduction
4 of anthraquinone, phthalocyanide and azo-dyes in effluents from textile factories [4], or
5 degradation of lignin [12] or phenols [9]}.

6 **1.2. Electrocatalytic Sensors**

7 Electrocatalysis uses electrodes to enhance chemical reactions (Fig. 2). Antimony-doped
8 anode SnO₂ [13], PbO₂ [14], Cu/CuO [15] and BDD [14, 16] give linear relationships with
9 COD_{Cr}. AgO-CuO graphite electrodes give around 80% of COD_{Cr} [17]. The highest oxidation
10 rates have been achieved in presence of hypochlorite electro-generated from chlorides [13].
11 BDD anodes present good stability allied with a wide potential window, and can totally oxidize
12 TOM [18] as phenols [14], PAHs [19] or dyestuffs [13, 20], yielding a COD removal rate
13 close to 100%.
14 The drawback is electrode inactivation by metals, requiring cleaning procedures {e.g.
15 polishing or the application of high-potential anodic polarization [21]}.

16 **1.3. Chemiluminescence (CL)**

17 Chemiluminescence (CL) is based on the measure of photons emitted by a chemical reaction.
18 Mn(VII) ions showing CL (at 690 nm) when reduced to Mn(II) state are used to determine
19 TOM [22]. The luminol-H₂O₂-CL reaction is used to amplify Mn(II) [23], surplus Mn(IV)
20 [24], or reduced Cr(III) [25, 26]. The combination of UV-photolysis and CL detection of free-
21 radicals gives results that match to COD_{Mn} [27]. The electro-regeneration of Ru(bpy)₃²⁺
22 suppresses reagent consumption and has been applied successfully to determine oxalate and
23 ethanol [28].

1 **1.4. Optical Sensors**

2 The fact that OM exhibits strong absorbance between 200 and 350 nm, and mainly at 254 nm
3 (UV_{254}), has meant that UV-Visible absorbance is widely used to quantify TOM in water.

4 UV-visible sensors allow multiparametric determinations without reagents, but their
5 applicability remains limited by the properties of the water matrix (turbidity, OM
6 composition, nitrate/nitrite absorbances), and mathematical data reprocessing is required.
7 Spectral deconvolution gives erratic correlations with COD, ranging from 0.57-0.58 to 0.90
8 [29], even for effluents of the same origin. The fluorescence properties of OM have been also
9 successfully used [30].

10 **1.5. Commercially available sensors**

11 Commercially available OM sensors couple UV-scanning with spectral deconvolution. The
12 Spectro-lyzer (s::scan, Vienna, Austria) gives a good correlation for low COD, although DOC
13 concentrations were not correlated [31]. The manufacturer's calibrations tend to
14 underestimate high concentrations and overestimate low concentrations. These deviations
15 could be reduced after adjustments based on known standards and further improved by
16 specific models integrating the major shifts in the water matrix [32].

17 Some authors have used an "off-line" calibration algorithm based on PLS-regression [33].

18 There is also a miniaturized voltammetric sensor comprising five working electrodes (Senset
19 AB, Linköping, Sweden) [34].

20 **2. Biodegradable Organic Matter**

21 **2.1. Respirometer**

22 Respirometry assesses metabolism rates in living organisms by measuring their oxygen
23 consumption. In rivers, oxygen consumption is closely related to microbial activity, which is

1 itself related to the amount of BOM, so biosensors have been developed based on
2 respirometry to measure the BOM content in water simply in just a few minutes. This
3 principle mirrors BOD₅, which is also a respirometric technique. The majority of
4 commercialized BOD equipment measures oxygen through a biofilm ([http://www.swift-](http://www.swift-wfd.com)
5 [wfd.com](http://www.swift-wfd.com)).

6 **2.1.1. Clark Electrode**

7 Microorganisms are entrapped on columns [35] or immobilized on membranes[36-43]. The
8 microorganisms used are pure strains with or without enzymes [36-39], consortia of mixed
9 strains , or inocula from wastewater-treatment plant (WWTPs) [39, 40], synthetic wastewater
10 [41], brackish waters [43] or standardized microbial cultures [42]. Inocula metabolize a
11 broader spectrum of substrates but present a less stable composition and are consequently less
12 constant over time. Furthermore, while dynamic measurements offer a quicker response and a
13 broader detection area, steady-state measurements give reliable results in the concentration
14 range 15–50 mgO₂/L [40]. BOM can also be monitored in anaerobic processes [44]. Various
15 papers have reported on biofilm optimization [45], immobilization mode [37, 38] and
16 inoculum renewal [41]. Electrolyte consumption and anodic oxidation limit the Clark
17 electrode lifetime, and require the anode surface to be ground of and regular electrolyte
18 renewal to avoid signal drift.

