Measure of Chemical Oxygen Demand by an Inexpensive Electrochemical Instrument.

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***Abstract*— This article describes the implementation of an inexpensive electrochemical instrument and its performance when it is used to measure the chemical oxygen demand (COD). Low cost precision electronic devices and electrochemical system were used to build it. Homemade copper electrode let made COD measurements in synthetic wastewater. Excellent results were achieved against conventional method for COD measurement.**

***Keywords*— low cost, electrochemical intrument; potentiostat; chemical oxygen demand (COD); potentiometry; copper electrode.**

I. Introduction

The COD is a fundamental parameter for determination of water pollution, the common way to measure it is through 5220B standard method [1]. However, this method has different disadvantages as long time of treatment, use of hazard chemical agents (Ag_2SO_4, H_2SO_4 con. $HgSO_4$), high cost instruments and others [2]. Due to these reasons, 5220B standard method is time consuming and expensive way to measure COD.

Based on these problems many researchers have developed alternative methods to measure COD [2-5]. One of the most attractive is the potentiometric method, which has had a widely developed on scientific community, because of its high sensibility, short analysis time, low cost operation, less use of hazard chemical agents and others. This method reduces the time and cost, hours to seconds and thousands to hundreds respectively.

The potentiometric method to measure COD uses a potentiostat as the main tool. It is a general-purpose instrument broadly used in the field of electrochemistry, which allow the study of redox processes at molecular level [6].

Potentiostats have a high price; above two thousand dollars and it represent a problem. Low budget laboratories cannot afford this kind of instruments. Based on it, researches had built an inexpensive electrochemical instrument (IEI), which can run experiments with high quality and precision as a commercial potentiostat.

Nowadays, there are a lot of information about how to build these kind of instruments, the most relevant information for the actual research was [7-10], with these was possible to developed and implement a high quality, and inexpensive electrochemical instrument.

The measurement of COD by potentiometry is a process in where the organic matter is reduced, for that a working electrode of Cu doped with nano-particles of Cu is needed. The electrode was made from electrical cable of 3 mm of diameter and it was polished until it had a homogenous surface.

Cupper electrode doped with nano-particles of Cu, in alkaline media oxide a very wide range of organic compounds, mainly responsible for the COD of natural water.

The electrochemical technique needed to measure the COD, is linear voltammetry, moreover cyclic voltammetry is needed to dope the working electrode with nano-particles of copper [11-12].

In addition, in order to prove the quality and performance of the proposed IEI, the signals generated by it were compare with the signals of a commercial potentiostat (CHI-1220B).

II. Materials

Materials to achieve the measurement of COD are divided in two groups, electronic and electrochemical.

A. Electronic

TABLE I
ELECTRONIC DEVICES

Device	Quantity	Price [$]	Total [$]
AD8625	3	9.74	29.22
TL071	1	0.33	0.33
OPA4188	1	4.50	4.50
DG612	2	1.20	2.40
2N3904	8	0.15	1.20
Shunts Resistors	12	1.20	14.40
RF Connector	3	3.30	9.90
Trimmer Resistor	1	2.50	2.50
ST32F407	1	20	20
PCB	1	60	60
Others	1	30	30
			174.45

With exception of the printed circuit board (PCB), which were custom ordered from SMELEKTRONIK, all the electronic devices to implement IEI could be obtained in any electronic store. Table I, shown the components to build it. The final cost of the electrochemical instrument implemented is about 200 dollars, versus CHI-1220B, which is traded about 4000 dollars.

B. Electrochemical

The chemical agents were pure reagent grade. Glucose from Merck was use as standard and sodium hydroxide (NaOH) 99% from Merck.

The electrochemical system used were, a Ag/AgCl as a reference electrode, platinum as counter electrode, and an electrical cable of 7.07 mm^2 of active area was used as working electrode.

To determine the better performance of analysis, were assessed two treatments to prepare the working electrode, one with NaOH to form oxides over the electrode surface, and other with CuSO4 in acid medium to form nanoparticles of Cu over the electrode surface.

