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Communication

COD Evaluation of Hospital Effluent by Means of UV-Spectral Deconvolution

The Chemical Oxygen Demand (COD) is an important parameter for the evaluation of the oxidizable matter in water and effluent in general. Although laborious and time-consuming, the Standard Method for COD determination employs very toxic pollutants, i.e., dichromate and mercury, which are now being gradually avoided or replaced. In general, the organic load of effluents usually shows absorbance in the UV-visible region, as a result of the presence of absorbing groups in its organic constituents, e.g., in the case of aromatic compounds, they show the well-known UV fingerprint. In this study, an attempt has been made to find a deconvolution correlation between the COD values of effluent samples from the Hospital of the Federal University of Santa Maria (HUSM) and their integrated UV-absorbances. Experimental procedures reveal a correlation of +0.567, classified as moderate positive and with a significancy of 0.0001, between the estimated and the determined values. Hence, a COD-estimation for hospital effluents is proposed, through a simple spectrophotometric measurement of the integrated absorbance in the 285 – 295 nm range.
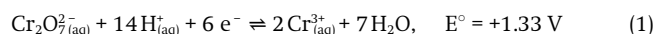
1 Introduction

The pollution caused by chemical analysis laboratories and chemicals is an issue of great concern today. Constant efforts are being made to seek new analytical methods that can avoid or minimize the causes of contamination and the generation of toxic effluents.

The discharge of organic loads into surface waters leads to the consumption of the dissolved oxygen by means of biochemical and chemical oxidation. Since chemical oxygen demand (COD) is used to determine the amount of oxidizable organic matter in effluents, it is now the most widespread procedure employed for environmental monitoring.

The traditional methods for COD determination rely on the action of a strong oxidant such as permanganate or dichromate ions. The decomposition of dichromate during the oxidation of organic loads can be expressed as given in Eq. (1):

$$Cr_2O_{7\,(aq)}^{2-} + 14\,H_{(aq)}^+ + 6\,e^- \rightleftharpoons 2\,Cr_{(aq)}^{3+} + 7\,H_2O, \quad E^\circ = +1.33\,V \tag{1}$$

Some new methods have been suggested for COD determination, e.g., photolytic degradation [1], TiO_2 photocatalytic sensors [2], or even prediction through a Gray System Theory (GST) method [3]. A recent project carried out by the current research team addressed the problem of COD determination of industrial effluents with a high content of chlorides [4].

Deconvolution has been an important and powerful tool in the development of new methods, e.g., determination of the secondary structure of peptides [5], interpretation of overlapping chromatographic signals [6, 7], studies of complex formation together with their coordination structures [8], and the determination of nitrate and organic carbon in soils [9]. The UV-spectral deconvolution (UVSD) method is a procedure that uses the integrated area of the UV-spectrum for the quantitative determination of compounds that absorb in this range. The relation between COD and absorbance is well known, e.g., Mrkva demonstrated this correlation for river water samples [10]. Results obtained by Thomas et al. [11] provide evidence that the total organic carbon (TOC) and the UV-spectrophotometric absorbance are linked and complementary, and could be used to monitor the quality of wastewater. Suryani et al. [12] discussed the quality control of water and wastewater and the usefulness of spectrophotometry aided by deconvolution methods.

Most organic compounds, as well as some soluble inorganic compounds, absorb in the UV region, making the UVSD a more suitable technique for determining these types of compounds than traditional ones, since it is faster and easier to apply. Ferree and Shannon [13] studied methods that depend on the second derivative of the obtained UV-spectrum to determine nitrate and the total amount of nitrogen. Muzio et al. [14] demonstrated that it may also be possible to determine biological oxygen demand (BOD) since it uses the integrated absorbance of pulp and paper mill effluents.

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Abbreviations: COD, Chemical Oxygen Demand; UVSD, UV-spectral deconvolution; HUSM, Hospital of the Federal University of Santa Maria; GST, Gray System Theory; TOC, Total organic carbon; BOD, Biological oxygen demand

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For this reason, an attempt is made to determine if there was a correlation between the obtained COD values and the related absorbance areas of the electromagnetic spectrum in the UV range. This is undertaken to enable COD determinations in samples of hospital effluents and similar samples, and thus, result in the ability to avoid the cumbersome adoption of the pollutant standard method.