19 Ozonation, or photocatalytic oxidation on TiO₂ before passing over a biofilm, gives a variant
20 of chemical bio-sensor or photo-biosensor. However, these hybrid techniques partially attack
21 refractory OM {e.g., tannic or humic acids, which can be biodegraded up to 51.8% and
22 38.4%, respectively [39]}, and overestimating BOM introduces confusion between TOM and
23 BOM.

24 **2.1.2. Optical Biosensors**

1 Optical respirometric biosensors measure microbial growth (1) directly from emitting bacteria
2 or (2) indirectly via an oxygen-sensitive colored indicator.

3 Naturally-emissive bacteria such (e.g., *Photobacterium phosphoreum*) are applied for BOM
4 measurement [46], and the commercially-available toxicity analyzer Microtox employs the
5 emitting strain *Vibrio fischeri* as test organism. Bioluminescent biosensors can also use
6 genetically-engineered heterotrophic microorganisms, in which the *lux* genes from *V. fischeri*
7 are integrated to measure microbial growth [47].

8 Another direct optical approach is to measure NAD(P)H (reduced forms of NAD(P))
9 coenzymes present in all living organisms for redox reactions. While NAD(P)H are
10 fluorescent (340/460 nm), their oxidized counterparts are not. Since NAD(P)H concentrations
11 depend on living cell count and their metabolic activities, the fluorescence intensity from
12 NAD(P)H reflects the amount of BOM [48].

13 In indirect techniques, microorganisms are immobilized on an optical fiber covered with a
14 fluorescent indicator. The presence of oxygen, acting as a quencher, attenuates the
15 fluorescence intensity of the indicator [49-54].

16 These respirometric biosensors give readings within minutes, against the five days required
17 for BOD₅. However, the protocol requires sowing and inoculum acclimatization. Moreover,
18 careful maintenance is required when reproducing active consortia, including continuous
19 feeding during prolonged storage. Additionally, fluctuating in-sample oxygen levels cause
20 poor reproducibility unless an oxygen supply is incorporated. The major advantage of optical
21 sensors over the Clark electrode is that they show good long-term stability.

22 **2.2. Microbial fuel cell**

23 The microbial fuel cell (MFC) system converts OM into electricity (Fig. 3). Electron transfer
24 from the microbial cell to the anode occurs either via membrane-associated components

1 (unmediated biosensors) or via soluble electron shuttles termed mediators (mediated
2 biosensors).

3 **2.2.1. Unmediated electron transfer**

4 Some sulfate-reducing bacteria (e.g., *Clostridium* sp.) are metal-reducers, able to directly
5 transfer electrons to the anode. Their cytochromes, localized on the outer membrane, can
6 reduce metals. Some species (e.g., *Geobacter* sp.) have *pili* (*pilus*: microbial nanowire) on
7 their outer membrane that are able to transfer their electrons.

8 Activated sludge contains significant amounts of metal-reducing bacteria that can be used as
9 biocatalysts in mediator-less MFC [55-59]. Continuous anaerobic feeding avoids the latency
10 following OM addition and population drift due to starvation, and extends the lifespan of
11 consortium to five years [60]. However, without rigorous maintenance, all MFC are instable
12 and have a limited lifespan.

13 **2.2.2. Mediated electron transfer**

14 Most strains are electrochemically inactive, which means mediators have to be used to extract
15 electrons from the cell and transfer them to the anode. These mediators are low-molecular-
16 weight redox couples. Hydrophilic mediators {e.g., potassium hexacyanoferrate(III)
17 (ferricyanide), ruthenium hexamine and ferrocene carboxymethylate} are hydrosoluble and
18 cannot cross the cell membrane to enter the cytoplasm, so they are not expected to be able to
19 mediate catabolism in eukaryotic cells. However, lipophilic mediators can cross the cell
20 membrane, enter the cytoplasm, and interact with electron-transport chains. This group
21 includes menadione and benzoamines [61]. Ferricyanide is the most widely used, either alone
22 [62-65] or with menadione [66]. Some natural mediators, including humic acids,
23 Fe(II)/Fe(III), or sulfur/sulfide, are found in activated sludge [67].

