Assessment of an *in situ* Real Time UV/VIS Based Spectrometry System for Chemical Oxygen Demand Measurement in a Wastewater Anaerobic Treatment Reactor

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Abstract

Analysis of physical and chemical parameters is more and more important for operation checking and performance control in wastewater treatment plants (WWTP). Recently developed UV/VIS spectrometry based sensors are being used for measurement of parameters like chemical oxygen demand (COD). The aim of this work is to report results of real time *in situ* COD measurement using a spectrophotometric system in a wastewater treatment plant with upflow anaerobic sludge blanket (UASB). The studies

focused a medium size WWTP (wastewater average flow around 319 L/s) located in Paraná State (Brazil), and used several statistical tools, like as relative error, boxplot charts, statistical dispersion, Student's t-test (significance level $\alpha = 0.05$) and bilateral test, to compare measurement system results with laboratorial analyses. The results indicate that sensor monitoring can be effective for the UASB affluent, as the probe measurement results and laboratorial analyses of COD showed no statistical significant difference for three different calibration scenarios. Linear local calibration showed the best performance in the assessed WWTP, with mean error being 4.32%, standard deviation $\sigma = 2.76\%$ and determination coefficient $R^2 = 0.7667$. For the UASB reactor effluent the behavior has not shown the expected adherence: only the offset calibration, among four assessed methods, showed no significant difference, with mean error being 27.53%, standard deviation $\sigma = 24.11\%$ and determination coefficient $R^2 = 0.1246$. COD removal efficiency in the WTP was between 56% and 60%.

Keywords: UV/VIS Spectrophotometry, COD, UASB, Probe, Sanitation System.

Introduction

In the wastewater treatment plants of Brazil, and of Paraná State in particular, the upflow anaerobic sludge blanket (UASB) treatment method is prevailing, due to its low energy consumption, reduced area requirement and higher operational simplicity. Besides, UASB reactors have low sludge production and reduced implantation cost (CHERNICHARO *et al.*, 1999).

Sampling and analysis are more and more important for treatment plants operation assessment, since the high-quality data of present systems allow plant monitoring. Traditional approach is based on punctual short runs for sampling and later laboratory analyses, which use to be lengthy, demand expensive and/or toxic reagents and produce residues needing later treatment (VANROLLEGHEM, LEE, 2003; BRITO *et al.*, 2014).

Usually assessed parameters, like as temperature, pH and conductivity among others, can be continuously monitored. In the last few years some papers reported the monitoring of total organic carbon (TOC), total suspended solids (TSS) and chemical oxygen demand (COD) using spectrometric techniques (BRITO *et al.*, 2014).

The chemical oxygen demand is a global parameter very used as indicator of oxygen content in design and control of UASB anaerobic treatment systems (CHERNICHARO *et al.*, 2015). Aisse *et al.* (2002) obtained $\text{COD} = 151 \pm 64 \text{ mg/L}$ as a typical value for the effluent of domestic wastewater treated in UASB reactor. Considering a value of $453 \pm 147 \text{ mg/L}$ for COD in the affluent the authors determined a removal efficiency of 69%. The volumetric organic load (VOL) can be assumed to be $1.80 \text{ kg(COD).m}^{-3}.\text{day}^{-1}$, for a hydraulic retention time of 8 hours.

The full UV spectrum has been used for the TOC, COD and biochemical oxygen demand (BOD₅) estimation in wastewater (THOMAS *et al.*, 1997). The spectrometry in the ultraviolet and visible ranges (UV/VIS) allows to obtain relevant information (VAN DEL BROEKE *et al.*, 2006; BRITO *et al.*, 2014). It is a fast and easy to implement technique, used for wastewater quality assessment (THOMAS *et al.*, 2005). The used wavelength varies from 200 to 800 nm, and it is possible to relate the radiation absorbance features (absorption wavelength ranges) with the compounds that account for COD values.

In the measurement process it is very important to consider the sample peculiarities (matrix effect) and assessment of the error, which can be reduced with previous calibration and with control of local sampling variables, such as flow fluctuation, coarse solids and equipment cleansing. A good monitoring depends on true results. Van der Broke *et al.* (2006) affirm that online spectra acquisition has been implemented in most WWTP. One can admit that measurement instruments must deal with additional challenges, due to water quality matrix variability and to facility related operation and safety issues (BRITO *et al.*, 2014). There are few works in Brazil that support the installation of *in situ* COD real time probes in UASB reactors based WWTP.

