Partenariat ***2009*** **–** *Domaine Qualité de l'eau***-** *Action 13 : Développement et optimisation des méthodes physico-chimiques*

Capteurs pour la mesure de la matière organique totale et biodégradable dans les eaux

Rapport final

Philippe Namour*, Université de Lyon / Cemagref*
Nicole Jaffrezic-Renault*, Université de Lyon*

Décembre 2009

Contexte de programmation et de réalisation

Ce document correspond à l'action 13 « Développement et optimisation des méthodes physico-chimiques » (cf Fiches 1 à 5 et 8, programme AQUAREF 2009 – Chimie), domaine Qualité de l'eau (cours d'eau, plans d'eau, masses d'eau de transition).

Les auteurs

Philippe Namour
Ingénieur d'Etudes
Email philippe.namour@adm.univ-lyon1.fr
Localisation Université de Lyon, UMR 5180

Nicole Jaffrezic-Renault
Directeur de Recherche
Email nicole.jaffrezic@univ-lyon1.fr
Localisation Université de Lyon, UMR 5180

Les correspondants

Onema : *Pierre-Francois Staub, ONEMA-DAST, pierre-francois.staub@onema.fr*

Cemagref : *Marina Coquery, Cemagref Lyon, marina.coquery@cemagref.fr*

Droits d'usage :	*Confidentiel avant publication*
Couverture géographique :	*internationale*
Niveau géographique [un seul choix] **:**	*international*
Niveau de lecture [plusieurs choix possibles] **:**	*experts*
Nature de la ressource :	*article scientifique (soumis)*

Capteurs pour la mesure de la matière organique totale et biodégradable dans les eaux

Rapport final

Philippe Namour & Nicole Jaffrezic-Renault

Sommaire

Capteurs pour la mesure de la matière organique totale et biodégradable dans les eaux

Philippe Namour & Nicole Jaffrezic-Renault

RESUME

Résumé

Ce document soumis à publication correspond à l'action 13 « Développement et optimisation des méthodes physico-chimiques » (cf. Fiches 1 à 5 et 8, programme AQUAREF 2009 – Chimie), domaine Qualité de l'eau (cours d'eau, plans d'eau, masses d'eau de transition). Il résume les publications scientifiques publiées ces deux dernières décennies portant sur la mesure des matières organiques totale et biodégradable dans les eaux. Il rapporte l'état de l'art des techniques les plus importantes. Bien que son objectif porte sur la mesure *in situ*, des techniques d'analyse en ligne pouvant conduire à l'élaboration de capteurs sensu stricto sont également discutées comme technologies émergentes.

Le rapport est divisé en deux sections : 1) matière organique totale ; 2) matière organique biodégradable. Chaque technique est décrite rapidement avant l'analyse de la littérature publiée. Nous concluons avec des recommandations sur les choix technologiques selon les objectifs de recherche.

Mots clés *:* Matière Organique, capteur, eau, rivière, DBO, DCO

Sensors for measuring biodegradable and total organic matter in water

Philippe Namour & Nicole Jaffrezic-Renault

ABSTRACT

ABSTRACT

This critical review spanning the past two decades outlines sensors developed for measuring total and biodegradable organic matter (OM) in water. It reports the state-of-the-art of the most significant technologies. Although the focus is on in situ devices, on-line techniques able to lead to sensors sensu stricto are also mentioned and discussed as possible emerging technologies.

The review is divided into two sections: (1) Total OM (TOM); and (2) Biodegradable OM (BOM). Each technique is first outlined in brief before following with analysis of the published literature. We conclude with recommendations on the technological choices geared to specific research topics.

Key words: Organic Matter, sensor, water, river, BOD, COD

Capteurs pour la mesure de la matière organique totale et biodégradable dans les eaux

Philippe Namour & Nicole Jaffrezic-Renault

Synthèse pour l'action opérationnelle

La surveillance de l'environnement constitue le premier pilier des politiques de gestion, de protection et de restauration des eaux de surface et des ressources souterraines des bassins versants. La Directive Cadre sur l'Eau (EU, 2000) entre en application et va amplifier à terme le marché de la métrologie environnementale. Devant le coût prohibitif des analyses de laboratoire requises et les artefacts possibles lors de la séquence prélèvement-conditionnement-transport, il est nécessaire de concevoir de nouvelles stratégies de surveillance des milieux. Une des voies possibles passe par le déploiement d'instrumentations à bas coûts, d'acquisition de données de masses et d'outils de validation, de gestion et d'interprétation de ces données. Toutefois actuellement ce nouveau type d'instrumentation ne couvre pas encore la totalité des paramètres de la Directive Cadre sur l'Eau (EU, 2000, 2008a, b), et cela ne sera sans doute pas encore totalement le cas avant 2015, ni même 2021, si un tel déploiement de capteurs est possible, voire souhaitable. L'ampleur de ce défi métrologique demande un changement de paradigme afin de concevoir une nouvelle approche de la surveillance des masses d'eau.

Cette synthèse n'aborde que la matière organique en tant que polluant global et non molécule par molécule. La seule distinction opérée sera entre matière organique totale et matière organique assimilable. Nous n'abordons pas notamment les substances organiques prioritaires de la DCE, qui font l'objet d'une veille bibliographique séparée, ni les substances dites émergentes quoique certaines soient potentiellement utilisables comme traceurs de matière organique d'origine anthropique comme les stérols ou la caféine, ainsi que nous le verrons en fin de rapport. Suite à ces précisions, nous aborderons les différentes techniques aujourd'hui envisagées pour évaluer globalement la matière organique dans les eaux.

La matière organique peut varier considérablement qualitativement et quantitativement et cette variabilité ne peut être estimée qu'à partir d'analyse statistique d'un nombre important de mesures judicieusement placées et rapprochées, afin d'intégrer les éventuelles pollutions ponctuelles intermittentes, causes de dommages souvent majeurs aux hydro-systèmes. Aussi il apparaît que seuls des méthodes rapides en continu en augmentant la fréquence de mesure et le nombre de points analysés permettent une meilleure surveillance de la qualité de l'eau.

Aussi notre rapport bibliographique est-il focalisé sur les méthodes *in situ* mises en œuvre à l'aide de capteurs directement immergés dans l'eau, sans échantillonnage. Les données sont recueillies et stockées automatiquement et éventuellement télé-transmises. Les méthodes d'analyse en ligne (analyseur placé sur le bord de la masse d'eau) ne sont pas abordées.

Actuellement la surveillance de la qualité des eaux s'appuie essentiellement sur des méthodes de laboratoire normalisées. Les méthodes d'analyse *in situ*, de développement récent, n'ont pas la reconnaissance des méthodes de laboratoire normalisées depuis plus de 30 ans et ne sont que timidement utilisées malgré leurs avantages.

Nous avons sélectionné dans notre étude certains critères de la norme ISO 15839 relative au matériel d'analyse/capteurs directs pour l'eau – spécifications et essais de performance. Toutefois les caractéristiques de fonctionnement demandées sont rarement, voire jamais, toutes données, notamment toutes celles concernant la dynamique de réponse du capteur. Aussi avons nous limité notre comparaison sur les caractéristiques générales comme la gamme de mesure, le limite de détection, le temps de mesure (qui donne une idée de la dynamique du système) et la répétabilité de la mesure.

Un grand nombre d'approches est en cours d'exploration et la partie détection ne semble pas poser de problème majeur, quoique les capteurs fondés sur la respirométrie semblent plus délicats à l'usage en raison de la présence des matériels biologiques. Parmi les capteurs étudiés, les capteurs virtuels constituent une approche prometteuse qui demande encore des développements surtout mathématiques. Cette technologie conduit à une simplification du réseau de capteurs et donc à une plus grande robustesse du dispositif.

Les seuls capteurs de matière organique commercialisés sont des capteurs optiques fondés sur une mesure de l'UV-visible suivie d'un traitement mathématique des spectres, généralement des déconvolutions de spectres. Toutefois à l'expérience, ce type de capteur optique nécessite un effort important d'étalonnage et des recherches sont encore nécessaires (sélection automatique d'étalonnages, ré-étalonnage en fonction des changements de matrices). Enfin nous abordons également l'utilisation de capteurs dédiés à la mesure de traceurs d'origine de la matière organique.

Les principes de détection ne semblent pas constituer un facteur limitant au développement de micro-capteurs pour l'environnement. Les verrous scientifiques et technologiques à lever, pour aboutir à des réseaux de micro-capteurs opérationnels sur le terrain, se situent plutôt au niveau de la miniaturisation car un grand nombre de capteurs sont encore au stade d'encombrants prototypes de laboratoire. Il s'agirait donc d'améliorer la chaîne transducteur - transmetteur. A terme l'encombrement des capteurs ne devrait par excéder la taille d'une clef USB. Les autres verrous sont la diminution de la consommation énergétique et aborder la possibilité d'extraction d'énergie *in situ* ; il est également indispensable d'améliorer la gestion du flux de données généré par ces réseaux de capteurs et la validation automatique. Ajoutons que des préoccupations comme la géo-localisation des capteurs, la surveillance de leurs communications et de la transmission des données commencent à émerger. Enfin un effort doit être mené dans le sens de l'homologation de ces capteurs pour la surveillance des milieux aquatiques afin qu'ils bénéficient de la même reconnaissance que les méthodes analytiques de laboratoire, qui bénéficient actuellement de l'effort de près de trois décennies de normalisation. La norme ISO 15389 devrait aider à cette reconnaissance des capteurs et à leur plus grande utilisation.

En résumé, les principaux axes de progrès des micro-capteurs sont :

- La miniaturisation : poursuivre l'intégration des différents modules (récepteur, transducteur et transmetteur) sur une même puce. Cela conduit à une baisse de l'énergie consommée et semble avoir, au moins sur les électrodes de conductivité, un effet bénéfique sur la sensibilité.

- La robustesse et notamment la résistance aux conditions environnementales et à l'encrassage. Ce dernier point n'est pas un objet de recherche aussi développé que la détection et des percées devraient être possible dans le domaine du traitement des surfaces sensibles et du nettoyage par ultrasons.

- La communication, entre les micro-capteurs et la station d'acquisition et entre les micro-capteurs entre eux. Un réseau de micro-capteurs devrait avoir la possibilité de se géo-localiser (recherche des micro-capteurs dispersés après une crue notamment), vérifier l'état des communications avec la station d'acquisition et avec les micro-capteurs, valider la qualité des données avant leur transmission, alerter en cas de situation anormale. Deux modes de communication seraient à étudier : les ultrasons ou les radiofréquences.

- L'autonomie à augmenter par la diminution de la consommation énergétique des capteurs ou développer les possibilités d'une alimentation in situ (les biopiles ou les hydroliennes seraient une voie à explorer).
- L'éco-conception doit être intégrée dès le choix des principes de mesure. Dans l'éventualité de perte dans l'environnement, la composition des micro-capteurs doit bannir l'utilisation de substances toxiques ou dangereuses pour l'environnement. La notion de cycle de vie du micro-capteur doit également être intégrée.