1 **2.3. Optical sensors**

2 OM has optical properties that make it possible to use rapid and reagentless techniques
3 requiring little sample preparation. These optical sensors are either “intrinsic” [measuring the
4 optical properties of OM (e.g., UV-visible absorbance)] or “extrinsic” [measuring the optical
5 properties of a suitable oxygen-detecting dye placed on an optical fiber]. Extrinsic sensors
6 were covered under the section on respirometric methods.

7 **2.3.1. *UV-visible absorption***

8 UV-visible absorption is also used to monitor BOM, but the technique remains relatively
9 inaccurate since refractory structures (e.g. aromatic cycles) exhibit stronger absorption than
10 the BOM (e.g. sugars and fatty acids do not absorb in UV).

11 Association between BOD₅ and UV₂₈₀ decrease across WWTP, from r^2 : 0.73, to r^2 : 0.49 and
12 r^2 : 0.11 in raw influent wastewater, primary effluent, effluent from the nitrification settling
13 basin, respectively [68].

14 The variable relationship between BOD₅ and UV₂₄₅ or UV₂₈₀ highlighted needs to consider
15 water matrix, as for TOM.

16 **2.3.2. *Fluorimetry***

17 Some biodegradable compounds are fluorescent, and synchronous fluorescence spectrum has
18 been applied to selected major peaks related to biodegradable and refractory components, in
19 both treated and untreated sewage samples [30, 69], in order to differentiate anthropogenic
20 and natural OM or trace groundwater [70, 71]. This technique shows three different peaks,
21 identified as protein-like (248-280/340-350 nm), fulvic-like, and humic-like peaks. Treated
22 sewage water shows a substantial reduction of the protein-like peak [69], and the fluorescence
23 intensities of the 270/350 nm [71] or 220/350 nm [72] peaks correlate with BOD₅. Obviously,

1 this technique for differentiating anthropogenic from natural OM is insensitive to nonaromatic
2 pollutants {e.g., the propylene glycol used as deicer on airplanes [72]}. Some portable
3 spectrofluorometers using multiple LEDs as excitation sources allow in-field fluorescence
4 analysis [73].

5 **2.4. Tracers or chemical indicators**

6 A tracer is a chemical compound that unambiguously elucidates the source and magnitude of
7 pollution. There is a sharp dichotomy between: (1) animal and bacterial OM (anthropogenic
8 OM) of proteinic type and (2) plant OM of lignocellulosic type. It is therefore possible to
9 differentiate natural inputs from residual inputs where the microbial imprint is more
10 pronounced. However, the discrimination is fine-tunable, and compounds are already in use
11 for tracing anthropogenic inputs into the water environment. The organic compounds used as
12 anthropogenic tracers of OM include sterols and endocrine-disrupting chemicals, detergents
13 and whitening agents {e.e., linear alkyl benzene sulfonate (LSA: a major household anionic
14 detergent)}, and caffeine. There are few sensors currently under development that can
15 monitor these tracers.

16 **2.4.1. Proteins**

17 Proteins are related to microbial activity, and generally speaking, high protein levels are
18 characteristic of allochthonous origins {e.g., sewer overflows, WWTP discharge or farm
19 waste [74]}. Proteins can therefore be used as a proxy for BOM quantification, particularly
20 for significant anthropogenic sources. The fluorescence peak of proteinaceous materials at
21 290/350 nm correlated well with BOM [71]. A conductometric biosensor based on protease
22 activities and tested on river and sewer samples showed good relationships with DOC.
23 Modifying its electrode design improves LoDs 2.2-fold [75].

24 **2.4.2. Sterols and phenolic endocrine-disrupting chemicals**

1 Sterol biomarker fingerprinting has been used to trace sewage plumes and identify sewage
2 origins [76, 77]. An enzymatic biosensor associating tyrosinase immobilized on carbon past
3 electrode and amperometric detection was built for the determination of phenolic endocrine-
4 disrupting chemicals (e.g. nonylphenol, a detergent). But unfortunately, no response was
5 registered for nonylphenol (nor for diethylstilbestrol, a synthetic nonsteroidal estrogen) for
6 concentrations lower than 1 mM [78]. Since environmental conditions can influence
7 metabolic processes and overlap the anthropogenic sterols, a useful sensor should ideally give
8 a kind of sterol fingerprint. We can imagine for example a set of sterol cross-reactive sensing
9 elements on microplate and pattern recognition by data processing.