In this respect, the objective of this work is to report the results of using a spectrophotometric measurement system for real time *in situ* COD determination

in a wastewater treatment plant with up flow anaerobic sludge blanket reactor.

Metodology

Location of Study

This study took place in a medium size WWTP with average flow of 319 L/s, located in Curitiba, PR. The wastewater pretreatment occurs in a system composed of 20 mm manual screen, 3 mm mechanical screen, grit removal system, Parshall flume and the biological treatment is done in six UASB reactors, each one with rated capacity of 70 L/s. Post treatment of anaerobic effluent post-treatment could take place in aerated facultative ponds.

Wastewater COD Concentration Meter (Probe)

The COD measurement system, Carbolysar model supplied by S::can (shown in Figure 1) is composed of a probe and a control unit. The system can determine concentrations between 100 and 3,250 mg(COD)/L using UV/VIS spectrophotometry. The probe measures the difference between optical intensity emitted by a lamp inside the measuring window and the optical intensity that reaches the detector, after crossing the waste water flow. The probe is 0.6 m in length and 44 mm in diameter, operates in a wavelength range between 200 and 750 nm and uses a xenon lamp.

Figure 1 – COD probe installation layout. Notes: (1) Carbolysar probe (spectrophotometer); (2) Equipment control display.

The installation of the instrument in the WTP allowed the assessment of affluent to and effluent from the UASB reactor, using an automated pumping system for alternate sampling of affluent and effluent flows.

The COD measurement system has a compressed air self-cleaning system with maximum pressure of 5 bar; manual cleaning is also allowed. The cleaning procedure, developed for the removal of solid deposits from the measurement hollow, includes the use of lukewarm water, pure ethanol and brushes provided by the manufacturer. The frequency of the manual cleaning was increased from biweekly to two times a week after day 14 reading.

Calibration Methods and Comparison with Laboratory Analyses

Besides the real-time measurements, collected wastewater samples were analyzed in laboratory, through procedures preconized in the APHA Standard Methods (APHA, 2012). At laboratory the samples were transferred to a digestion flask at 150°C for 2 hours. COD was determined by colorimetric method based on absorbance measurement at 620 nm in a workbench spectrophotometer DR6000 (Hach Industries) and previous calibration curve. Total 25 affluent and 29 effluent samples were collected in different days, between 9:00 and 11:00 am and during summer and autumn of 2016.

The calibration of the COD measurement system installed in the WTP was done so that the samples covered the historic variation of wastewater concentration values. Three scenarios were outlined for affluent COD readings: 1) global calibration (from factory), 2) local offset calibration (for both field and laboratory measurements, used to fit the global calibration to present situation, shifting the position but not the inclination of global calibration curve), and 3) local linear calibration (from two field samples and two laboratory results, global calibration inclination and alignment change). For the effluent COD recording 4 scenarios were proposed: 1) global calibration (from factory), 2) local offset calibration, 3) local linear calibration, and 4) new calibration curve supplied by the manufacturer.

Results were analyzed with statistical tools such as percentage mean error, boxplot charts, scatter plots, Student's

t-test, for two samples with presumed equivalent variances and significance level $\alpha = 0.05$, and bilateral test, to compare results obtained from measurement system at WTP with laboratory analyses.

Results and Discussion

Figure 2 shows the relative error between values registered by measurement system installed in WTP and values obtained in the laboratory analyses, for wastewater affluent samples. Mean relative error values is $64.7\% \pm 64.0\%$ for global calibration (reading days #1 to #11), $38.3 \pm 40.5\%$ for offset calibration (#11 to #20) and $4.3 \pm 2.8\%$ for local linear calibration (#21 to #25). The improved probe performance from day #16 can be attributed to the increased cleaning frequency (from biweekly to two times a week) from day #14.

Figure 2 – Relative error scatter plot for the affluent in the calibration modes: global, offset and local linear.

Figure 3 shows the COD boxplot charts for the wastewater affluent, measured by the probe and in the laboratory. For global calibration (Figure 3a) the average probe measured COD is 708 ± 252 mg/L and 486 ± 250 mg/L at the laboratory; in the case of offset calibration (Figure 3b) probe average COD is 705 ± 152 mg/L and laboratory average, 562 ± 190 mg/L; for the local linear calibration (Figure 3c), probe average COD is much closer to laboratory average: 650 ± 52 mg/L (probe) and 651 ± 73 mg/L (laboratory). The linear calibration has shown the best results among the three scenarios.