III. Methodology

Measurement of COD could be done by linear voltammetry, besides, to dope working electrode with particles of nCu, cyclic voltammetry is needed. Hence, IEI must execute these electrochemical techniques.

Typical linear voltammetry response curve is shown in Fig. 1a. In simple terms, the wave form is just a ramp function, which starts at some start potential (Ei) and increases (become more negative) or decreases (become more positive) until some finish potential (E) [6].

Cyclic voltammetry is the most widely practiced method of all electrochemical methods. The waveform for it is a symmetrical triangular wave; this is carried out by switching the direction of the scan at certain time. The waveform is shown in Fig. 2a. and its result is shown in Fig. 2b [6].

The generation of the waveforms for linear and cyclic voltammetry was done by software through a 12-bit digital to analog converter (DAC), a peripherical included in the microcontroller (STM32F407VG).

To implement these two electrochemical techniques, the potentiostat use a system of three electrodes. The three electrodes are:

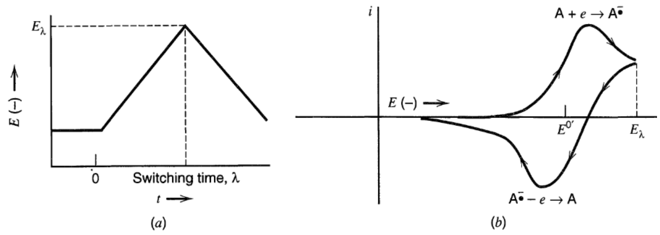

Fig. 2 (a) Cyclic voltammetry wave form. (b) Resulting cyclic voltammogram

- Working electrode (WE): where all chemical reactions occur.
- Reference electrode (RE): has a constant and self-governing potential.
- Counter electrode (CE): let close the electronic circuit.

The accomplishment of the electrochemical experiments could be done by to mains tasks. First, IEI must control the potential between working and reference electrode and second, it must measure the current that flows through counter and working electrode.

The circuit for control the voltage was derived from the circuit shown in Fig. 3. Since the electrochemical cell could be modeled as a network of impedances [6], The current through the cell is controlled by the amplifier U1 then the reference electrode is always at $-e_i\ vs\ ground$, because working electrode is grounded.

Voltage follower (U2) has been inserted into the feedback loop to avoid the current flow between counter electrode and reference electrode. The follower output is also available to measure continuously the potential between reference and working electrode.

Additionally, to measure the current through the cell, the working electrode was connected to a current to voltage converter (U5), whose voltage output is proportionally to the input current. Notice that the working electrode is still connected to ground, an essential condition for the operation of the system [9]. The electronic circuit is shown in Fig. 4.

The electrochemical instrument implemented was very sensible to noise; the source of noise could be inherent to the electronic system, electrochemical cell and environmental conditions [9]. The best way to reduce it was implementing a filter.

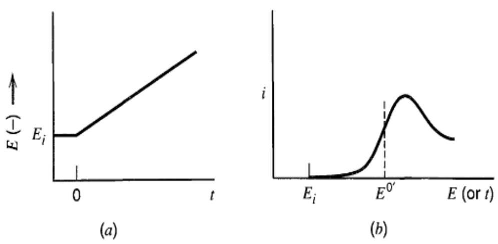

Fig. 1 (a) Linear voltammetry wave form starting at Ei. (b) Resulting $i-E$ curve.

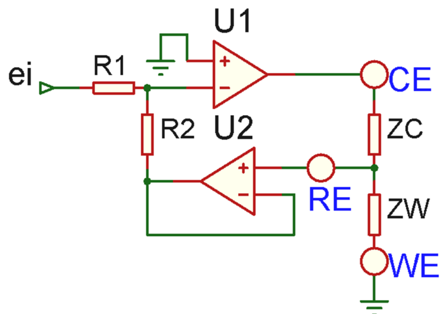

Fig. 3 Circuit for control the potential.