10 **2.4.3. Detergents & whitening agents**

11 Some sensors have been reported for anionic detergent made up of an immobilized LAS
12 degrading yeast (*Trichosporon cutaneum*) in a column-reactor type biosensor and an oxygen
13 electrode. This system was able to detect 0.2 mg/L LAS, but *T. cutaneum* being a
14 heterotrophic yeast, the measure must be corrected of organic matter content [79].

15 Detergent-selective electrodes comprising an ionophore in PVC membrane and
16 potentiometric detection measured anionic detergents in industrial wastewater. The LODs for
17 LSA detergents were at μM level [80], and for nonionic detergents [e.g., octylphenol
18 decaethylene glycol ether (Triton X-100) or polyethylene glycol lauryl ether (Brij 35)], were
19 5.6 μM and 33 μM respectively. [81].

20 Although cationic detergents seem to interfere strongly on the response of this last sensor, no
21 sensor gives a global measure of the detergent content (anionic, non-ionic and cationic all
22 together).

1 Recently a fluorescence sensor was proposed for rapid quantification of ionic and non-ionic
2 detergents in solution at sub μM concentrations [82]. Strangely, there is no article about
3 optical sensors to detect fluorescent whitening agents.

4 **2.4.4. Caffeine**

5 Caffeine from beverages and food products is clearly a ubiquitous anthropogenic indicator in
6 domestic wastewater. Caffeine concentrations will depend on regional conditions, and they
7 decrease with increasing efficiency of WWTPs [83].

8 A biosensor based on *Pseudomonas alcaligenes* and oxygen electrode can detect caffeine over
9 a concentration range 0.1 to 1 g/L [84]. But, as all heterotrophic organisms, *P. alcaligenes*
10 also consumes OM present in sample and OM interferes with caffeine measure. A more
11 specific sensor, based on Cytochrome P450 oxidase enzyme system, would be more suitable.

12 **3. Future developments**

13 As environmental parameters present strong coherence due to the dynamic balances inherent
14 in an ecosystem, a structured group of parameters can be exploited to deduce a particular
15 quantity without necessarily measuring it. Also, there is emerging a new global approach,
16 which, avoiding development of a more specific sensor, is centered on mathematical
17 processing of signal from sensor network with the aim of deducing the monitored variable
18 indirectly. This virtual sensor, otherwise known as “soft sensor” or “smart sensor”, comprises
19 an array of simple and reliable sensors that are not analyte specific but can be linked by a
20 computer programmed to process certain sample features and build a proxy of the “unsensed”
21 parameter [34]. Virtual sensors will soon measure a ‘fingerprint’ that can be analyzed by a
22 pattern recognition system. Any sensor can be integrated into a virtual sensor system and its
23 data pooled and processed.

1 The quality of this approach lies in how the data from the sensor networks is mathematically
2 processed. These processing steps span chemometrics to artificial neural networks (ANNs)
3 and genetic algorithms, and can be clustered under two main objectives:

4 1) to determine structure and data correlations using principal component analysis (PCA)
5 and/or canonical analysis;

6 2) to establish a model from the data that can be used in predictive mode. In this second
7 approach, the techniques used are projections to latent structures and partial least squares
8 (PLS) regression that generalize and fuse the PCA, and the multiple regression methods, or
9 ANNs.

10 Nowadays, the majority of the statistical treatments used bring only qualitative information,
11 and not quantitative. But some results suggest that it might be feasible to use a virtual sensor
12 to monitor OM in drinking water production plants [85], WWTPs [86] or rivers [87].

13 Interestingly, the very same measurement set-up can be used for accurate determinations of
14 TOC, simply by making a few changes to the regression model.

15 A virtual sensor array can also detect changes in the BOM content of wastewater [88]. More
16 recently, a model based on experimental data from five pilot-scale constructed wetland units,
17 used in conjunction with ANN model, predicted BOD₅ removals in horizontal subsurface
18 flow constructed wetlands [86].

19 In WWTPs, an ANN's model gave reasonable estimates for the BOD₅ predicted for a WWTP
20 with average absolute relative errors of 10% and for a river with a relative standard deviation
21 of 44% [89].

22 At present, the virtual sensor technology is still under development. But already, and despite
23 the expected difficulties associated with this strongly transdisciplinary approach, some
24 promising results have been obtained.

1 OM sensors are still in their infancy, and many approaches are being explored. This
2 flourishing research stream offers advantages, since it enables study into OM under different
3 angles. The study objective has to guide the choice of sensor, so, before choosing a technique,
4 the question to ask is what functions are being studied and what is the goal? Functionality can
5 be studied by selecting the most relevant technology.