The application of Student's t-test in all the three calibration scenarios has not shown significant differences. Nevertheless, it is clear from Figures 2 and 3c that linear calibration is the best one in comparison with global (manufacturer) and offset calibrations, based on its lowest relative error, equal to 4.3%, and on the lowest difference between probe and laboratory averages.

Figure 4 shows the scatter plots of affluent COD results obtained with laboratory analyses *versus* measurements obtained with the probe at WTP, assessed with the three different calibration scenarios. The following determination coefficient (R^2) values were found: 0,6178 for global calibration (Figure 4a), 0,4612 for local offset calibration (Figure 4b) and 0,7667 for local linear calibration. Again, the local linear calibration scenario is the more adequate to the studied situation.

(a)

(b)

(c)

Figure 3 – Boxplot charts for the affluent: (a) global calibration; (b) local offset calibration; (c) linear local calibration.

(a)

(b)

(c)

Figure 4 – Affluent CODlaboratory vs. probe dispersion scatter plots: (a) global calibration; (b) local offset calibration; (c) local linear calibration.

The relative error between the probe and the laboratory values for the effluent are shown in Figure 5.

Between readings #1 and #9 (manufacturer global calibration) the observed average error is $51.66\% \pm 35.60$;

for the measurement days from #10 to #19 (local offset calibration) the found error is $27.53 \pm 24,11\%$; for the samples #20 to #24 the recalibrated probe (local linear calibration) has shown an average error of $10.09 \pm 1.95\%$.

Figure 5 – Effluent COD relative error dispersion scatter plot for: (a) global calibration; (b) local offset calibration; (c) local linear calibration; (d) new global calibration.

As for the effluent samples, the increased cleaning frequency improved the probe performance for effluent samples from collection day #14. Besides the previous three calibration scenarios, a new global calibration was supplied by the probe manufacturer, with average relative error of $44.14 \pm 10.25\%$. The effluent COD values can be seen in Figure 6, for the four different calibration conditions.

The probe has not shown the expected adherent behavior for the wastewater effluent. For global calibration (Figure 6a) measurements with the probe showed average COD of 319 ± 73 mg/L and laboratory results of 225 ± 68 mg/L. For local offset calibration (Figure 6b) the results were 277 ± 60 mg/L with the probe and 241 ± 53 mg/L at the laboratory. Local linear calibration results (Figure 6c) were

242 ± 4 mg/L with the probe and 270 ± 9 mg/L at the laboratory. Finally, average COD results were 114 ± 43 mg/L with the probe and 204 ± 74 mg/L at the laboratory for the new global calibration.

The application of Student's t-test indicated that only offset calibration has not showed significant difference between probe and laboratory measurements, rejecting the other three conditions.

Figure 7 shows the determination coefficient R^2 for the effluent in the four studied calibration scenarios. The R^2 equals 0,3845 for global calibration (Figure 7a), 0,1246 for local offset calibration (Figure 7b), 0,5566 for local linear calibration (Figure 7c) and 0,7927 for the new global calibration (Figure 7d).

Figure 6 – Effluent boxplot charts for the different calibration scenarios: (a) global calibration; (b) local offset calibration; (c) local linear calibration; (d) new global calibration.

Other Comments

One possible explanation for the difference between probe and laboratory measurements is that the spectrophotometer detects only the organic matter fraction absorbing in the UV/VIS range, e.g. organic acids and carbon hydrates. The laboratory analysis detects sulfide, chloride and Fe(II) ions by dichromate oxidation. If the probe spectrophotometer has not the ability to detect ion species, field measurements

should give lower COD values. According Figures 4 and 7, this is the case only for the wastewater effluent and only for local linear and new global calibrations.

The probe has the important ability to measure, besides COD, total suspended solids. Joint calibration can allow fitting the parameters of the initially built intrinsic software model (Gruber *et al.*, 2006). This can improve the supplier's global calibration, which has not shown reliable values for the effluent.

(a)

(b)

(c)

(d)

Figure 7 – Dispersion scatter plots for calibration modes: (a) global calibration, (b) local offset calibration, (c) local linear calibration, (d) new global calibration.

It is worth mentioning that this study is the first attempt to use spectrophotometry for assessment of COD in wastewater treatment UASB reactors, a successful technology for urban drainage. The local linear calibration is the best adapted configuration for affluent wastewater monitoring and it also has shown the smaller relative errors for effluent samples.