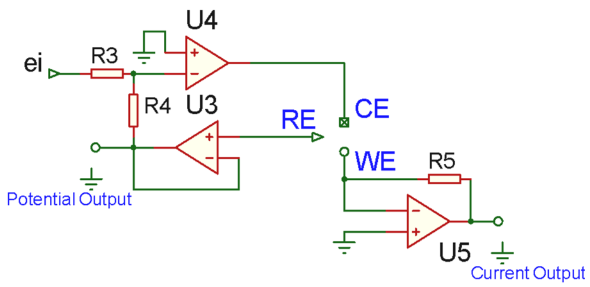

Fig. 4 Potentiostat: electronic circuit.

The range of working frequencies per experiments are from 0.25 Hz to 10 Hz. knowing this range, the filter was determined, it was: fourth order low pass filter with cut-off frequency at 10 Hz [13].

The analog filter helps to reduce the noise from electrochemical system and environmental conditions. The noise inherent to the electronic system depend mainly on the quality of the electronic devices.

Once all analog electronic was made, the digitalization of measurements of voltage and current was possible. An analog to digital converter (ADC) of 12-bit was use, this peripheral is also include in STM32F407VG.

Before the measurements were sent to user interface by STM32F407VG, a digital filter treated these data in order to reduce the noise inherent in electronic systems, a Butterworth low pass digital filter was implemented, and it was designed according the parameters mentioned before, in Matlab [14]. This kind of filter completes the last step of filtering and help to obtain a clearly measurement of voltage and current.

The software for STM32F407 was develop on C through CooCox, and the user interface was develop on JAVA with NeatBeans. The implemented hardware of IEI is shown in Fig. 5, then with software and hardware settled, the performance was verified and the first experiments were run.

IV. Results and Discussions

The first step was to compare the quality of signals between the IEI and CHI-1220B. The electrochemical technique used to probe this was cyclic voltammetry; the solution was potassium ferricyanide (FeCN6K3) at 0.1 Molar with a glassy carbon as a working electrode.

The Fig. 6 shown the result of this experiment. Visually the difference between the voltammograms is slightly different.

Fig. 5 Inexpensive Electrochemical Instrument

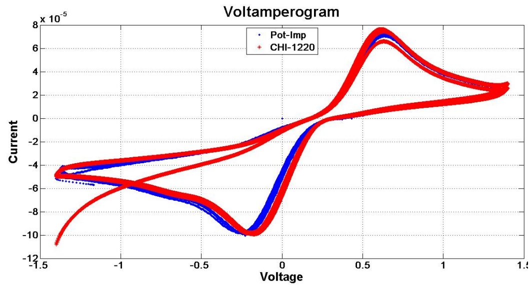

Fig. 6 Voltamperogram of the 0.1 M potassium ferricyanide using a working electrode of Carbon Glass, a counter electrode of Platinum, and electrode reference of Ag/AgCl. Implemented potentiostat (Blue) vs commercial Potentiostat (Red).

Statistically the correlation between each other is greater than 0.99, this means that the quality of the signals generated and measure by the implemented instrument is good enough to developed electrochemical experiments more complex.

Since IEI had satisfactory results, a cyclic voltammetry was performed from -1.0 V to 0.8 V with cooper electrode as working electrode in a solution of NaOH at 0.1 M to dope it with nano-particles of Cu.

This stage is important because in it is produced a layer of copper oxide (CuO) in the surface of the electrode, which allow the reading of organic matter. The treatment of Cu electrode was realized in both, the implemented instrument and CHI-1220B, given the same result for both.

The next step was use this electrode with a solution of glucose (Synthetic wastewater) at different concentrations of COD (from 0 to 1000 mg/L), and run linear voltammetry from 0 V to 0.7 V vs Ag/AgCl with sweep speed of 80 mV.s-1, the results of these experiments are shown in Fig. 7. It could be seen, if the concentration of COD has increased thus the output current will increase for the same range of potential.