6 To study BOM, sensors based on respirometry are preferable. They measure oxygen
7 consumption and, more indirectly, the bioavailable OM. However, they remain hampered by
8 reliability issues. The development of new microbial strains coupled with novel techniques
9 (e.g., stabilized enzymes) will help improve the performance of these sensors. Finally, since
10 respirometry sensors have different oxidation strengths, this diversity could be used to
11 discriminate various classes of lability.

12 Spectral methods are specifically adapted to the measurement of aromatic structures that are
13 present in the compounds rather than refractory to their biodegradation (e.g., humic
14 substances). This makes them seemingly better candidates for determining OM origin. Almost
15 all commercialized devices are based on UV-visible spectrometry. However, these sensors
16 require a major calibration effort, and further research needs to be directed towards the
17 automatic selection of the re-calibrations imposed by matrix changes.

18 Virtual sensors are a promising concept, but they are still at the R&D stage. By deferring the
19 sensor specificity to mathematical processing, this technology leads to a simplification of
20 sensing elements and to a more robust sensor network. It also allows the design of sensor
21 networks specifically tailored to studying individual OM properties.

22 Molecular tracers are useful in studying OM origin, but, as a prerequisite, they need good
23 knowledge of the OM composition. In general, a good tracer associates a narrow specificity to

1 good stability. Labile compounds (e.g., carbohydrates or proteins) are chemical indicators that
2 are better geared to studying early diagenesis.

3 The sensor technologies that have emerged from environmental sciences in the last couple of
4 decades now require validation. Water quality monitoring is currently based on standardized
5 laboratory methods. Sensors, despite being developed more recently, do not have the same
6 recognition capacities and are only seldom used, despite their advantages. Field validations
7 are needed in order to boost their credibility. ISO standard 15839 (released in 2003) provides
8 a consistent protocol for characterizing these sensors, should facilitate their adoption for
9 routine use by regulatory bodies. Further work is required to increase their operational period,
10 and particularly to prevent bio-fouling and clogging. Other technological challenges include
11 miniaturization of on-chip modules, cutting energy consumption, developing *in situ* fuelling,
12 eco-design, geolocation, communication checking, and data validation and transmission. It is
13 equally imperative to improve data management. Clearly, there is plenty of room for
14 progression.

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Table 1: Methods for TOM determination in water

Description	Application	Range	LoD	Time	RDS	References
		O ₂ mg/L	O ₂ mg/L	min	%	
Photocatalysis under UV-lamps						
Flow system with TiO ₂ beads, Clark electrode	Lake water	10	0.12		4.4	[1]
Flow system with a TiO ₂ film electrode, photocurrent measurement	Synthetic wastewater, glucose	235	0.30	1	1.42	[2]
Fluorinated TiO ₂ , Mn(IV) at 525nm	Tap and lake water, wastewater (paper industry)	280	0.02	10	1.1	[3]
TiO ₂ beads, Cr(III) at 610nm	Food, sewage, chemical wastewater (glucose-spiked)	100	nd	10	6.3	[5]
TiO ₂ beads O ₂ Clark electrode	Synthetic wastewater, lake water	7.6	0.12	3-4	6.8	[6]
TiO ₂ film, Cr(III) at 590nm	Wastewater (glucose-spiked)	500	20	40	5	[7]
ZnO/TiO ₂ film, Mn(IV) at 525nm	Groundwater	0.25–10.0	0.1	40	2.35	[8]
Electrocatalysis						
TiO ₂ thin-film electrode thin-layer cell	Agri-food, dyes, industrial wastewaters	100-360	1-0.2	1-5	0.8-1.2	[10]
Ti/TiO ₂ /PbO ₂	Agri-food, industrial wastewaters, dyes	2 500	15	1	7%	[11]
Cu/CuO in 0.1M NaOH	Soft drinks industry wastewater	2 800	20	1	0.2	[15]
BDD in 1M NaOH	Glucose	1 900	95	1	6	[16]
AgO-CuO in graphite polystyrene anodes in 0.1M NaOH	Glucose solution, winemaking wastewater	1 400	5	1	8.5	[17]
Cu, with a grinding device cleaning its surface, in 0.1M NaOH	Glucose solution, wastewater (1 st sedimentation tank)	1 000	10	10	nd	[21]
Chemiluminescence						
Flow system measuring Mn(II) concentrated on-column	Lake waters	4 000	4	1.5	4.4	[23]
Microplate reader measuring Mn(IV) at 640 nm	Natural waters, drug wastewater	19	0.1	<1	4	[24]
Photodiode detects Cr(III)	Dyes, garbage leakage, wastewaters	700	2	nd	4.5	[25]
Flow system measuring Cr(III)	Wastewaters	10 000	100	nd	2.7	[26]
A flow injection system integrating UV photolysis	Certified freshwaters, lake waters	20	0.08	10	2.7	[27]