Enfin il convient de mentionner la nécessiter de développer les technologies de l'information et de la communication (TIC) dans le but de gérer les flux de données générés par un réseau de micro-capteurs de façon optimale.

Capteurs pour la mesure de la matière organique totale et biodégradable dans les eaux

Philippe Namour & Nicole Jaffrezic-Renault

Corps du document

Although "Organic Matter" (OM) is a term that appears easy to decipher, it paradoxically resists all attempts at formal chemical definition. Thus, since the beginnings of organic chemistry, OM has been defined by its oxidizability, originally by calcination (volatile suspended solid) and then, early in the twentieth century, by wet oxidation methods: chemical oxygen demand (CODCr) to determine total OM (TOM) and five-day biochemical oxygen demand (BOD5) to determine biodegradable OM (BOM). The CODCr method uses a two-hour reflux reaction in hot sulfuric acid and two highly toxic ions: Cr(VI) as oxidant reagent, and Hg(II) as masking agent camouflaging the interference from the chloride. These two toxic substances condemn this method. Furthermore, running a back-titration of the excess dichromate is too insensitive for measuring TOM in river samples (LD=30 mg/L). The BOD5 method is based on the aerobic microbial consumption of BOM at a temperature of 20°C, in the dark and over an elapsed period of five days. It is cheap but time-consuming (five-day incubation period) and labor-intensive, requiring skill to get reproducible results. Its precision is around 15% (Kim, M. et al., 2003; Liu et al., 2004a). Moreover, BOM is highly unstable and is partly destroyed during sampling, transport, storage, and test preparation. Even when using a refrigerated sampler, up to 20% of BOM in raw sewage can be lost within the space of 24 hours. In the second half of the twentieth century, these limitations prompted the development of instrumental methods based on elemental analysis of OM, such as total or dissolved organic carbon (TOC or DOC) or nitrogen (TON or DON). These analyses do offer alternatives to COD, but unfortunately there is no elemental method for BOD5. The major drawbacks of these methods are the acquisition and operation costs, and the need for sampling and sample handling before laboratory analysis.

All current conceptual river models focus on daily and seasonal quantitative and qualitative OM variations. The growing focus on the protection, remediation and restoration of aquatic environments has generated an urgent need for advanced monitoring technology, especially in response to new legislation. However, instrumental techniques cannot affordably deliver the large datasets demanded by these new legislations. The urgent need for continuous, in situ monitoring techniques has driven the search for simple, continuous and in-situ measurement of OM content and time-course evolution. Sensors meet these needs.

This article focuses on sensors for TOM (section I, Table 1) and BOM (section II). Table 2 recaps sensors that use Clark electrodes while Table 3 recaps the other techniques. Note that there is confusing overlap in some publications between CODCr and the permanganate method (CODMn). CODMn has 40-50% lower oxidation power, and therefore sometimes gives lower results than BOD5. Another source of confusion is the use of various organic compounds as standards, from glucose through to phthalic acid, which skews conclusions on the oxidizing power of the methods proposed.

Total Organic Matter

Photocatalytic Sensors

These sensors use light to oxidize OM (Figure 1). TiO2 is used either alone (Lee et al., 2000; Kim et al., 2001; Ai et al., 2004b; Chen et al., 2005; Li et al., 2006a; Zhu et al., 2006; Chatzisymeon et al., 2008; Harrelkas et al., 2008) or mixed with other oxides (Kansal et al., 2007; Zhang et al., 2007). ZnO alone gives good results (Pardeshi & Patil, 2008). Photocatalysis presents the low detection limits (COD>1 mg/L) needed for river monitoring, with satisfactory reproducibility (Table 1), but lacks oxidizing power compared to CODCr. An Australian team (Zhang et al., 2004; Zhao et al., 2004; Zhang et al., 2006; Zhao et al., 2007) coined the acronym PECOD for "photoelectrochemical demand in oxygen", a technique based on a photoelectrocatalytic degradation process in a thin-layer photoelectrochemical cell. The method is rapid, at around 2 min for phthalic acid, and concurs well with CODCr (Jiang et al., 2007). Chloride interference is insignificant when [Cl-]<26.6 mg/L and concentration ratio [Cl-]/[MO] is <5 (Zhang & Zhao, 2008). Ti/TiO2/PbO2 electrodes gives good results compared with CODCr, and the relative bias is below 6.0% (Li et al., 2006b;2007). Some authors have compared their results with CODMn values (Lee et al., 2000; Kim et al., 2001; Zhu et al., 2006; Zhang et al., 2007) or used readily-oxidizable standards like glucose or glutamic acid (Chen et al., 2005; Li et al., 2006a; Zhang et al., 2007). Finally, photocatalysis requires close contact between sample and catalyst, and an injection device has to push the sample through these sensors. However photocatalysis has found industrial applications as a pretreatment for toxic industrial wastewater: chemical reduction of anthraquinone, phthalocyanide and azo-dyes in effluents from textile factories (Harrelkas et al., 2008), or degradation of lignin (Kansal et al., 2008) or phenols (Pardeshi & Patil, 2008).

Electrocatalytic Sensors

Electrocatalysis uses electrodes to enhance chemical reactions (Figure 2). Antimony-doped anode SnO2 (Mao et al., 2008), PbO2 (Ai et al., 2004a; Awad & Galwa, 2005; Mao et al., 2008; Weiss et al., 2008), Cu/CuO (Lee et al., 1999a; Lee et al., 1999b; Silva et al., 2009) and BDD (Lee & Park, 2005; Cañizares et al., 2006; Panizza & Cerisola, 2008; Weiss et al., 2008) give linear relationships with CODCr (Lee et al., 1999a; Lee et al., 1999b; Ai et al., 2004a). AgO-CuO graphite electrodes give around 80% of CODCr (Orozco et al., 2008). The highest oxidation rates have been achieved in presence of hypochlorite electro-generated from chlorides (Awad & Galwa, 2005; Mao et al., 2008). BDD anodes present good stability allied with a wide potential window, and can totally oxide TOM (Martinez-Huitle & Ferro, 2006) as phenols (Cañizares et al., 2006; Weiss et al., 2008), PAHs (Wang et al., 2008) or dyestuffs (Awad & Galwa, 2005; Mao et al., 2008; Panizza & Cerisola, 2008), yielding a COD removal rate close to 100%. The drawback is electrode inactivation by metals, requiring cleaning procedures like polishing (Jeong, B.G. et al., 2007) or the application of high-potential anodic polarization.

Chemiluminescence (CL)

Chemiluminescence (CL) is based on the measure of protons emitted by a chemical reaction. Mn(VII) ions showing chemiluminescence (at 690 nm) when reduced to Mn(II) state are used to determine TOM (Fujimori et al., 1998). The luminol-H2O2-CL reaction is used to amplify Mn(II) (Li et al., 2003), surplus Mn(IV) (Yao et al., 2009), or reduced Cr(III) (Hu & Yang, 2004; Liu et al., 2008). The combination of UV-photolysis and CL detection of free-radicals gives results that match to CODMn (Su et al., 2007). The electro-regeneration of Ru(bpy)32+ suppresses reagent consumption and has successfully been applied to determine oxalate and ethanol (Lin et al., 2002).

Virtual or Soft Sensors

Environmental parameters present strong coherence due to the dynamic balances inherent to an ecosystem. Consequently, a structured group of parameters can be exploited to deduce a particular quantity without necessarily measuring it. Virtual sensors, otherwise known as "soft sensors" or "smart sensors", consist of an array of simple and reliable sensors that are not analyte-specific but can be linked by a computer programmed to process certain sample features and build a proxy of the "unsensed" parameter (Bourgeois et al., 2003; Winquist, 2008; Winquist et al., 2008). Virtual sensors will soon measure a 'fingerprint' that can be analyzed by a pattern recognition system. In fact, any sensor can be integrated into a virtual sensor system and its data pooled and processed.

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

1) to determine structure and data correlations using principal component analysis (PCA) (58-61) and/or canonical analysis (Stuetz et al., 1999a; Stuetz et al., 1999b; Villanueva et al., 2006; Villanueva et al., 2008);

2) to establish a model from the data that can be used in predictive mode. In this second approach, the techniques used are projections to latent structures and partial least squares (PLS) regression that generalize and fuse the PCA, and the multiple regression methods, or ANNs (Lee & Park, 1999; Pai et al., 2007; Akratos et al., 2008; Dogan et al., 2008).

It has been suggested that it might be feasible to use a virtual sensor to monitor OM in drinking water production plants (Krantz-Rülcker et al., 2001), wastewater treatment plants (Lee & Park, 1999; Stuetz et al., 1999a; Yoo & Lee, 2004; Tønning et al., 2005; Akratos et al., 2008) or rivers (Yang et al., 2008). Interestingly, the very same measurement set-up can be used for accurate determinations of TOC, simply by making a few changes to the regression model.

Optical Sensors

The fact that OM exhibits strong absorbance between 200 and 350 nm, and mainly at 254 nm (UV254), has meant that UV-Visible absorbance is widely used to quantify TOM in water. UV-visible sensors allow multiparametric determinations without reagents, but their applicability remains limited by the properties of the water matrix (turbidity, OM composition, nitrate/nitrite absorbances), and mathematical data reprocessing is required (Thomas et al., 1999). Spectral deconvolution gives erratic correlations with COD, ranging from 0.57-0.58 (Stumwohrer et al., 2003; Martins et al., 2008) to 0.90 (76), even for effluents of the same origin. ANN analysis gives better results (Jeong, H.S. et al., 2007; Yang et al., 2008). The fluorescence properties of OM have been also successfully used (Tartakovsky et al., 1996; Lee & Ahn, 2004).

Commercially available sensors

Commercially available OM sensors couple UV-scanning with spectral deconvolution (Greenwood & Roig, 2006). The Spectrolyzer Scan (Vienna, Austria) gives a good correlation for low COD, although DOC concentrations were not correlated (Rieger et al., 2004; Maribas et al., 2008). The manufacturer's calibrations tend to underestimate high concentrations and overestimate low concentrations. These deviations could be reduced after adjustments based on known standards and further improved by specific models integrating the major shifts in the water matrix (Rieger et al., 2006). Some authors have used an "off-line" calibration algorithm based on PLS-regression (Bertrand-Krajewski et al., 2007; Torres & Bertrand-Krajewski, 2008; Winkler et al., 2008). There is also a miniaturized voltammetric sensor comprising five working electrodes (SensET AB) (Winquist, 2008).

Biodegradable Organic Matter

Respirometer

Respirometry assesses metabolism rates in living organisms by measuring their oxygen consumption. In rivers, oxygen consumption is closely related to microbial activity, which is itself related to the amount of BOM. Therefore, biosensors have been developed based on respirometry to measure the BOM content in water simply and in the space of just a few minutes. This principle mirrors BOD5, which is also a respirometric technique. The majority of commercialized BOD equipment measures oxygen through a biofilm (Nakamura & Karube, 2003; Greenwood & Roig, 2006).

