Fast electrochemical COD (eCOD) measurement on polluted water

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Abstract:
COD is one of the main parameters for assessment of water quality. There are many procedures to determine COD but most of them are time expensive because a digestion step is included to complete the oxidation of organic matter by chemical reactants. The proposed method uses the same technology as for preparative electrochemical oxidation of pollutants but here with an analytical purpose. A flow-cell with laminar path is designed to circulate the water and it was tested with standard solutions in a continuous amperometric technique. A single analysis takes only 4 minutes and no reactants are consumed, only electrical energy. The range of electrochemical-COD (eCOD) that can be detected goes from 0.1 to 1200 ppm, and a LOD of 0.03 ppm and an RSD% below 0.3 are calculated. Similar results were found by checking for different organic pollutants. These results are compared with those obtained by using the dichromate standard method (COD-Cr) and no significative differences are observed.

Keywords:
wastewater; COD; amperometry; flow detector; electrochemistry; electroanalysis

1. Introduction

Beyond the increasingly urgent need to maintain the quality of natural water bodies, to design processes that minimize water consumption and, once used, to return the water in the same or better condition than it was originally in, there are several countries that use the Chemical Oxygen Demand (COD) level in a regulatory manner for assessment water quality, and they set threshold for drinking waters around 10 mg/L. Also, maximum limits ranging from 120 to 200 mg/L depending on every country [1], [2], [3] should be considered for wastewater before that water can be returned to the environment.

The standard method to measure the COD is the ISO 6060:1989 [4] but from december-2023 this method is withdrawal. So, the most used method to measure COD in water samples is the 4-hour method whose basis is the complete oxidation of dissolved organic matter by an excess of potassium dichromate in acidic and hot conditions and quantification of remanent dichromate by titration or colorimetry. Such method has several weaknesses as their interferents (Cl^-, NO_2^-, S^{2-}, Fe^{2+}…) or the limited range of determination (typically from 300 to 600 ppm for the best accuracy), without forgetting the time consumed for each measurement (a digestion 4-hour period is included). Several of such limitations can be avoided if an electrochemical method is used to determine the COD (eCOD) [5]. Also, the flow approach, both for colorimetric [6], [7] and electrochemical [8], [9] determinations, contributes to greatly increasing the frequency of sampling but also the range of determination will be seriously stretched and restricted to lower levels of COD, mainly for Flow Injection strategies.

To develop electrochemical methods to determine the eCOD on waters, several materials can be used as anode, the working electrode for such determinations, and expensive Boron-doped-diamond (BDD) [8], complex 3D-structured [10], nano-modified [11], [12], [13], [14], composite [15], [16] or low-cost [13], [17] materials can be found in bibliography. Regarding the geometry of electrochemical cells, most batch methods use three cylindrical electrodes immersed in the cell but also thin layer working electrodes have been used [18], [19]. For flow approaches, a thin-layer flow-through cell with small circular working electrodes [8], [9], [20] exposed to the carrier/sample solution and reference electrode sets downstream out of cell is the preferred configuration. Also, microelectrode-arrays having medium-large exposed surface have been used [15].

In this work we propose a new flow-cell design having a great electrode-surface exposed to the smallest liquid volume by using a laminar sandwich setup for the working electrode, the flowing liquid and the counter electrode. In addition, the reference electrode is located inside the cell, minimizing the iR drop and helping to potentiostat stabilization. The material selected as working electrode must be shaped as a plate, but its surface can be modified in a variety of ways, resulting in a very adaptable setup that can be tunned according to the requirements of every problem. The overall cell size doesn't exceed 3x4x6 cm, making the proposal very portable and suitable for field measurements. The time for each measurement can be reduced to 4 minutes and the limit of eCOD detection is as low as 30 ppb with a range of response from 0.1 to 1200 ppm, suitable both for analysis of drinking waters and highly contaminated wastewater and without consuming any kind of reactants, only electrical energy.

2. Materials and Methods

2.1 Reactants, solutions and methods

Eating sugar is used as saccharose source for standard COD solutions. A concentrated solution of saccharose is prepared by dissolving 10 g in 1 L of distilled water. Appropriated dilutions were made to obtain standard solutions with adequate concentration.

A carrier solution with Na_2SO_4 0.1 M is used instead of net water to provide an electrolyte conductive enough to apply the electrochemical method properly.

Pharmaceutical Secondary Standards are used as sources of Diclofenac potassium salt and Ibuprofen. Concentrated 200 mg/L solutions are prepared for both reactants as standard solutions.

All reactants are used as they are commercially available, without further purification. Distilled water is used to make all solutions. All standard solutions are dairy prepared. The reactant solutions are prepared and stored on glass laboratory bottles at room temperature.