Table 2: Sensors for BOM using a Clark electrode

Description	Applications	Range	LoD	Time	RDS	References
		O ₂ mg/L	O ₂ mg/L	min	%	
WWTP consortium on beads in-column	Tap water, diluted wastewaters	12	0.15	>180	5.7-22.6	[35]
<i>Klebsiella</i> sp. from activated sludge and enzymes immobilized on membrane	Monosaccharides	nd	nd	30	nd	[36]
<i>P. syringae</i> in highly porous micro-cellular polymer	Glucose-glutamic acid	100	3.3	3-5	3	[37]
Encapsulated <i>S. cerevisiae</i> on calcium alginate	Glucose-glutamic acid	40	nd	3		[38]
Flow system combining photocatalysis on TiO ₂ and passage on <i>P. putida</i>	River waters	8	1	5-10	12	[39]
WWTP consortium	OECD synthetic wastewater	230	15	1.5-2	7.5	[40]
Consortium from synthetic wastewater in flow cell	Synthetic wastewaters	700	5	60	7.3	[41]
Reference consortium (DONSEED) on nylon membrane	Brewery wastewaters	90	1	15	4	[42]
Bacteria from brackish waters on polyurethane membrane, fixed on a Clark electrode or optical fibre	Monosaccharides, disaccharides	1.9-96	1.9	15-120	10	[43]
WWTP consortium	Food, tannery, paper industry wastewaters	60	1	5-7	5%	[45]
<i>Ph. phosphoreum</i> on a bio-chip, measured by digital camera	Domestic, industrial wastewaters	16	1	20	3	[46]
Recombinant <i>E. coli</i> containing <i>lux</i> genes from <i>V. fischeri</i>	Domestic, industrial wastewaters	200	3	60-120	14.2	[47]

Table 3: Biosensors for BOM without a Clark electrode

Description	Applications	Range	LoD	Time	RDS	References
		O ₂ mg/L	O ₂ mg/L	min	%	
Marine microorganisms on silicate film with Ru(II)	Seawater	40	0.1	3	3	[49]
Marine strains on silicate film with a Ru (II)	Seawater	40	0.18	20	3.6	[50]
Microorganisms on silicate film with Ru(II)	Seawater	40	0.2	13	1.2	[51]
<i>P. fluorescens</i> on nylon membrane onto optical fibre	Synthetic wastewaters	10	0.5	15	20	[52]
Microorganisms in polymer and Ru(II)	Seawater	200	4	nd	4	[53]
<i>B. subtilis</i> and consortium from activated sludge, fluorimetry on Ru(II),	Domestic wastewaters	60	nd	50	18	[54]
Single-chamber MFC with an air cathode, consortium from WWTP	Artificial and diluted wastewaters	350	50	60	0.5	[55]
On-line MFC WWTP inoculum	Wastewaters	150	10	45	1.6	[56]
Flow MFC WWTP inoculum feed with wastewater	Synthetic wastewater	100	nd	60	10	[57]
Flow MFC WWTP inoculum feed with synthetic wastewater	Synthetic wastewater	100	20	5	nd	[58]
Flow MFC oligotrophic inoculum feed with river water	Surface water & synthetic wastewater	nd	nd	nd	nd	[59]
<i>P. vulgaris</i> on polyvinyl acetate, (ferricyanide)	Wastewaters	19-150	4.8	60	nd	[62]
Marine microorganisms on a functionalized glassy carbon electrode (ferricyanide)	GGA standard solution, seawater	40	1.2	30	7.7	[63]
<i>P. fluorescens</i> on cellulose acetate membrane, (ferricyanide)	Wastewaters	260	5	20	10.5	[64]
Yeasts from pulp mill effluent on glassy carbon electrodes (ferricyanide)	Pulp mill effluents	100	2	5	10	[65]
<i>S. cerevisiae</i> and double mediator system (ferricyanide & menadione)	Synthetic water	220	6.6	15	9.1	[66]
MFC feed with anaerobic sludge from biogas reactor	Glucose	25,000	25	3-5	7.2	[67]