Clark Electrode

Microorganisms are either immobilized on membranes (Nomura et al., 1998a; Liu & Mattiasson, 2002) or entrapped on columns (Khan et al., 2003). The microorganisms used are either pure strains with or without enzymes (Iranpour et al., 1997; Chee et al., 1999a; Chee et al., 1999b; Chee et al., 2000;2001; Kim & Park, 2004; Chee et al., 2005; Kara et al., 2009; Seo et al., 2009), consortia of mixed strains (Tan & Wu, 1999; Kim & Park, 2001; Dai et al., 2004; Jiang et al., 2006), or inocula from WWTPs (An et al., 1998; Konig et al., 1999; Khan et al., 2003; Rastogi et al., 2003a; Rastogi et al., 2003b; Chee et al., 2005; Velling & Tenno, 2009), synthetic wastewater (Liu et al., 2004a), brackish waters (Koster et al., 2006) or standardized microbial cultures (Dhall et al., 2008). Inocula metabolize a broader spectrum of substrates (Kim & Park, 2001; Kwok et al., 2005) but present a less stable composition and are consequently less constant over time. Furthermore, while dynamic measurements offer a quicker response and a broader detection area, steady-state measurements give reliable results in the concentration range of 15–50 mgO2/L (Velling & Tenno, 2009). BOM can also be monitored in anaerobic processes (Kumlanghan et al., 2008). Various papers have reported on biofilm optimization (Rastogi et al., 2003a; Rastogi et al., 2003b), immobilization mode (Kara et al., 2009; Seo et al., 2009) and inoculum renewal (Liu et al., 2004a;b). Electrolyte consumption and anodic oxidation limit the Clark electrode lifetime, and require grinding of the anode surface and regular electrolyte renewal to avoid signal drift.

Ozonation (Chee et al., 1999a), or photocatalytic oxidation on TiO2 (Chee et al., 2001;2005) before passing over a biofilm, gives a variant of a chemical- or photo-biosensor. However, these hybrid techniques partially attack refractory OM like tannic or humic acids, which can be biodegraded up to 51.8% and 38.4%, respectively (Chee et al., 2005), and overestimating BOM introduces confusion between TOM and BOM.

Optical Biosensors

Optical respirometric biosensors measure microbial growth (1) directly from emitting bacteria or (2) indirectly via an oxygen-sensitive colored indicator. Naturally-emissive bacteria such as Photobacterium phosphoreum are applied for BOM measurement (Sakaguchi et al., 2007), and the commercially available toxicity analyzer Microtox employs the emitting strain Vibrio fischeri as test organism. Bioluminescent biosensors can also use genetically-engineered heterotrophic microorganisms, in which the lux genes from V. fischeri are integrated to measure microbial growth (Sakaguchi et al., 2003). Another direct optical approach is to measure NAD(P)H (reduced forms of NAD(P)) coenzymes present in all living organisms for redox reactions. While NAD(P)H are fluorescent (340/460 nm), their oxidized counterparts are not. Since NAD(P)H concentrations are dependent on living cell count and their metabolic activities, the fluorescence intensity from NAD(P)H reflects the amount of BOM (Tartakovsky et al., 1996; Ju & Nallagatla, 2003; Huang & Ju, 2007).

In indirect techniques, microorganisms are immobilized on an optical fibre covered with a fluorescent indicator. The presence of oxygen, acting as a quencher, attenuates the fluorescence intensity of the indicator (Chee et al., 2000; Dai et al., 2004; Kwok et al., 2005; Jiang et al., 2006; Lin et al., 2006; Xin et al., 2007).

These respirometric biosensors give readings within minutes, against the five days required for BOD5. However, the protocol requires sowing and inoculum acclimatization. Moreover, careful maintenance is required when reproducing active consortia, including continuous feeding during prolonged storage (Liu et al., 2004a). Additionally, fluctuating in-sample oxygen levels cause poor reproducibility unless an oxygen supply is incorporated. The major advantages of optical sensors over the Clark electrode is that they show good long-term stability.

Microbial fuel cell

The microbial fuel cell (MFC) system converts OM into electricity (Figure 3). Electron transfer from the microbial cell to the anode occurs either via membrane-associated components (unmediated biosensors) or via soluble electron shuttles termed mediators (mediated biosensors).

Unmediated electron transfer

Some sulfate-reducing bacteria such as Clostridium sp. (Kim et al., 2002) are metal-reducers able to directly transfer electrons to the anode. Their cytochromes, localized on the outer membrane, can reduce metals. Some species, such as Geobacter sp., have pili (pilus: microbial nanowire) on their outer membrane that are able to transfer their electrons. Activated sludge contains significant amounts of metal-reducing bacteria that can be used as biocatalysts in mediator-less MFC (Kang et al., 2003; Kim, M. et al., 2003; Chang et al., 2004; Moon et al., 2004; Di Lorenzo et al., 2009). Continuous anaerobic feeding avoids the latency following OM addition and the population drift due to starvation (Kim et al., 2004; Kumlanghan et al., 2007), and extends the lifespan of consortium to five years (Kim, B.H. et al., 2003). However, without rigorous maintenance, all MFC are instable and have a limited lifespan.

Mediated electron transfer

Most strains are electrochemically inactive, which means mediators have to be used to extract electrons from the cell and transfer them to the anode. These mediators are low-molecular-weight redox couples. Hydrophilic mediators such as potassium hexacyanoferrate(III) (ferricyanide), ruthenium hexamine and ferrocene carboxymethylate are hydrosoluble and cannot cross the cell membrane to enter the cytoplasm, so they are not expected to be able to mediate catabolism in eukaryotic cells. Lipophilic mediators, though, are able to cross the cell membrane, enter the cytoplasm, and interact with electron transport chains. This group includes menadione and benzoamines (Chaubey & Malhotra, 2002). Ferricyanide is the most widely used, either alone (Pasco et al., 2000; Trosok et al., 2001; Yoshida et al., 2001a; Yoshida et al., 2001b; Pasco et al., 2004; Chen et al., 2008) or with menadione (Baronian et al., 2003; Nakamura et al., 2007). Some natural mediators, including humic acids, Fe(II)/Fe(III), or sulfur/sulfide, are found in activated sludge (Kumlanghan et al., 2007).

Optical sensors

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

UV-visible absorption

UV-visible absorption is used also to monitor BOM, but the technique remains relatively inaccurate since refractory structures (e.g. aromatic cycles) exhibit stronger absorption than the BOM (e.g. sugars and fatty acids do not absorb in UV). The relationship between BOD5 and UV245 (Reynolds & Ahmad, 1997) or UV280 (Brookman, 1997; Muzio et al., 2001; Nataraja et al., 2006) seems variable, ranging from r2=0.97 (Reynolds & Ahmad, 1997) to r2<0.80 (Brookman, 1997; Muzio et al., 2001), thus highlighting the need to consider the water matrix, as is the case for TOM.

Fluorimetry

Some biodegradable compounds are fluorescent, and synchronous fluorescence spectrum has been applied to selected major peaks related to biodegradable and refractory components, in both treated and untreated sewage samples (Reynolds, 2002; Lee & Ahn, 2004), in order to differentiate anthropogenic and natural OM (Spencer et al., 2007; Hudson et al., 2008; Hur et al., 2008) or trace groundwater (Baker & Lamont-Black, 2001). This technique shows three different peaks, identified as protein-like (248-280/340-350 nm), fulvic-like, and humic-like peaks. Treated sewage water shows a substantial reduction of the protein-like peak (Reynolds & Ahmad, 1997; Ahmad & Reynolds, 1999; Reynolds, 2002), and the fluorescence intensities of the 270/350 nm (Hur et al., 2008) or 220/350 nm (Baker & Inverarity, 2004) peaks correlate with BOD5. Obviously, this technique for differentiating anthropogenic from natural OM is insensitive to nonaromatic pollutants, such as the propylene glycol used as deicer on airplanes (Baker & Inverarity, 2004). Some portable spectrofluorometers using multiple LEDs as excitation sources allow in-field fluorescence analysis (Hart & JiJi, 2002; Obeidat et al., 2008).

Virtual sensors

With the focus on TOM sensors in the above section, virtual sensors appear a suitable approach for BOM determination (Stuetz et al., 1999a; Stuetz et al., 1999b; Tønning et al., 2005; Akratos et al., 2008; Dogan et al., 2008; Dogan et al., 2009).

Tracers or chemical indicators

A tracer is a chemical compound that unambiguously elucidates the source and magnitude of pollution. There is a sharp dichotomy between (1) animal and bacterial OM (anthropogenic OM) of proteinic type and (2) plant OM of lignocellulosic type. It is therefore possible to differentiate natural inputs from residual inputs where the microbial imprint is more pronounced (Namour, 1999). However, the discrimination is fine-tunable, and compounds are already in use for tracing anthropogenic inputs into the water environment. The organic compounds used as anthropogenic tracers of OM include sterols, detergents, whitening agents and caffeine. There are few sensors currently under development that can monitor these tracers.

Proteins

Proteins are related to microbial activity, and generally speaking, high protein levels are characteristic of allochthonous origins like sewer overflows, WWTP discharge or farm waste (Namour, 1999; Baker, 2001). Therefore, proteins can be used as a proxy for BOM quantification, particularly for significant anthropogenic sources. The fluorescence peak of proteinaceous materials at 290/350 nm correlated well with BOM (Arunachalam et al., 2005; Hur et al., 2008). A conductometric biosensor based on protease activities and tested on river and sewer samples showed good relationships with DOC (Marrakchi et al., 2005; Marrakchi et al., 2007; Khadro et al., 2009). Modifying its electrode design improves detection limits 2.2-fold (Khadro et al., 2008), whereas an ISFET sensor proved less sensitive (Marrakchi et al., 2006).

Caffeine

Caffeine from beverages and food products is clearly a ubiquitous anthropogenic indicator in domestic wastewater (Ferreira, 2005; Sankararamakrishnan & Guo, 2005; Buerge et al., 2006). Caffeine concentrations will depend on regional conditions, and they decrease with increasing efficiency of WWTPs (Buerge et al., 2006). Biosensors can detect caffeine over a concentration range from 0.1 to 1 mg/mL (Babu et al., 2007).

Sterols

Sterol biomarker fingerprinting has been used to trace sewage plumes and identify sewage origins (Jarde et al., 2007a; Jarde et al., 2007b; Cordeiro et al., 2008). Unfortunately, there are no reports of sterol-specific sensors. Since environmental conditions can influence metabolic processes and overlap the anthropogenic sterols, a useful sensor should ideally give a kind of sterol fingerprint.