To determine the COD-Cr concentrations a modification of method described by Li et al. [21] is used. Briefly, in a screw-capped glass vial 3 mL of sample/standard water is mixed with 3 mL of reactant solution containing 9.20 g/L of $K_2Cr_2O_7$, 1.65 g/L of Ag_2SO_4 and 33% v/v of concentrated H_2SO_4. The filled vial is kept at 70 ºC for at least 8 hours to complete the reaction and absorbance is measured at 575 nm after room temperature is reached. The absorbance is translated to COD-Cr ppm by using a calibration equation previously determined with standard solutions.

A single-line manifold (Figure 1) is used for calibrating the amperometric measurement method. It includes sequentially a 250 mL baker containing 100 mL of carrier solution and a magnetic stirrer, a peristaltic pump configured to impel the liquid with a flow rate of 48 mL/s, and the home-made flow cell described in the 2.3 section below connected to the potentiostat. The output of cell is returned to the baker in a closed loop circuit. All the tubing used are flexible crystal-clear Tygon 0.5 mm ID. A potential higher than 1300 mV is applied to the working electrode, enough to oxidize the organic pollutants presents on water but below water oxidation values to avoid the gas evolution inside the cell, and an amperometric method is configured to register the current evolution on time. After a steady state is reached and current values are stabilized (4 minutes should be adequate) 1.0 mL of standard solution is added to the baker and a new steady state is awaited.

Before the amperometric method is applied, electrochemical cleaning of working electrode should be made by cycling potentials from -100 to 1800 mV at 100 mV/s (20 cycles), so a new and reproducible PbO_2 surface is obtained coating the lead plate used to making the working electrode. The electrolyte used to fill the flow cell for this cleaning procedure is the carrier solution flowing at 48 mL/s. An auxiliary electrode made from a plate of Stainless Steele and an Ag/AgCl reference electrode are used to configure the three-electrodes set.

2.2 Apparatus

A potentiostat/galvanostat OGF500 from Origalys Electrochem SAS (France) is used to drive the detector. The dedicated software OrigaMaster is used to configure experiments and collect data.

The Blue-Wave miniature fiber-optic spectrometer and SL5 light source with Tungsten Halogen and Deuterium lamps by StellarNet Inc (FL - USA) are used to measure the absorbance for COD-Cr determinations, a sample-holder for measuring directly on cylindrical 2 cm OD vials was designed and 3D-printed in black PLA in our laboratory, the dedicated SpectraWiz software is used to collect the absorption spectra.
A Gilson Minipuls 3 peristaltic pump (WI - USA) is used to drive liquids through the cell.

2.3 Cell design

The cell is made in two transparent PMMA blocks for easy inspection of leakages and bubbles. Both are milled to make a recess for electrode allocation (see Figure 2). At the bottom part the counter electrode is placed (B in Figure 2). Beside a silicone rubber spacer is placed (C in Figure 2) and then the working electrode (D in Figure 2), a gasket to seal liquids (E in Figure 2) is placed on top the working electrode. The spacer placed-in between working and counter electrodes seals the liquids, delimits the effective area of working electrode contacting liquids and in addition sets the width of liquid layer (the content of liquid inside the cell with such design is less than 130 mm^3, with 1 mm of clearance from working to counter electrodes). The working electrode has three holes to enable the inlet and outlet of liquids and to allocate the reference electrode. These holes reduce the effective surface of working electrode but 56 mm^2 remains in contact with water.
A pair of 1/4-28" coupling is aligned with the working holes by upper block to connect the Tygon tubbing used to circulate liquid through the cell. The reference electrode is a commercial Ag/AgCl (BioLogic RE-1S) and is adjusted to body cell by the gasket, to avoid leakage. Placing the reference electrode in the middle of water path inside the cell minimises the iR drop by reducing its distance from the working electrode, and the potentiostat used to set the electrode potential is more stable than with other configurations. A pair of bolts and nuts tighten all parts together.
To make electrical connections from external instrumentation to electrodes, they have a side flap that are located one on each side of cell to make clamp connections easier, avoiding short-circuits.

3. Results and Discussion

3.1. Potential determination

In general terms the potential applied to working electrode must be selected by voltametric tests. Once the electrochemical cleaning of working electrode is performed (Figure 3), the highest potential that doesn't evolute gas from water dissociation will be the better option, so any organic pollutant present should be oxidized. An alternative method can also be made by adding a pollutant aliquot to carrier solution and observing the emerging anodic wave. Such test was performed and the working potential selected for amperometrical measurements was 1300 mV, 1350 mV and 1450 mV for saccharose, ibuprofen and diclofenac solutions respectively.