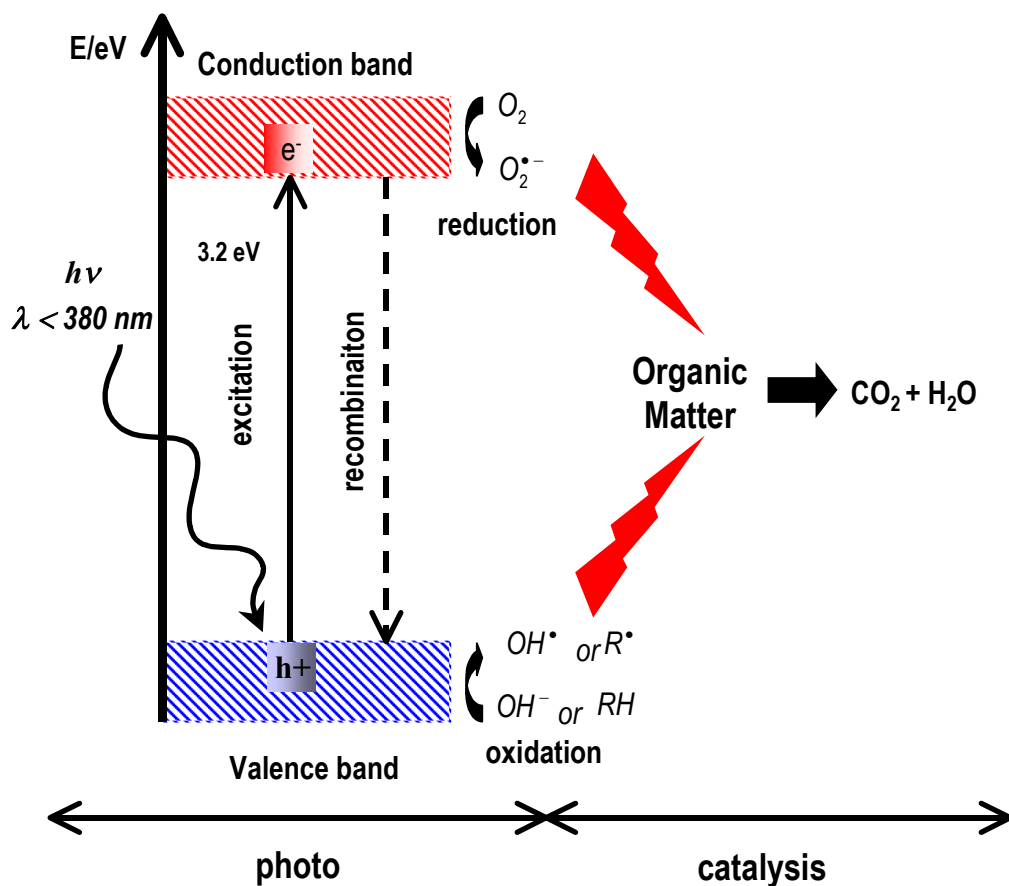


Figure 1: Photocatalytic mechanism on a semiconductor surface illuminated with energy $> 3.1\text{eV}$ (380 nm). An electron jumps from the valence band to the conduction band, leaving a positive hole. This electron can be transferred to oxygen (or H^+ ; chlorinated compounds), initiating various reactions. The hole can produce hydroxyl radical (or, with water: organic compounds). Free-radicals are strong oxidants, able to mineralize OM.