Other tracer compounds

Others candidate tracers include endocrine-disrupting chemicals, linear alkyl benzene sulfonate (a major household anionic surfactant), fluorescence whitening agents or fluorides (Sankararamakrishnan & Guo, 2005). Biosensors have been reported for anionic surfactants (Nomura et al., 1998b) and industrial wastewater (Sak-Bosnar et al., 2006), or for nonylphenol (Andreescu & Sadik, 2004) determination.

Conclusions

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

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

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

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

Molecular tracers are useful in studying OM origin, yet they need good prerequisite knowledge of the OM composition. In general, a good tracer associates a narrow specificity and good stability. Labile compounds like carbohydrates or proteins are chemical indicators that are better geared to studying early diagenesis.

The sensor technologies that have emerged from environmental sciences in the last couple of decades now require validation. Water quality monitoring is currently based on standardized laboratory methods. Sensors, despite being developed more recently, do not have the same recognition capacities and are only seldom used, despite their advantages.

Field validations are needed in order to boost their credibility. ISO standard 15839 (released in 2003) develops a consistent protocol for characterizing these sensors, which should facilitate their adoption for routine use by regulatory bodies. Further work is required to increase their operational period, and particularly to prevent bio-fouling and clogging. Other technological challenges are include miniaturization of the various on-chip modules, cutting energy consumption, developing in situ fuelling, eco-design, geolocation, communication checking, data validation and transmission. It is equally imperative to improve data management. Clearly, there is plenty of room for progression.

Table 1: Methods for TOM determination in water

Description	Application	Range	LOD	Time	Reproducibility	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	(Kim *et al.*, 2001)
TiO_2 beads O_2 Clark electrode	Synthetic wastewater, lake water	7.6	0.12	3-4	6.8	(Lee *et al.*, 2000)
TiO_2 beads, Cr(III) at 610nm	Food, sewage, chemical wastewater (glucose-spiked)	100	nd	10	6.3	(Ai *et al.*, 2004)
Flow system with a TiO_2 film electrode, photocurrent measurement	Synthetic wastewater, glucose	235	0.30	1	1.42	(Chen *et al.*, 2005)
Fluorinated TiO_2, Mn(IV) at 525nm	Tap and lake water, wastewater (paper industry)	280	0.02	10	1.1	(Zhu *et al.*, 2006)
TiO_2 film, Cr(III) at 590nm	Wastewater (glucose-spiked)	500	20	40	5	(Li *et al.*, 2006)
ZnO/TiO_2 film, Mn(IV) at 525nm	Groundwater	0.25–10.0	0.1	40	2.35	(Zhang *et al.*, 2007)
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	(Zhang *et al.*, 2006, Zhang *et al.*, 2004, Zhao *et al.*, 2004, Zhao *et al.*, 2007)
$Ti/TiO_2/PbO_2$	Agri-food, industrial wastewaters, dyes	2500	15	1	7%	(Li *et al.*, 2006, Li *et al.*, 2007)
PbO_2, in 10mM Na_2SO_4	Synthetic water, wastewater (glucose-spiked)	500	2.5	5	5.4	(Ai *et al.*, 2004)
Sandwich-type thin layer working electrode made of Cu	Synthetic, lake water	50	1	10	nd	(Lee *et al.*, 1999)
Cu working electrode in chamber separated with Nafion membrane, in 0.1M NaOH	Synthetic, river, lake waters	10	1	30	nd	(Lee *et al.*, 1999)
Cu/CuO in 0.1M NaOH	Soft drinks industry wastewater	2800	20	1	0.2	(Silva *et al.*, 2009)
BDD in 1M NaOH	Glucose	1900	95	1	6	(Lee and Park, 2005)
AgO-CuO in graphite polystyrene anodes in 0.1M NaOH	Glucose solution, winemaking wastewater	1400	5	1	8.5	(Orozco *et al.*, 2008)
Cu, with a grinding device cleaning its surface, in 0.1M NaOH	Glucose solution, wastewater (1st sedimentation tank)	1000	10	10	nd	(Jeong *et al.*, 2007)
Chemiluminescence						
Flow system measuring Mn(II)	Gallic acid, rivers, pond waters	120	0.8	5	2	(Fujimori *et al.*, 1998)
Flow system measuring Mn(II) concentrated on-column	Lake waters	4,000	4	1.5	4.4	(Li *et al.*, 2003)
Microplate reader measuring Mn(IV) at 640 nm	Natural waters, drug wastewater	19	0.1	<1	4	(Yao *et al.*, 2009)
Photodiode detects Cr(III)	Dyes, garbage leakage, wastewaters	700	2	nd	4.5	(Hu and Yang, 2004)
Flow system measuring Cr(III)	Wastewaters	10,000	100	nd	2.7	(Liu *et al.*, 2008)
A flow injection system integrating UV photolysis	Certified freshwaters, lake waters	20	0.08	10	2.7	(Su *et al.*, 2007)

Table 2: Sensors for BOM using a Clark electrode

Description	Applications	Range	LOD	Time	Reproducibility	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	(Khan *et al.*, 2003)
Trichosporon cutaneum yeast on membrane,	Pharmaceutical, food industry wastewaters	200	50	30		(Iranpour *et al.*, 1997)
P. putida biofilm, sample ozonation	River and wastewaters		0.2	5		(Chee *et al.*, 1999)
P. fluorescens on nitrate cellulose membrane	River waters	10	0.5	2-	10	(Chee *et al.*, 1999)
Flow system combining photocatalysis on TiO_2 and passage on *P. putida*	River waters	8	1	5-10	12	(Chee *et al.*, 2001, Chee *et al.*, 2005)
Klebsiella sp. from activated sludge and enzymes immobilized on membrane	Monosaccharides	nd	nd	30	nd	(Kim and Park, 2004)
P. syringae in highly porous micro-cellular polymer	Glucose-glutamic acid	100	3.3	3-5	3	(Kara *et al.*, 2009)
Encapsulated *S. cerevisiae* on calcium alginate	Glucose-glutamic acid	40	nd	3		(Seo *et al.*, 2009)
Biofilm of the killed cells of a BODSEED	Dairy-, industrial wastewater	45	0.08	45-	12	(Tan and Wu, 1999)
WWTP consortium	Chemical, food-industry wastewater	33	3	6	1.3	(An *et al.*, 1998)
Nitrifying strains from WWTP	Wastewater	0.23–1.4	0.23	6-12	3.7	(Konig *et al.*, 1999)
WWTP consortium	Food, tannery, paper industry wastewaters	60	1	5-7	5%	(Rastogi *et al.*, 2003, Rastogi *et al.*, 2003)
WWTP consortium	OECD synthetic wastewater	230	15	1.5-2	7.5	(Velling and Tenno, 2009)
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	(Koster *et al.*, 2006)
Reference consortium (DONSEED) on nylon membrane	Brewery wastewaters	90	1	15	4	(Dhall *et al.*, 2008)
WWTP consortium on alginate gel	Latex industry wastewaters	60	0.2	10-15	3.9	(Kumlanghan *et al.*, 2008)
Consortium from synthetic wastewater in flow cell	Synthetic wastewaters	700	5	60	7.3	(Liu *et al.*, 2004)
Ph. phosphoreum on a bio-chip, measured by digital camera	Domestic, industrial wastewaters	16	1	20	3	(Sakaguchi *et al.*, 2007)
Recombinant *E. coli* containing *lux* genes from *V. fischeri*	Domestic, industrial wastewaters	200	3	60-120	14.2	(Sakaguchi *et al.*, 2003)

Table 3: Biosensors for BOM without a Clark electrode

Description	Applications	Range	LOD	Time	Reproducibility	References
		O_2 mg/L	O_2 mg/L	min	%	
On-line MFC WWTP inoculum	Wastewaters	150	10	45	1.6	(Kim *et al.*, 2003)
S. cerevisiae and double mediator system (ferricyanide & menadione)	Synthetic water	220	6.6	15	9.1	(Nakamura and Karube, 2003)
P. fluorescens on nylon membrane onto optical fibre	Synthetic wastewaters	10	0.5	15	20	(Chee *et al.*, 2000)
Microorganisms in polymer and Ru(II)	Seawater	200	4	nd	4	(Dai *et al.*, 2004)
Marine microorganisms on silicate film with Ru(II)	Seawater	40	0.1	3	3	(Jiang *et al.*, 2006)
B. subtilus and consortium from activated sludge, fluorimetry on Ru(II),	Domestic wastewaters	60	nd	50	18	(Kwok *et al.*, 2005)
NAD(P)H fluorescence on commercial sensor (340/460nm)	Synthetic wastewaters					(Huang and Ju, 2007)
Microorganisms on silicate film with Ru(II)	Seawater	40	0.2	13	1.2	(Lin *et al.*, 2006)
Marine strains on silicate film with a Ru (II) (Liu *et al.*, 2004)	Seawater	40	0.18	20	3.6	(Xin *et al.*, 2007)
Flow MFC oligotrophic inoculum feed with river water	Surface water & synthetic wastewater	nd	nd	nd	nd	(Kang *et al.*, 2003)
Flow MFC WWTP inoculum feed with wastewater	Synthetic wastewater	100		60	10	(Chang *et al.*, 2004)
Flow MFC WWTP inoculum feed with synthetic wastewater	Synthetic wastewater	100	20	5		(Moon *et al.*, 2004)
Single-chamber MFC with an air cathode, consortium from WWTP	Artificial and diluted wastewaters	350	50	60	0.5	(Di Lorenzo *et al.*, 2009)
MFC feed with anaerobic sludge from biogas reactor	Glucose	25,000	25	3-5	7.2	(Kumlanghan *et al.*, 2007)
Flow MFC WWTP consortium (starch-processing plant) feed with river water	Starch industry wastewater	206	2.6	30	3-12	(Kim *et al.*, 2003, Kim *et al.*, 2004)
P. fluorescens on cellulose acetate membrane, (ferricyanide)	Wastewaters	260	5	20	10.5	(Yoshida *et al.*, 2001)
Yeasts from pulp mill effluent on glassy carbon electrodes (ferricyanide)	Pulp mill effluents	100	2	5	10	(Trosok *et al.*, 2001)
P. vulgaris on polyvinyl acetate, (ferricyanide)	Wastewaters	19-150	4.8	60	nd	(Pasco *et al.*, 2004)
Marine microorganisms on a functionalized glassy carbon electrode (ferricyanide)	GGA standard solution, seawater	40	1.2	30	7.7	(Chen *et al.*, 2008)