2 Materials and Methods

The experiments were conducted with samples of effluent generated in the emergency service at the University Hospital of the Federal University of Santa Maria (PA-HUSM). The effluent sampling was undertaken in accordance with international criteria [15]. Sampling was carried out over a period of 10 days, from Monday to Friday, five times a day (at 08:00, 09:30, 11:00, 12:30, and 14:00) during August 2007, which resulted in a total of 50 samples.

After the sampling procedure, the samples were filtered and then submitted to COD, conductimetric and spectrophotometric determinations.

2.1 Reagents and Solutions

When preparing the solutions, analytical grade reagents and distilled-deionized water were used, following the Standard Methods [15]. The used reagents were: 95 to 98% H_2SO_4 (F. Maia Indústria e Comércio Ltda, Quimex®), extra pure Ag_2SO_4 (Merck®), 98% $HgSO_4$ (Vetec Química Fina Ltd., Vetec®), 99% $K_2Cr_2O_7$ (Labsynth Produtos para Laboratório Ltd., Synth®) and 98.5 to 101.5% $Fe(NH_4)_2(SO_4)_2 \cdot 6 H_2O$ (Labsynth Produtos para Laboratório Ltda., Synth®). Solutions of 65% HNO_3 (Vetec Química Fina Ltda., Vetec®) and 99% NaOH (Belga Importação e Exportação de Produtos Químicos Ltda., Belga®) were used for pH adjustment.

2.2 Characterization of the Hospital Effluent

2.2.1 COD Determination

The COD measurements were conducted in accordance with Standard Methods and by means of titrimetry after digestion of the organic load with potassium dichromate, at 170°C, in acidic medium [15]. The oxidation process was conducted in a Licit® digestion block (www.licit.com.br). The COD values were calculated by means of Eq. (2):

$$COD_{K_2Cr_2O_7} = \frac{(B - A).M.8000}{VS} \qquad (2)$$

where B is the volume (mL) of the solution of $Fe(NH_4)_2(SO_4)_2$ used for titration of the blank solution, A is the spent volume (mL) of the solution of $Fe(NH_4)_2(SO_4)_2$ in the COD determinations, M is the molar concentration of the solution of $Fe(NH_4)_2(SO_4)_2$, and VS is the sample volume (mL).

2.2.2 Conductivity Determination

A Conductivimeter Digimed® CD-21 (www.digimed.com) equipped with a thermopair for temperature compensation was employed to determine the conductivity.

2.2.3 Obtaining the UV-Spectra

The absorbance spectra were obtained with the aid of a diode array Shimadzu® UV-visible Spectrophotometer Multispec-1501 (www.shi-

Figure 1. Spectra obtained for samples of hospital effluent at different pH, in the range of 200 to 750 nm.

madzu.com). A quartz cuvette of 1 cm length and 1 nm slit were employed. The region of the UV exploited was 200 to 350 nm while taking into account that, according to Pons at al. [16], in this part of the electromagnetic spectrum, most anthropogenic substances, e. g., tensides, urine constituents and other components of urban sewage, show characteristic absorptions. In addition, according to the norm DIN 38404-C3, the Spectral Absorbance Coefficient (SAC254) refers to the absorbance at 254 nm.