To know the relation between current and concentration of COD, data of the area under the curve of each line was plotted against its respective concentration. The results obtained shown a linear relation between the current and COD in synthetic wastewater, with this relation was possible to determine a calibration curve for the IEI.

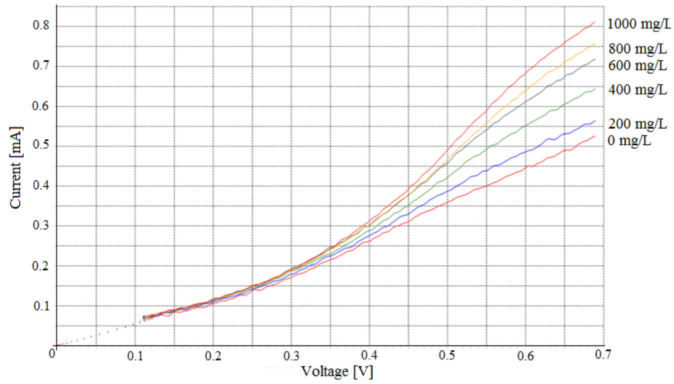

Fig. 7 Results of linear voltammetry for synthetic wastewater at different concentrations of COD.

The measures obtained were very satisfactory and they are shown in Fig. 8. The correlation coefficient of the curve is

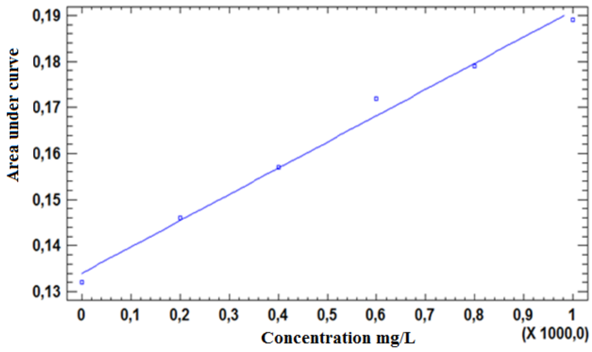

Fig. 8 Measurement of COD from 0 to 1000 mg/L.

0.9887, this income in the potential use of IEI for measure COD in real water and use it in researches that are more complex.

However, the results obtained with CHI-1220B were similar, but with a correlation coefficient of 0.9814, less than the correlation obtained with IEI. This is because CHI-1220B is a general-purpose instrument, then for measure the area under the curve the researcher has to select the beginning point and the ending point of the curve with the mouse, carrying with it a tiny amount of errors.

Finally, the expected time for one measurement is about 15 minutes, 10 minutes for treatment of the copper electrode and about 5 minutes for reading the COD, being faster compared to 5220 B standard method with an operating time is 2-4 hours. The outcomes shown in the present article are about the measure of COD in synthetic wastewater, the outcomes for measurement of COD in real wastewater will be shown in next articles.

V. Conclusions

It was possible to implement an inexpensive electrochemical instrument, which was used in measurement of COD in synthetic and real wastewater; moreover, it reproduces linear and cyclic voltammetry techniques with high accuracy enabling it to run experiments that are more complex.

The implementation of an inexpensive electrochemical instrument (less than 200 American dollars), which can measure COD and run several electrochemical experiments, implies an important breakthrough, because it enables the applications of rapid and less pollutant chemical analysis techniques. Furthermore, its cost makes it accessible to low budget laboratories.

The quality of signal generated by DAC of STM32F407VG was good enough to achieve the measurement of COD, but it has a disadvantage, it has not repetitively among time and it is a problem, because at different time DAC changed its output voltage for the same digital data.

The main problem to achieve good measurements of voltage and current was the noise, the implementation of analog and digital filter help reducing it but cannot be eliminated at all.

Future Works

Test the IEI with real wastewater and in field conditions to study and correct external agents like solar light, electric noise, human vibration, temperature, etc.

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