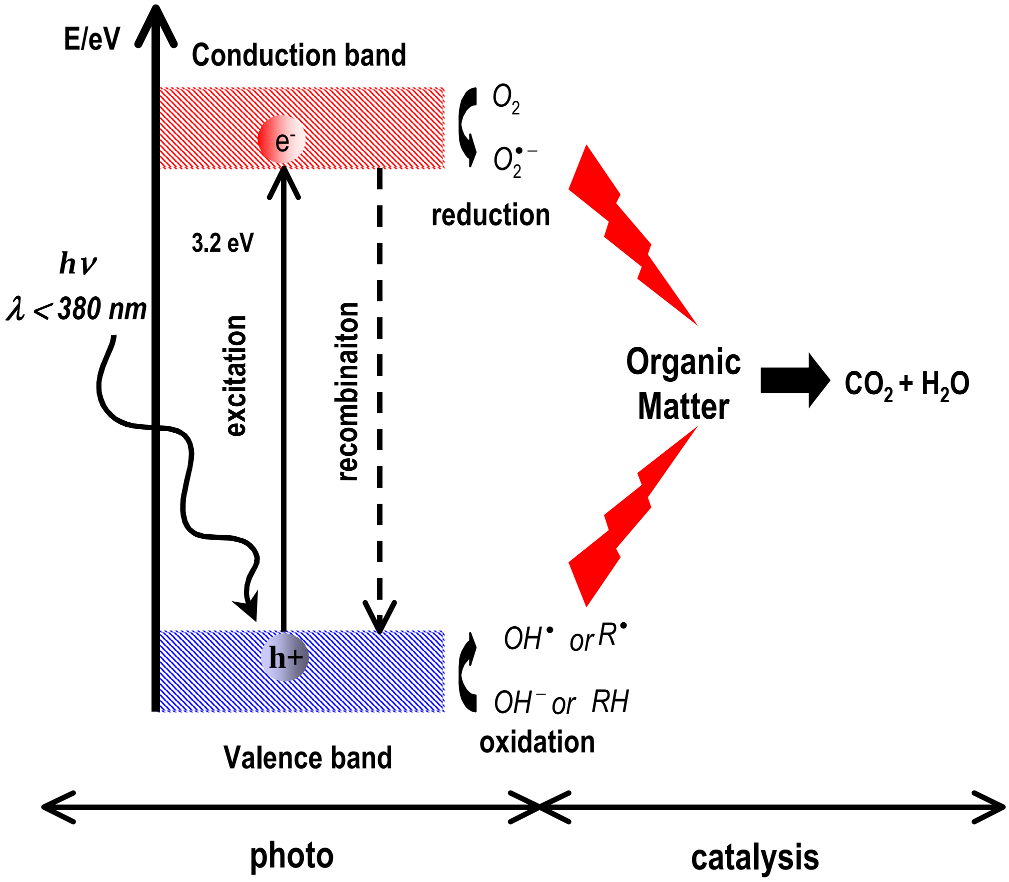

Figure 1: Photocatalytic mechanism on a semiconductor surface illuminated with energy > 3.1eV (380 nm). An electron jumps from the valence band to the conduction band, leaving a positive hole. This electron can be transferred to oxygen (or H+; chlorinated compounds), initiating various reactions. The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

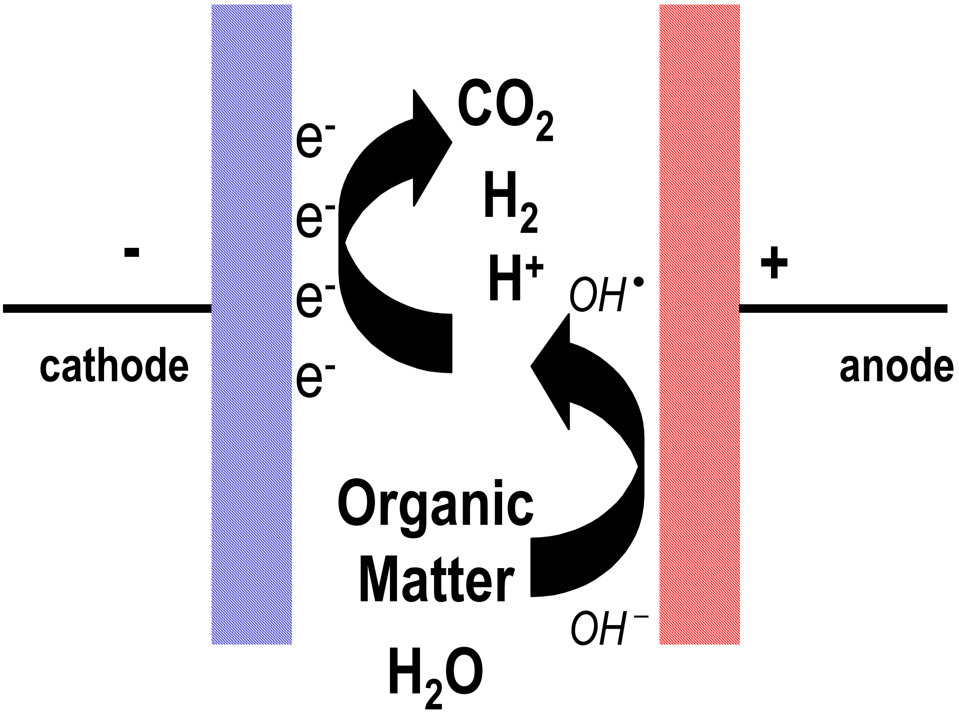

Figure 2: The principle of electrocatalysis is based on a powerful oxidizing activity generated at the electrode surface. The electrons released during oxidation can be measured as an electrical current proportional to the quantity of OM oxidized.

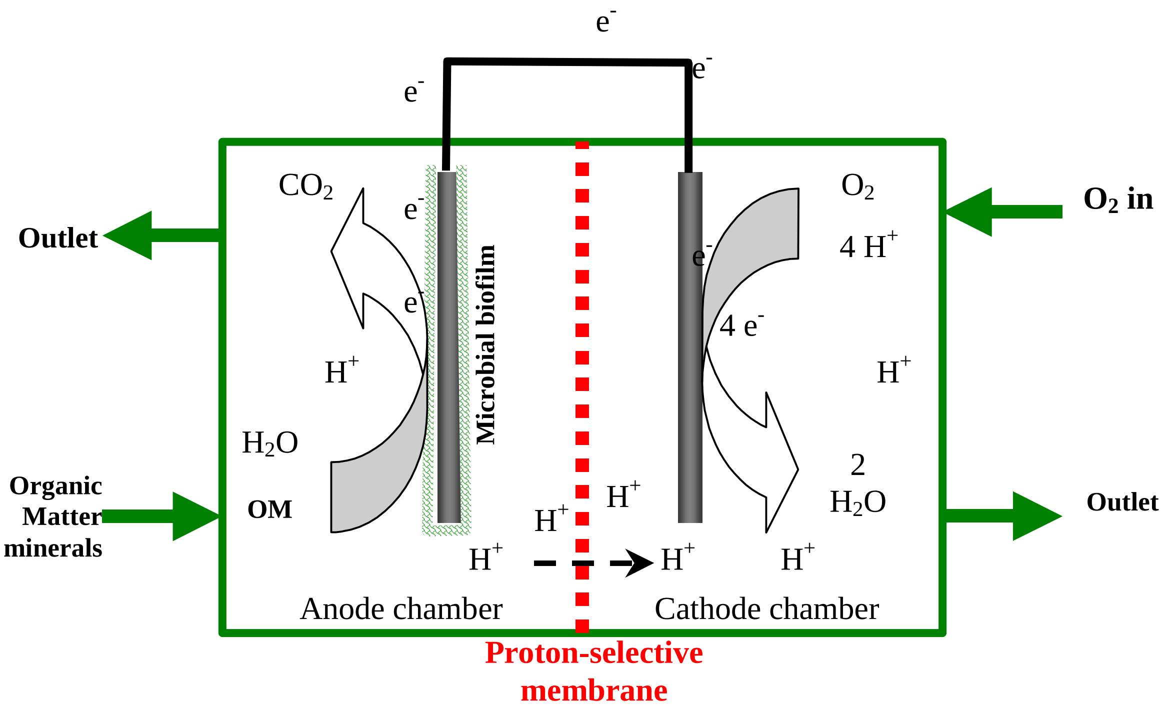

Figure 3: A microbial fuel cell consists of an anaerobic chamber with an anode, and an aerobic chamber with a cathode, the two separated by a proton-exchange membrane. In the anaerobic chamber, the anode short-circuits the natural electron acceptors, such as oxygen or nitrate. The protons then pass through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

References

Ahmad, S.R., Reynolds, D.M. 1999, Monitoring of water quality using fluorescence technique: Prospect of on-line process control. Water Research, 33:2069-2074.

Ai, S.Y., Gao, M.N., Yang, Y., Li, J.Q., Jin, L.T. 2004a, Electrocatalytic sensor for the determination of chemical oxygen demand using a lead dioxide modified electrode. Electroanalysis, 16:404-409.

Ai, S.Y., Li, J.Q., Ya, Y., Gao, M.N., Pan, Z.S., Jin, L.T. 2004b, Study on photocatalytic oxidation for determination of chemical oxygen demand using a nano-TiO2-K2Cr2O7 system. Analytica Chimica Acta, 509:237-241.

Akratos, C.S., Papaspyros, J.N.E., Tsihrintzis, V.A. 2008, An artificial neural network model and design equations for BOD and COD removal prediction in horizontal subsurface flow constructed wetlands. Chemical Engineering Journal, 143:96-110.

An, L.C., Niu, H., Zeng, H. 1998, A new biosensor for rapid oxygen demand measurement. Water Environment Research, 70:1070-1074.

Andreescu, S., Sadik, O.A. 2004, Correlation of analyte structures with biosensor responses using the detection of phenolic estrogens as a model. Analytical Chemistry, 76:552-560.

Arunachalam, R.S., Shah, H.K., Ju, L.K. 2005, Monitoring aerobic sludge digestion by online scanning fluorometry. Water Research, 39:1205-1214.

Awad, H.S., Galwa, N.A. 2005, Electrochemical degradation of Acid Blue and Basic Brown dyes on Pb/PbO2 electrode in the presence of different conductive electrolyte and effect of various operating factors. Chemosphere, 61:1327-1335.

Babu, V.R.S., Patra, S., Karanth, N.G., Kumar, M.A., Thakur, M.S. 2007, Development of a biosensor for caffeine. Analytica Chimica Acta, 582:329-334.

Baker, A. 2001, Fluorescence excitation-emission matrix characterization of some sewage-impacted rivers. Environmental Science & Technology, 35:948-953.

Baker, A., Inverarity, R. 2004, Protein-like fluorescence intensity as a possible tool for determining river water quality. Hydrological Processes, 18:2927-2945.

Baker, A., Lamont-Black, J. 2001, Fluorescence of dissolved organic matter as a natural tracer of ground water. Ground Water, 39:745-750.

Baronian, K., Downard, A., Lowen, R., Pasco, N. 2003, Detection of two distinct substrate-dependent catabolic responses in yeast cells using a mediated electrochemical method. Applied Microbiology and Biotechnology, 60:108-113.

Bertrand-Krajewski, J.L., Winkler, S., Saracevic, E., Torres, A., Schaar, H. 2007, Comparison of and uncertainties in raw sewage COD measurements by laboratory techniques and field UV-visible spectrometry. Water Science and Technology, 56:17-25.