The samples were submitted to a spectrophotometric determination after being filtered through qualitative filter paper (www.jprolab.com.br) and adjustment of the pH to 5, 7, and 9, with the aid of HNO_3 and NaOH solutions, using a potentiometer Phtek® model PHS-3 (Tecscience, www.tecscience.com.br), equipped with a glass pH electrode and thermopair for temperature compensation.
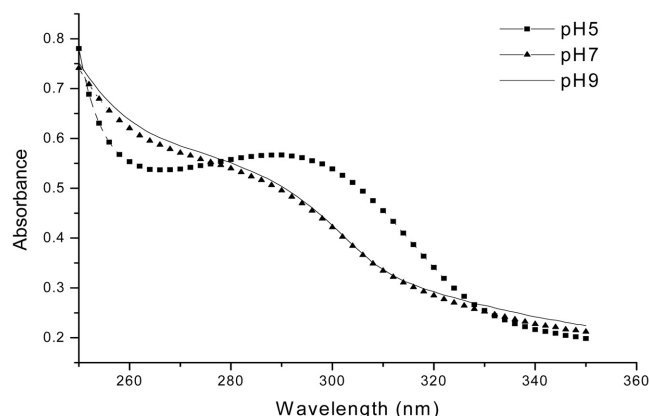
The determination of the spectral area was carried out by means of commercial software that allowed for the collection and statistical evaluation of the data.

3 Results and Discussion

The results obtained from the COD determinations and the UV-visible scanning procedures, as well as the conductivity measurements, were evaluated and utilized in the search for a linear correlation, which could replace the unsatisfactory standard method using dichromate by providing a simple, direct reading of the absorbance in the ultraviolet region.

3.1 Choice of the Spectral Range

Initially, scanning procedures were undertaken in the 200 to 700 nm region, see Fig. 1, to determine the profile of absorbances of the hospital effluent samples. The obtained spectra showed that there was no significant absorbance in the visible range. At wavelengths of 250 and 350 nm, the absorbances of the effluent samples at pH 5, 7, and 9 are similar, which means that there is no significant pH influence at these points. As a result, this interval was chosen for the subsequent spectrophotometric determinations, see Fig. 2. As can be seen from Fig. 2, the effluent sample at pH 5 shows a higher absorbance (between 285 and 295 nm), which leads to a broader band area than those corresponding to pH 7 and 9. This spectral range was used for subsequent determinations with the aim of correlating integrated absorbance with COD values. However, each hos-

Figure 2. Spectra obtained for samples of hospital effluent at pH values 5, 7, and 9, in the range of 200 to 750 nm.

Figure 3. Conductivity and COD variations for samples of hospital effluent, collected over a period of 10 days, with 5 daily samplings.

Figure 4. COD values correlated to the integrated absorbances of the samples of hospital effluent (285 to 295 nm, pH 5).

pital effluent has its own characteristics, and thus, it is recommended that the UV-spectrum of the effluent is run at different pH, e. g., 5 to 9, to verify which pH region gives the highest absorbance values, and is likely to provide the best calibration curve for COD vs. integrated absorbance.
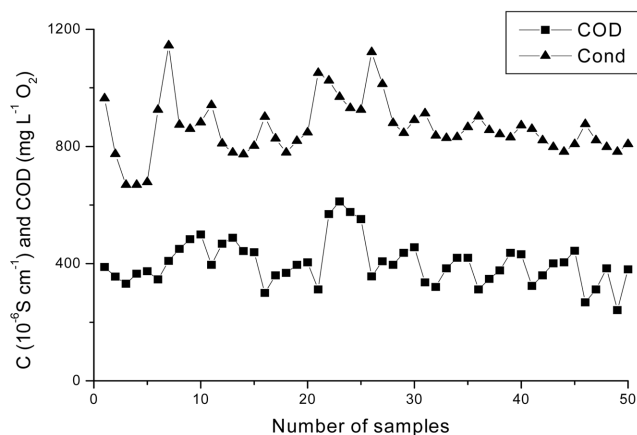
3.2 Conductivity and COD

The conductivity of a solution depends on the amount of ions present, in particular inorganic ions, which are mainly responsible for the conducting process. Many of these compounds can be oxidized, e. g., Fe^{2+} ions. These species increase the COD values, since they can be oxidized together with the organic load. Some studies estimate that ca. one third of the COD value of a solution arises from the oxidation of inorganic compounds [17]. Consequently, the conductivity of the effluent samples was measured and related to the COD values. The scanned samples were also submitted to COD determination. The COD values and the variation of conductivity are shown in Fig. 3.