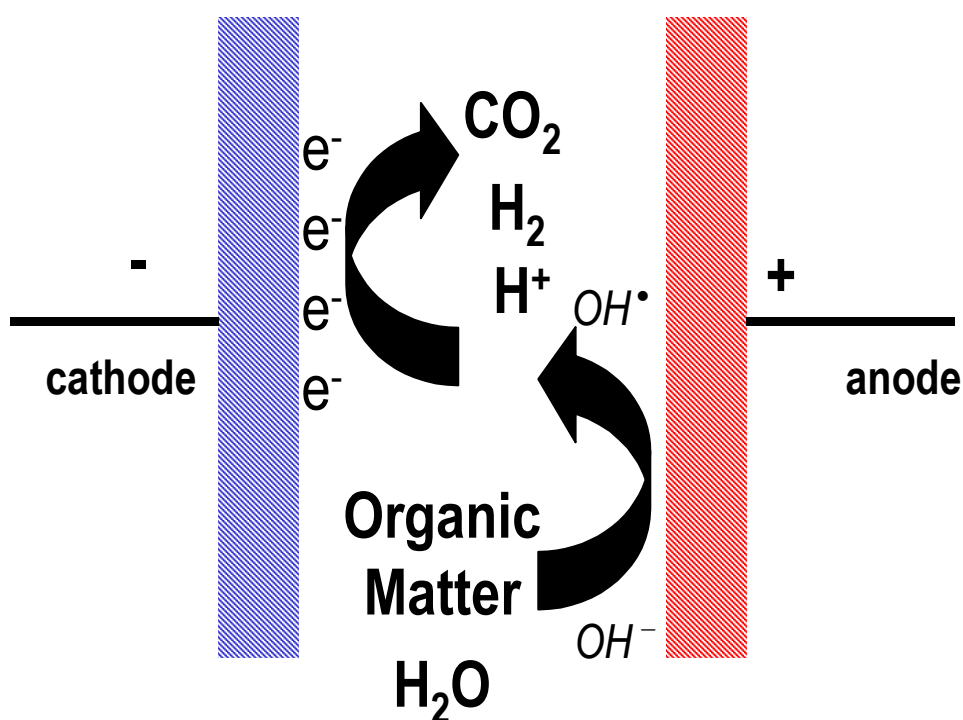


Figure 2: The principle of electrocatalysis is based on a powerful oxidizing activity generated at the electrode surface. The electrons released during oxidation can be measured as an electrical current proportional to the quantity of OM oxidized.

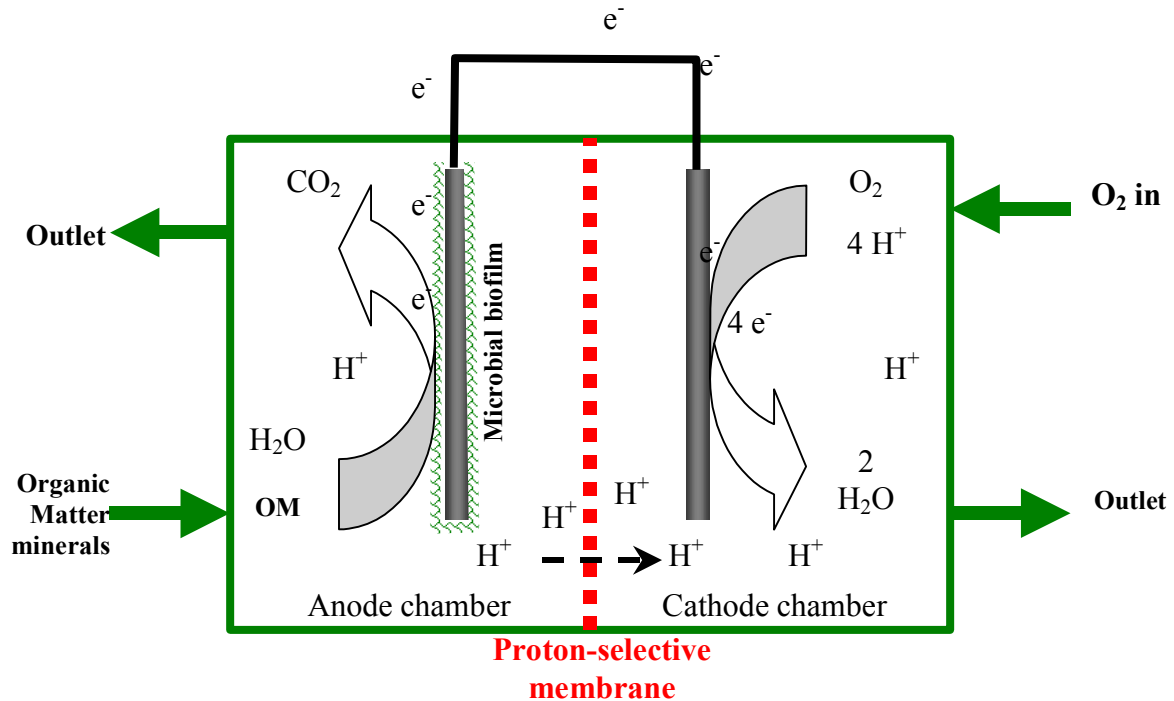


Figure 3: A microbial fuel cell consists of an anaerobic chamber with an anode, and an aerobic chamber with a cathode, the two separated by a proton-exchange membrane. In the anaerobic chamber, the anode short-circuits the natural electron acceptors, such as oxygen or nitrate. The protons then pass through the proton-selective membrane toward the aerobic chamber. The electrons produced are transferred to the cathode, where they reduce oxygen to form water.