Bourgeois, W., Romain, A.C., Nicolas, J., Stuetz, R.M. 2003, The use of sensor arrays for environmental monitoring: interests and limitations. Journal of Environmental Monitoring, 5:852-860.

Brookman, S.K.E. 1997, Estimation of biochemical oxygen demand in slurry and effluents using ultra-violet spectrophotometry. Water Research, 31:372-374.

Buerge, I.J., Poiger, T., Muller, M.D., Buser, H.R. 2006, Combined sewer overflows to surface waters detected by the anthropogenic marker caffeine. Environmental Science and Technology, 40:4096-4102.

Cañizares, P., Sáez, C., Lobato, J., Rodrigo, M.A. 2006, Detoxification of synthetic industrial waste-waters using electrochemical oxidation with boron-doped diamond anodes. Journal of Chemical Technology and Biotechnology, 81:352-358.

Chang, I.S., Jang, J.K., Gil, G.C., Kim, M., Kim, H.J., Cho, B.W., Kim, B.H. 2004, Continuous determination of biochemical oxygen demand using microbial fuel cell type biosensor. Biosensors and Bioelectronics, 19:607-613.

Chatzisymeon, E., Stypas, E., Bousios, S., Xekoukoulotakis, N.P., Mantzavinos, D. 2008, Photocatalytic treatment of black table olive processing wastewater. Journal of Hazardous Materials, 154:1090-1097.

Chaubey, A., Malhotra, B.D. 2002, Mediated biosensors. Biosensors & Bioelectronics, 17:441-456.

Chee, G.J., Nomura, Y., Ikebukuro, K., Karube, I. 1999a, Development of highly sensitive BOD sensor and its evaluation using preozonation. Analytica Chimica Acta, 394:65-71.

Chee, G.J., Nomura, Y., Ikebukuro, K., Karube, I. 2000, Optical fiber biosensor for the determination of low biochemical oxygen demand. Biosensors and Bioelectronics, 15:371-376.

Chee, G.J., Nomura, Y., Ikebukuro, K., Karube, I. 2001, Biosensor for the evaluation of biochemical oxygen demand using photocatalytic pretreatment. Sensors and Actuators, B: Chemical, 80:15-20.

Chee, G.J., Nomura, Y., Ikebukuro, K., Karube, I. 2005, Development of photocatalytic biosensor for the evaluation of biochemical oxygen demand. Biosensors and Bioelectronics, 21:67-73.

Chee, G.J., Nomura, Y., Karube, I. 1999b, Biosensor for the estimation of low biochemical oxygen demand. Analytica Chimica Acta, 379:185-191.

Chen, H., Ye, T., Qiu, B., Chen, G., Chen, X. 2008, A novel approach based on ferricyanide-mediator immobilized in an ion-exchangeable biosensing film for the determination of biochemical oxygen demand. Analytica Chimica Acta, 612:75-82.

Chen, J.S., Zhang, J.D., Xian, Y.Z., Ying, X.Y., Liu, M.C., Jin, L.T. 2005, Preparation and application of TiO2 photocatalytic sensor for chemical oxygen demand determination in water research. Water Research, 39:1340-1346.

Cordeiro, L.G.S.M., Carreira, R.S., Wagener, A.L.R. 2008, Geochemistry of fecal sterols in a contaminated estuary in southeastern Brazil. Organic Geochemistry.

Dai, Y.J., Lin, L., Li, P.W., Chen, X., Wang, X.R., Wong, K.Y. 2004, Comparison of BOD optical fiber biosensors based on different microorganisms immobilized in ormosil matrixes. International Journal of Environmental Analytical Chemistry, 84:607-617.

Dhall, P., Kumar, A., Joshi, A., Saxsena, T.K., Manoharan, A., Makhijani, S.D., Kumar, R. 2008, Quick and reliable estimation of BOD load of beverage industrial wastewater by developing BOD biosensor. Sensors and Actuators, B: Chemical, 133:478-483.

Di Lorenzo, M., Curtis, T.P., Head, I.M., Scott, K. 2009, A single-chamber microbial fuel cell as a biosensor for wastewaters. Water Research, 43:3145-3154.

Dogan, E., Ates, A., Yilmaz, E.C., Eren, B. 2008, Application of artificial neural networks to estimate wastewater treatment plant Inlet Biochemical Oxygen Demand. Environmental Progress, 27:439-446.

Dogan, E., Sengorur, B., Koklu, R. 2009, Modeling biological oxygen demand of the Melen River in Turkey using an artificial neural network technique. Journal of Environmental Management, 90:1229-1235.

Ferreira, A.P. 2005, Caffeine as an environmental indicator for assessing urban aquatic ecosystems. Cadernos de saúde pública, Rio de Janeiro, 21:1884-1892.

Fujimori, K., Takenaka, N., Bandow, H., Maeda, Y. 1998, Continuous monitoring method for organic pollutants in water based on chemiluminescence reaction with potassium permanganate. Analytical Communications, 35:307-308.

Greenwood, R., Roig, B. 2006, SWIFT Report , Deliverable 5: Directory of "Screening tools" - A toolbox of existing and emerging methods for chemical and ecological status monitoring under the WFD, European Union 238.

Harrelkas, F., Paulo, A., Alves, M.M., El Khadir, L., Zahraa, O., Pons, M.N., van der Zee, F.P. 2008, Photocatalytic and combined anaerobic-photocatalytic treatment of textile dyes. Chemosphere, 72:1816-1822.

Hart, S.J., JiJi, R.D. 2002, Light emitting diode excitation emission matrix fluorescence spectroscopy. Analyst, 127:1693-1699.

Hu, Y.G., Yang, Z.Y. 2004, A simple chemiluminescence method for determination of chemical oxygen demand values in water. Talanta, 63:521-526.

Huang, L., Ju, L.K. 2007, Sludge settling and online NAD(P)H fluorescence profiles in wastewater treatment bioreactors operated at low dissolved oxygen concentrations. Water Research, 41:1877-1884.

Hudson, N., Baker, A., Ward, D., Reynlds, D.M., Brunsdon, C., Carliell-Marquet, C., Browning, S. 2008, Can fluorescence spectrometry be used as a surrogate for the Biochemical Oxygen Demand (BOD) test in water quality assessment? An example from South West England. Science of the Total Environment, 391:149-158.

Hur, J., Hwang, S.J., Shin, J.K. 2008, Using synchronous fluorescence technique as a water quality monitoring tool for an urban river. Water Air and Soil Pollution, 191:231-243.

Iranpour, R., Straub, B., Jugo, T. 1997, Real time BOD monitoring for wastewater process control. Journal of Environmental Engineering-Asce, 123:154-159.

Jarde, E., Gruau, G., Mansuy-Huault, L. 2007a, Detection of manure-derived organic compounds in rivers draining agricultural areas of intensive manure spreading. Applied Geochemistry, 22:1814-1824.

Jarde, E., Gruau, G., Mansuy-Huault, L., Peu, P., Martinez, J. 2007b, Using sterols to detect pig slurry contribution to soil organic matter. Water, Air, and Soil Pollution, 178:169-178.

Jeong, B.G., Yoon, S.M., Choi, C.H., Kwon, K.K., Hyun, M.S., Yi, D.H., Park, H.S., Kim, M., Kim, H.J. 2007, Performance of an electrochemical COD (chemical oxygen demand) sensor with an electrode-surface grinding unit. Journal of Environmental Monitoring, 9:1352-1357.

Jeong, H.S., Lee, S.H., Shin, H.S. 2007, Feasibility of on-line measurement of sewage components using the UV absorbance and the neural network. Environmental Monitoring and Assessment, 133:15-24.

Jiang, D.L., Zhang, S.Q., Zhao, H.J. 2007, Photocatalytic degradation characteristics of different organic compounds at TiO2 nanoporous film electrodes with mixed anatase/rutile phases. Environmental Science and Technology, 41:303-308.

Jiang, Y., Xiao, L.L., Zhao, L., Chen, X., Wang, X., Wong, K.Y. 2006, Optical biosensor for the determination of BOD in seawater. Talanta, 70:97-103.

Ju, L.K., Nallagatla, P.B. 2003, Monitoring and kinetic study of ammonia oxidation using dissolved oxygen electrode and NAD(P)H fluorometer. Water Research, 37:188-196.

Kang, K.H., Jang, J.K., Pham, T.H., Moon, H., Chang, I.S., Kim, B.H. 2003, A microbial fuel cell with improved cathode reaction as a low biochemical oxygen demand sensor. Biotechnology Letters, 25:1357-1361.

Kansal, S.K., Singh, M., Sud, D. 2007, Studies on photodegradation of two commercial dyes in aqueous phase using different photocatalysts. Journal of Hazardous Materials, 141:581-590.

Kansal, S.K., Singh, M., Sud, D. 2008, Studies on TiO2/ZnO photocatalysed degradation of lignin. Journal of Hazardous Materials, 153:412-417.

Kara, S., Keskinler, B., Erhan, E. 2009, A novel microbial BOD biosensor developed by the immobilization of P. Syringae in micro-cellular polymers. Journal of Chemical Technology and Biotechnology, 84:511-518.

Khadro, B., Namour, P., Bessueille, F., Leonard, D., Jaffrezic, N. 2009, Validation of a conductometric bienzyme biosensor for the detection of proteins as marker of organic matter in river samples. Journal of Environmental Sciences--CHINA, 21:545-551.

Khadro, B., Santha, H., Nagy, P., Harsanyi, G., Jaffrezic-Renault, N. 2008, Comparison of the performances of conductometric microsensors for different technologies and designs of interdigitated electrodes. Sensor Letters, 6:413-416.

Khan, E., Babcock, R.W., Jongskul, S., Devadason, F.A., Tuprakay, S. 2003, Determination of biodegradable dissolved organic carbon using entrapped mixed microbial cells. Water Research, 37:4981-4991.

Kim, B.H., Chang, I.S., Gil, G.C., Park, H.S., Kim, H.J. 2003, Novel BOD (biological oxygen demand) sensor using mediator-less microbial fuel cell. Biotechnology Letters, 25:541-545.

Kim, B.H., Park, H.S., Kim, H.J., Kim, G.T., Chang, I.S., Lee, J., Phung, N.T. 2004, Enrichment of microbial community generating electricity using a fuel-cell-type electrochemical cell. Applied Microbiology and Biotechnology, 63:672-681.

Kim, H.J., Park, H.S., Hyun, M.S., Chang, I.S., Kim, M., Kim, B.H. 2002, A mediator-less microbial fuel cell using a metal reducing bacterium, Shewanella putrefaciense. Enzyme and Microbial Technology, 30:145-152.

Kim, M., Youn, S.M., Shin, S.H., Jang, J.G., Han, S.H., Hyun, M.S., Gadd, G.M., Kim, H.J. 2003, Practical field application of a novel BOD monitoring system. Journal of Environmental Monitoring, 5:640-643.