The conductivity values remain within a certain range with some regular variations and show a mean value of 862.1 μS cm^{-1}. Most of the COD values remain within the range of 300 to 500 mg L^{-1} de O_2. It can be seen that both parameters vary in a very similar way, which suggests that the oscillations of conductivity are following the corresponding COD values. This behavior suggests that the occurrence of inorganic ions in the hospital effluent is responsible for a rise in the COD values obtained.
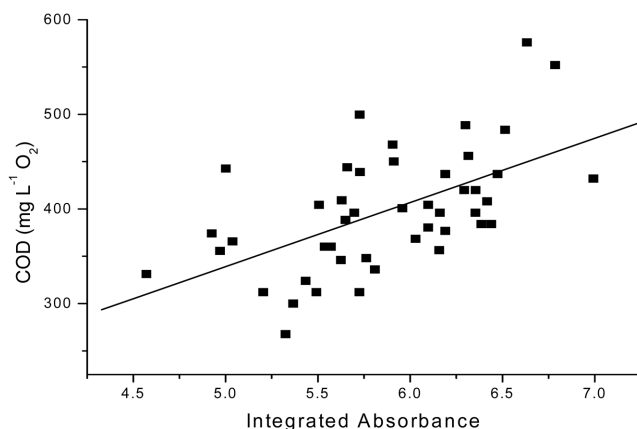
In an attempt to find a link between conductivity and integrated absorbance, calculations were carried out that led to a correlation coefficient of – 0.1731 with a significance of 0.2292, and for conductivity and COD values, a correlation coefficient of +0.1886 with a significance of 0.1897. However, it has been pointed out in the literature by Miller and Miller [18] and Miller [19], that these values do not guarantee the existence of a reliable correlation.

3.3 COD and Integrated Absorbance

The COD values obtained for the collected samples of hospital effluent were correlated with the corresponding integrated absorbance and the results are shown in Fig. 4. As can be seen in Fig. 4, there is a linear correlation between the obtained COD values and the respec-

tive integrated band areas. The angular and linear coefficients were 67.82155 and – 0.08061, respectively. The resulting determination coefficient was +0.321, and the correlation coefficient was +0.567. The value of this correlation coefficient can be classified as moderately positive and shows little dispersion. The resulting significance of this correlation was 0.0001, which demonstrates that there was a good correlation between both parameters [18 – 20]. It was not possible to validate the method since there was a great deal of variation of effluent composition from one hospital to another. Each hospital effluent has its own integrated absorbance and COD value ranges. However, the coefficients of determination obtained and the correlation for the evaluated parameters allow an estimate of the COD to be made by means of the integrated absorbance in a specific spectrum region, in this case, between 285 and 295 nm. It should also be taken into account that the COD values do not represent absolute values, but an estimate of the oxidizable matter present in the medium. In general, this can be attributed to the prevailing organic load. The COD variations are directly linked to the composition of the medium, which is much more variable. The studies of Pai et al. [3] achieved a minimum prediction accuracy of 55.11% for the models that were employed, which demonstrates how difficult it is to predict COD for real samples. The viability of this method is suggested by the measurable integrated absorbance values, which are

also dependent on the occurrence of organic and inorganic loads. This method would most probably not be useful in cases of effluents containing no (or very low concentrations of) absorbing substances, since the consequent low integrated absorbances would not allow a good correlation with COD values.

4 Conclusions

The UV-spectral deconvolution method proved to be effective in correlating the COD values of the hospital effluent samples with their corresponding integrated absorbances. On the basis of the results obtained, it can be concluded that there is a moderately positive correlation between COD values and the integrated absorbances, with low significance, which facilitates the estimation of the COD values of the studied samples by means of the measurement of the integrated absorbance between 285 to 295 nm, preferably at pH 5.

The values obtained for COD and the conductivity of these samples lie within a defined range and also show that the composition of the hospital effluent is relatively stable.

Apart from allowing the unsatisfactory standard titrimetric method to be replaced with a simple absorbance method involving scanning in the UV region, in addition, this rapid and practical determination of COD values in samples of hospital effluent by means of deconvolution makes it possible to avoid the use of toxic chemicals and prevent their subsequent deposition in the environment.

Acknowledgements

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