Operational Aspects

It is mandatory to avoid air bubbles, optical window hindrance and other measurement interfering phenomena (VANROLLEGHEM *et al.*, 2003). These phenomena were recurrent in this study, including obstruction and clogging of the pipeline connecting the effluent/affluent boxes to the probe site. The frequency of retention valves cleaning and pumps maintenance was increased to mitigate these problems. Feeding pump flow speeds lower than 3 m/s ensured the measurement quality. Weekly maintenance and cleaning of submersible pumps kept the optical window free of impurities, which could encumber the measurement. Additionally, distilled water and detergent together with manual brushing completed the cleaning process.

Air cleaning systems are an important requirement spectrophotometer reliability. If cleaning air systems are not able to remove the grime deposited on the

measurement window COD values tend to be increased (drift) (GRUBER *et al.*, 2005). According to Langengraber *et al.* (2004), Gruber *et al.* (2005). Air cleaning systems should prevent film formation and growth, but in this study case it was not enough to eliminate the film formed at the window, even using the maximum allowed pressure (5 mbar). The UASB wastewater characteristics could be the reason for this phenomenon, and additional studies are needed.

Cleaning issues were a specific variable in this study and can be related to calibration modes. Manufacturer global calibration is based on standard algorithms developed for typical applications, but wastewater quality matrix can vary with location and wastewater origin. Local calibration can reflect this variability and produce better estimation results (LANGERGRABER *et al.*, 2004; BRITO *et al.*, 2014). The present study indicates the importance of local calibration adapted to the Brazilian wastewater matrix.

Assessment of Removal Efficiency for UASB reactor

Table 1 summarizes the UASB reactors performance, with lowest relative error being the choice criterion of collection days. For the chosen collection days, the relative error between probe and laboratory measurements were 10% for the affluent and 13% for the effluent.

Table 1 – UASB reactor performance assessment⁽¹⁾.

Parameter	Unit	COD affluent ⁽²⁾	COD effluent ⁽³⁾	TSS affluent	TSS effluent	COD efficiency	TSS efficiency
Probe	mg/L	682	271	–	–	60%	–
Laboratory	mg/L	613	267	196	82	56%	58%

Notes: (1) observation period from January to May 2016, collection schedule from 9 to 11 am; (2) values for collection day #16 on; (3) values for collection days #14 and #24.

One can notice that both measurement techniques provided similar COD removal efficiency values (56% and 60%). For the entire assessment period (January to May 2016) COD removal measured at the laboratory was 56.76%, with average of 541 mg/L at reactor entry and 234 at the exit. These efficiency values are similar to the lower limit COD reported by Aisse *et al.* (2002) and Chernicharo *et al.* (2015), authors who compiled the performance of anaerobic treatment plants in large scale, with focus on brazilian plants. The assessed WTP operates with hydraulic retention times close by the rated value.

Conclusions

The scope of this study was to assess the real time *in situ* utilization of a spectrophotometric measurement system with COD probe in UASB reactor entry and exit of a wastewater treatment plant located in the Paraná State.

Results allow to conclude that monitoring can be effective for the UASB affluent. COD values obtained with spectrophotometric

probe and laboratory colorimetric analysis have shown no statistically significant difference for three different calibration scenarios. Linear local calibration is the most adequate to the WTP wastewater conditions, with average relative error equal to 4.32%, standard deviation of 2.76% and 0.7667 for the determination coefficient.

The probe has not shown the expected adherence for the UASB reactor effluent. Global calibration has not shown any reliable value for the effluent and only the local offset calibration, among four calibration scenarios, has shown no significant difference (average relative error of 27.53%, standard deviation of 24.11% and determination coefficient of 0.1246). COD removal efficiency values were between 56% and 60%, close by the lower limit reported in the literature for brazilian wastewater treatment plants.

Therefore, the application of spectrophotometer techniques consists of an advancement to the real time *in situ* monitoring of brazilian wastewater treatment plants. Even then the spectrophotometric

probes could not be considered as wastewater quality indicators, they allow real time monitoring wastewater treatment plants. However, it is necessary to first define the best practices to obtain more reliable results. The development of cleaning procedures is an example of a better practice adequate for the UASB reactor WTP.

Recommendations

The following recommendations will base future works on the use of spectrophotometer techniques in wastewater treatment plants:

- Improvement of the COD measurement for the effluent with probe operation changes, since the results were not conclusive in this case.

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- Building of global calibration curves adequate for the Brazilian wastewater condition, for example, UASB reactors effluent.
- Assessment of behavior and correlations for other variables, also measured with the probe, such as filtered COD and total suspended solids (for UASB affluent and effluent), and the different post-treatment configurations used for the anaerobic affluent.

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