Kim, M.N., Park, K.H. 2001, Klebsiella BOD sensor. Sensors and Actuators, B: Chemical, 80:9-14.

Kim, M.N., Park, K.H. 2004, Immobilization of enzymes for Klebsiella BOD sensor. Sensors and Actuators, B: Chemical, 98:1-4.

Kim, Y.C., Sasaki, S., Yano, K., Ikebukuro, K., Hashimoto, K., Karube, I. 2001, Photocatalytic sensor for the determination of chemical oxygen demand using flow injection analysis. Analytica Chimica Acta, 432:59-66.

Konig, A., Bachmann, T.T., Metzger, J.W., Schmid, R.D. 1999, Disposable sensor for measuring the biochemical oxygen demand for nitrification and inhibition of nitrification in wastewater. Applied Microbiology and Biotechnology, 51:112-117.

Koster, M., Gliesche, C.G., Wardenga, R. 2006, Microbiosensors for measurement of microbially available dissolved organic carbon: Sensor characteristics and preliminary environmental application. Applied and Environmental Microbiology, 72:7063-7073.

Krantz-Rülcker, C., Stenberg, M., Winquist, F., Lundström, I. 2001, Electronic tongues for environmental monitoring based on sensor arrays and pattern recognition: a review. Analytica Chimica Acta, 426:217-226.

Kumlanghan, A., Kanatharana, P., Asawatreratanakul, P., Mattiasson, B., Thavarungkul, P. 2008, Microbial BOD sensor for monitoring treatment of wastewater from a rubber latex industry. Enzyme and Microbial Technology, 42:483-491.

Kumlanghan, A., Liu, J., Thavarungkul, P., Kanatharana, P., Mattiasson, B. 2007, Microbial fuel cell-based biosensor for fast analysis of biodegradable organic matter. Biosensors and Bioelectronics, 22:2939-2944.

Kwok, N.Y., Dong, S., Lo, W., Wong, K.Y. 2005, An optical biosensor for multi-sample determination of biochemical oxygen demand (BOD). Sensors and Actuators, B: Chemical, 110:289-298.

Lee, D.S., Park, J.M. 1999, Neural network modeling for on-line estimation of nutrient dynamics in a sequentially-operated batch reactor. Journal of Biotechnology, 75:229-239.

Lee, J., Park, S.M. 2005, Direct electrochemical assay of glucose using boron-doped diamond electrodes. Analytica Chimica Acta, 545:27-32.

Lee, K.H., Ishikawa, T., McNiven, S., Nomura, Y., Sasaki, S., Arikawa, Y., Karube, I. 1999a, Chemical oxygen demand sensor employing a thin layer electrochemical cell. Analytica Chimica Acta, 386:211-220.

Lee, K.H., Ishikawa, T., McNiven, S.J., Nomura, Y., Hiratsuka, A., Sasaki, S., Arikawa, Y., Karube, I. 1999b, Evaluation of chemical oxygen demand (COD) based on coulometric determination of electrochemical oxygen demand (EOD) using a surface oxidized copper electrode. Analytica Chimica Acta, 398:161-171.

Lee, K.H., Kim, Y.C., Suzuki, H., Ikebukuro, K., Hashimoto, K., Karube, I. 2000, Disposable chemical oxygen demand sensor using a microfabricated Clark-type oxygen electrode with a TiO2 suspension solution. Electroanalysis, 12:1334-1338.

Lee, S., Ahn, K.H. 2004, Monitoring of COD as an organic indicator in waste water and treated effluent by fluorescence excitation-emission (FEEM) matrix characterization. Water Science and Technology, 50:57-63.

Li, B.X., Zhang, Z.J., Wang, J., Xu, C.L. 2003, Chemiluminescence system for automatic determination of chemical oxygen demand using flow injection analysis. Talanta, 61:651-658.

Li, J.Q., Li, L.P., Zheng, L., Xian, Y.Z., Jin, L.T. 2006a, Determination of chemical oxygen demand values by a photocatalytic oxidation method using nano-TiO2 film on quartz. Talanta, 68:765-770.

Li, J.Q., Zheng, L., Li, L.P., Shi, G.Y., Xian, Y.Z., Jin, L.T. 2006b, Photoelectro-synergistic catalysis at Ti/TiO2/PbO2 electrode and its application on determination of chemical oxygen demand. Electroanalysis, 18:2251-2256.

Li, J.Q., Zheng, L., Li, L.P., Shi, G.Y., Xian, Y.Z., Jin, L.T. 2007, Photoelectro-synergistic catalysis combined with a FIA system application on determination of chemical oxygen demand. Talanta, 72:1752-1756.

Lin, J.M., Qu, F., Yamada, M. 2002, Chemiluminescent investigation of tris(2,2'-bipyridyl) ruthenium(II) immobilized on a cationic ion-exchange resin and its application to analysis. Analytical and Bioanalytical Chemistry, 374:1159-1164.

Lin, L., Xiao, L.L., Huang, S., Zhao, L., Cui, J.S., Wang, X.H., Chen, X. 2006, Novel BOD optical fiber biosensor based on co-immobilized microorganisms in ormosils matrix. Biosensors and Bioelectronics, 21:1703-1709.

Liu, J., Mattiasson, B. 2002, Microbial BOD sensors for wastewater analysis. Water Research, 36:3786-3802.

Liu, J., Olsson, G., Mattiasson, B. 2004a, Short-term BOD (BODst) as a parameter for on-line monitoring of biological treatment process Part 1. A novel design of BOD biosensor for easy renewal of bio-receptor. Biosensors and Bioelectronics, 20:562-570.

Liu, J., Olsson, G., Mattiasson, B. 2004b, Short-term BOD (BODst) as a parameter for on-line monitoring of biological treatment process. Part II: Instrumentation of integrated flow injection analysis (FIA) system for BODst estimation. Biosensors and Bioelectronics, 20:571-578.

Liu, W., Zhang, Z.J., Zhang, Y.Y. 2008, Chemiluminescence micro-flow system for rapid determination of chemical oxygen demand in water. Microchimica Acta, 160:141-146.

Mao, X.H., Tian, F., Gan, F.X., Lin, A., Zhang, X.J. 2008, Comparison of the performances of Ti/SnO2-Sb, Ti/SnO2-Sb/PbO2, and Nb/BDD anodes on electrochemical degradation of azo dye. Russian Journal of Electrochemistry, 44:802-811.

Maribas, A., da Silva, M.D.L., Laurent, N., Loison, B., Battaglia, P., Pons, M.N. 2008, Monitoring of rain events with a submersible UV/VIS spectrophotometer. Water Science and Technology, 57:1587-1593.

Marrakchi, M., Dzyadevych, S.V., Biloivan, O.A., Martelet, C., Temple, P., Jaffrezic-Renault, N. 2006, Development of trypsin biosensor based on ion sensitive field-effect transistors for proteins determination. Materials Science and Engineering C, 26:369-373.

Marrakchi, M., Dzyadevych, S.V., Namour, P., Martelet, C., Jaffrezic-Renault, N. 2005, A novel proteinase K biosensor based on interdigitated conductometric electrodes for proteins determination in rivers and sewers water. Sensors and Actuators, B: Chemical, 111-112:390-395.

Marrakchi, M., Martelet, C., Dzyadevych, S.V., Namour, P., Jaffrezic-Renault, N. 2007, An enzyme biosensor based on gold interdigitated thin film electrodes for water quality control. Analytical Letters, 40:1307-1316.

Martinez-Huitle, C.A., Ferro, S. 2006, Electrochemical oxidation of organic pollutants for the wastewater treatment: direct and indirect processes. Chemical Society Reviews, 35:1324-1340.

Martins, A.F., Arsand, D.R., Brenner, C.B., Minetto, L. 2008, COD evaluation of hospital effluent by means of UV-spectral deconvolution. Clean-Soil Air Water, 36:875-878.

Moon, H., Chang, I.S., Kang, K.H., Jang, J.K., Kim, B.H. 2004, Improving the dynamic response of a mediator-less microbial fuel cell as a biochemical oxygen demand (BOD) sensor. Biotechnology Letters, 26:1717-1721.

Muzio, F.M., Budman, H.M., Robinson, C.W., Graff, S. 2001, BOD5 estimation for pulp and paper mill effluent using UV absorbance. Water Research, 35:1842-1850.

Nakamura, H., Karube, I. 2003, Current research activity in biosensors. Analytical and Bioanalytical Chemistry, 377:446-468.

Nakamura, H., Suzuki, K., Ishikuro, H., Kinoshita, S., Koizumi, R., Okuma, S., Gotoh, M., Karube, I. 2007, A new BOD estimation method employing a double-mediator system by ferricyanide and menadione using the eukaryote Saccharomyces cerevisiae. Talanta, 72:210-216.

Namour, P. 1999. Auto-épuration des rejets organiques domestiques, nature de la matière organique résiduaire et son effet en rivière. PhD thesis. Université de Lyon, Lyon (France).

Nataraja, M., Qin, Y., Seagren, E.A. 2006, Ultraviolet spectrophotometry as an index parameter for estimating the biochemical oxygen demand of domestic wastewater. Environmental Technology, 27:789-800.

Nomura, Y., Chee, G.J., Karube, I. 1998a, Biosensor technology for determination of BOD. Field Analytical Chemistry and Technology, 2:333-340.

Nomura, Y., Ikebukuro, K., Yokoyama, K., Takeuchi, T., Arikawa, Y., Ohno, S., Karube, I. 1998b, Application of a linear alkylbenzene sulfonate biosensor to river water monitoring. Biosensors and Bioelectronics, 13:1047-1053.

Obeidat, S., Bai, B., Rayson, G.D., Anderson, D.M., Puscheck, A.D., Landau, S.Y., Glasser, T. 2008, A multi-source portable light emitting diode spectrofluorometer. Applied Spectroscopy 62:327-332.

Orozco, J., Fernandez-Sanchez, C., Mendoza, E., Baeza, M., Cespedes, F., Jimenez-Jorquera, C. 2008, Composite planar electrode for sensing electrochemical oxygen demand. Analytica Chimica Acta, 607:176-182.

Pai, T.Y., Tsai, Y.P., Lo, H.M., Tsai, C.H., Lin, C.Y. 2007, Grey and neural network prediction of suspended solids and chemical oxygen demand in hospital wastewater treatment plant effluent. Computers and Chemical Engineering, 31:1272-1281.

Panizza, M., Cerisola, G. 2008, Removal of colour and COD from wastewater containing acid blue 22 by electrochemical oxidation. Journal of Hazardous Materials, 153:83-88.

Pardeshi, S.K., Patil, A.B. 2008, A simple route for photocatalytic degradation of phenol in aqueous zinc oxide suspension using solar energy. Solar Energy, 82:700-705.