3.2. Calibration procedure

To verify the analytical performance of the electrochemical detector toward quantitative determination of eCOD, several 1 mL additions of standard solutions are made to the reservoir of carrier solution and oxidation current are registered every 2 seconds. Figure 4 shows the chronoamperogram and the correspondent calibration

curve obtained for saccharose measures considering the current registered 4 minutes after each addition. Each data for the calibration curve is calculated as the mean value for the 30 current values nearest to the data logging time. The statistical figures extracted from the experimental results are the following: the linear response of detector goes from 0.1 to 1250 ppm of eCOD, having a limit of detection (LOD) of 0.03 ppm calculated as 3-fold the standard deviation of base line measures divided by the slope of the experimental response (3s/m); the sensitivity of method is 0.17 µA/ppm eCOD and the relative standard deviation (RSD) is only 0.3%; the eCOD-current equation is *Current* (µA) = 0.17 x *eCOD* (ppm) + 381.14 with a correlation coefficient (r^2) of 0.993.

Additionally, the COD-Cr for the same concentrations of saccharose are measured as described in section 2.1 and both sets of COD values are correlated up to 1250 ppm resulting (see Figure 5) in a strait behaviour with a slope of 1.001 and a correlation coefficient (r^2) of 0.99. These results validate the proposed electrochemical detector for quantitative determination of COD in water samples.

To ensure that the eCOD determination can be made regardless of the organic pollutant present in the water samples, calibration experiments have been repeated with two emerging pollutants, considered as recalcitrant because of their persistence and difficult removal by the usual water treatment procedures, such as Ibuprofen and Diclofenac. For Ibuprofen, the linear response of detector goes from 0.1 to 250 ppm of eCOD, having a limit of detection (LOD) of 0.02 ppm calculated as 3-fold the standard deviation of base line measures divided by the slope of the experimental response (3s/m); the sensitivity of method is 0.25 µA/ppm eCOD and the relative standard deviation (RSD) is only 0.3%; the eCOD-current equation is *Current* (µA) = 0.25 x *eCOD* (ppm) + 598.52 with a correlation coefficient (r^2) of 0.699. For Diclofenac, the linear response of detector goes from 0.1 to 250 ppm of eCOD, having a limit of detection (LOD) of 0.01 ppm calculated as 3-fold the standard deviation of base line measures divided by the slope of the experimental response (3s/m); the sensitivity of method is 1.04 µA/ppm eCOD and the relative standard deviation (RSD) is only 0.75%; the eCOD-current equation is *Current* (µA) = 1.04 x *eCOD* (ppm) + 559.69 with a correlation coefficient (r^2) of 0.95. These results demonstrate the ability to measure eCOD with the detector proposed in this work, whatever the organic pollutant present in the water samples.

4. Conclusions

This work proposes a new design of flow-cell intended for the determination of the electrochemical COD in water samples. Such cell was tested by using Saccharose, Ibuprofen and Diclofenac as organic pollutants and making their corresponding calibration curves by measuring the oxidation current in an amperometric procedure as successive aliquots of standard solutions were added to a water reservoir whose contents was circulated through the cell in a single-line closed-loop flow arrangement. In all the experiments an oxidation current proportional to the concentration of organic pollutants was measured, no matter what the organic contaminant was present in water samples. If such contaminant is highly soluble, the lineal response of the detector is broad enough to measure highly contaminated samples being the linear working range of our detector comparable to the broadest previously published. The high electrode area of detector also enables the detection of the lowest concentration

of contaminant, as is demonstrated by the small values of LOD, less than 30 ppb, obtained for the three molecules tested, such values are comparable to the lowest reported by bibliography, assessing the good performance of the detector both for high and low values of COD.
The eCOD results for saccharose were correlated with those obtained with an adaptation of the dichromate method, COD-Cr, for the same concentrations. A good correspondence for both sets of data in the whole range tested is obtained, so, both results are completely and directly interchangeable.

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Conceptualization, J.D.M; methodology, J.D.M.; software, A.M.G., C.M.M. and J.D.M.; validation, A.M.G., C.M.M. and J.D.M.; formal analysis, J.D.M.; investigation, A.M.G. and C.M.M.; resources, J.D.M.; data curation, J.D.M.; writing—original draft preparation, C.M.M. and J.D.M.; writing—review and editing, C.M.M. and J.D.M.; supervision, J.D.M.; project administration, J.D.M. All authors have read and agreed to the published version of the manuscript.

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Figure captions:

Figure 1. Suggested manifold for amperometric measurements. A) Reservoir; B) Stirrer; C) Peristaltic pump; D) Flow cell; E) Potentiostat

Figure 2. Exploded view of flow cell, showing all the parts included in: A) Bottom part, B) Counter electrode, C) Spacer, D) Working electrode, E) Gasket, F) Top part; G) Tube Fitters and nuts

Figure 3. Resulting voltammograms after working electrode cleaning procedure

Figure 4. A) Measurements of oxidation current for the first additions, and B) corresponding calibration curve for saccharose

Figure 5. eCOD and COD-Cr correlation chart