Pasco, N., Baronian, K., Jeffries, C., Hay, J. 2000, Biochemical mediator demand - A novel rapid alternative for measuring biochemical oxygen demand. Applied Microbiology and Biotechnology, 53:613-618.

Pasco, N., Baronian, K., Jeffries, C., Webber, J., Hay, J. 2004, MICREDOX® - Development of a ferricyanide-mediated rapid biochemical oxygen demand method using an immobilised Proteus vulgaris biocomponent. Biosensors and Bioelectronics, 20:524-532.

Rastogi, S., Kumar, A., Mehra, N.K., Makhijani, S.D., Manoharan, A., Gangal, V., Kumar, R. 2003a, Development and characterization of a novel immobilized microbial membrane for rapid determination of biochemical oxygen demand load in industrial waste-waters. Biosensors and Bioelectronics, 18:23-29.

Rastogi, S., Rathee, P., Saxena, T.K., Mehra, N.K., Kumar, R. 2003b, BOD analysis of industrial effluents: 5 days to 5 min. Current Applied Physics, 3:191-194.

Reynolds, D.M. 2002, The differentiation of biodegradable and non-biodegradable dissolved organic matter in wastewaters using fluorescence spectroscopy. Journal of Chemical Technology and Biotechnology, 77:965-972.

Reynolds, D.M., Ahmad, S.R. 1997, Rapid and direct determination of wastewater BOD values using a fluorescence technique. Water Research, 31:2012-2018.

Rieger, L., Langergraber, G., Siegrist, H. 2006, Uncertainties of spectral in situ measurements in wastewater using different calibration approaches. Water Science and Technology, 53:187-197.

Rieger, L., Langergraber, G., Thomann, M., Fleischmann, N., Siegrist, H. 2004, Spectral in-situ analysis of NO2, NO3, COD, DOC and TSS in the effluent of a WWTP. Water Science and Technology, 50:143-152.

Sak-Bosnar, M., Matesic-Puac, R., Madunic-Cacic, D., Grabaric, Z. 2006, New potentiometric sensor for determination of low levels of anionic surfactants in industrial effluents. Tenside Surfactants Detergents, 43:82-87.

Sakaguchi, T., Kitagawa, K., Ando, T., Murakami, Y., Morita, Y., Yamamura, A., Yokoyama, K., Tamiya, E. 2003, A rapid BOD sensing system using luminescent recombinants of Escherichia coli. Biosensors and Bioelectronics, 19:115-121.

Sakaguchi, T., Morioka, Y., Yamasaki, M., Iwanaga, J., Beppu, K., Maeda, H., Morita, Y., Tamiya, E. 2007, Rapid and onsite BOD sensing system using luminous bacterial cells-immobilized chip. Biosensors and Bioelectronics, 22:1345-1350.

Sankararamakrishnan, N., Guo, Q. 2005, Chemical tracers as indicator of human fecal coliforms at storm water outfalls. Environment International, 31:1133-1140.

Seo, K.S., Choo, K.H., Chang, H.N., Park, J.K. 2009, A flow injection analysis system with encapsulated high-density Saccharomyces cerevisiae cells for rapid determination of biochemical oxygen demand. Applied Microbiology and Biotechnology, 83:217-223.

Silva, C., Conceição, C.D.C., Bonifácio, V., Fatibello, O., Teixeira, M. 2009, Determination of the chemical oxygen demand (COD) using a copper electrode: a clean alternative method. Journal of Solid State Electrochemistry 13:665-669.

Spencer, R.G.M., Baker, A., Ahad, J.M.E., Cowie, G.L., Ganeshram, R., Upstill-Goddard, R.C., Uher, G. 2007, Discriminatory classification of natural and anthropogenic waters in two UK estuaries. Science of the Total Environment, 373:305-323.

Stuetz, R.M., Fenner, R.A., Engin, G. 1999a, Characterisation of wastewater using an electronic nose. Water Research, 33:442-452.

Stuetz, R.M., George, S., Fenner, R.A., Hall, S.J. 1999b, Monitoring wastewater BOD using a non-specific sensor array. Journal of Chemical Technology and Biotechnology, 74:1069-1074.

Stumwohrer, K., Matsche, N., Winkler, S. 2003, Influence of changes of the wastewater composition on the applicability of UV-absorption measurements at combined sewer overflows. Water Science and Technology, 47:73-78.

Su, Y.Y., Li, X.H., Chen, H., Lv, Y., Hou, X.D. 2007, Rapid, sensitive and on-line measurement of chemical oxygen demand by novel optical method based on UV photolysis and chemiluminescence. Microchemical Journal, 87:56-61.

Tan, T.C., Wu, C.H. 1999, BOD sensors using multi-species living or thermally killed cells of a BODSEED microbial culture. Sensors and Actuators B-Chemical, 54:252-260.

Tartakovsky, B., Lishman, L.A., Legge, R.L. 1996, Application of multi-wavelength fluorometry for monitoring wastewater treatment process dynamics. Water Research, 30:2941-2948.

Thomas, O., El Khorassani, H., Touraud, E., Bitar, H. 1999, TOC versus UV spectrophotometry for wastewater quality monitoring. Talanta, 50:743-749.

Tønning, E., Sapelnikova, S., Christensen, J., Carlsson, C., Winther-Nielsen, M., Dock, E., Solna, R., Skladal, P., Norgaard, L., Ruzgas, T., Emneus, J. 2005, Chemometric exploration of an amperometric biosensor array for fast determination of wastewater quality. Biosensors and Bioelectronics, 21:608-617.

Torres, A., Bertrand-Krajewski, J.L. 2008, Partial Least Squares local calibration of a UV-visible spectrometer used for in situ measurements of COD and TSS concentrations in urban drainage systems. Water Science and Technology, 57:581-588.

Trosok, S.P., Driscoll, B.T., Luong, J.H.T. 2001, Mediated microbial biosensor using a novel yeast strain for wastewater BOD measurement. Applied Microbiology and Biotechnology, 56:550-554.

Velling, S., Tenno, T. 2009, Different calibration methods of a microbial BOD sensor for analysis of municipal wastewaters. Sensors and Actuators, B: Chemical, 141:2336238.

Villanueva, S., Guadarrama, A., Rodriguez-Mendez, M.L., de Saja, J.A. 2008, Use of an array of metal oxide sensors coupled with solid phase microextraction for characterisation of wines. Study of the role of the carrier gas. Sensors and Actuators, B: Chemical, 132:125-133.

Villanueva, S., Vegas, A., Fernandez-Escudero, J.A., Iniguez, M., Rodriguez-Mendez, M.L., de Saja, J.A. 2006, SPME coupled to an array of MOS sensors. Reduction of the interferences caused by water and ethanol during the analysis of red wines. Sensors and Actuators, B: Chemical, 120:278-287.

Wang, B., Chang, X., Ma, H.Z. 2008, Electrochemical oxidation of refractory organics in the coking wastewater and Chemical Oxygen Demand (COD) removal under extremely mild conditions. Industrial and Engineering Chemistry Research, 47:8478-8483.

Weiss, E., Groenen-Serrano, K., Savall, A. 2008, A comparison of electrochemical degradation of phenol on boron doped diamond and lead dioxide anodes. Journal of Applied Electrochemistry, 38:329-337.

Winkler, S., Bertrand-Krajewski, J.L., Torres, A., Saracevic, E. 2008, Benefits, limitations and uncertainty of in situ spectrometry. Water Science and Technology, 57:1651-1658.

Winquist, F. 2008, Voltammetric electronic tongues - basic principles and applications. Microchimica Acta, 163:3-10.

Winquist, F., Krantz-Rulcker, C., Lundstrom, I. 2008, A miniaturized voltammetric electronic tongue. Analytical Letters, 41:917-924.

Xin, L.L., Wang, X.D., Guo, G.M., Wang, X.R., Chen, X. 2007, An optical biosensing film for biochemical oxygen demand determination in seawater with an automatic flow sampling system. Measurement Science and Technology, 18:2878-2884.

Yang, W., Nan, J., Sun, D. 2008, An online water quality monitoring and management system developed for the Liming River basin in Daqing, China. Journal of Environmental Management, 88:318-325.

Yao, H., Wu, B., Qu, H.B., Cheng, Y.Y. 2009, A high throughput chemiluminescence method for determination of chemical oxygen demand in waters. Analytica Chimica Acta, 633:76-80.

Yoo, C.K., Lee, I.B. 2004, Soft sensor and adaptive model-based dissolved oxygen control for biological wastewater treatment processes. Environmental Engineering Science, 21:331-340.

Yoshida, N., Hoashi, J., Morita, T., McNiven, S.J., Nakamura, H., Karube, I. 2001a, Improvement of a mediator-type biochemical oxygen demand sensor for on-site measurement. Journal of Biotechnology, 88:269-275.

Yoshida, N., Hoashi, J., Morita, T., McNiven, S.J., Yano, K., Yoshida, A., Nakamura, H., Karube, I. 2001b, Monitoring of the composting process using a mediator-type biochemical oxygen, demand sensor. Analyst, 126:1751-1755.

Zhang, S.Q., Jiang, D.L., Zhao, H.J. 2006, Development of chemical oxygen demand on-line monitoring system based on a photoelectrochemical degradation principle. Environmental Science & Technology, 40:2363-2368.

Zhang, S.Q., Zhao, H.J. 2008, A new approach prevailing over chloride interference in the photoelectrochemical determination of chemical oxygen demand. Analyst, 133:1684-1691.

Zhang, S.Q., Zhao, H.J., Jiang, D.L., John, R. 2004, Photoelectrochemical determination of chemical oxygen demand based on an exhaustive degradation model in a thin-layer cell. Analytica Chimica Acta, 514:89-97.

Zhang, Z.H., Yuan, Y., Fang, Y.J., Liang, L.H., Ding, H.C., Jin, L.T. 2007, Preparation of photocatalytic nano-ZnO/TiO2 film and application for determination of chemical oxygen demand. Talanta, 73:523-528.

Zhao, H.J., Jiang, D.L., Zhang, S.Q., Catterall, K., John, R. 2004, Development of a direct photoelectrochemical method for determination of chemical oxygen demand. Analytical Chemistry, 76:155-160.

Zhao, H.L., Jiang, D.L., Zhang, S.L., Wen, W. 2007, Photoelectrocatalytic oxidation of organic compounds at nanoporous TiO2 electrodes in a thin-layer photoelectrochemical cell. Journal of Catalysis, 250:102-109.

Zhu, L.H., Chen, Y., Wu, Y.H., Li, X.R., Tang, H.Q. 2006, A surface-fluorinated-TiO2-KMnO4 photocatalytic system for determination of chemical oxygen demand. Analytica Chimica Acta, 571:242-247.

Onema
Hall C – Le Nadar
5 square Félix Nadar
94300 Vincennes
01 45 14 36 00
www.onema.fr

Cemagref
Parc de Tourvoie
BP 44,
92163 Antony cedex
01 40 96 61 21
www.cemagref.fr