



Determination of chemical oxygen demand in aqueous samples with non-electrochemical methods



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ABSTRACT

Water contamination is a globally important environmental concern, with chemical oxygen demand (COD) being a criteria in water quality assessment, providing information on the availability of chemically degradable fractions of organic pollutants. However, the standard method for COD analysis is time-consuming and results may vary between laboratories. Efforts to resolve these problems have mostly focussed on improvements to both digestion and detection techniques and this review addresses recent trends in the determination of COD in aqueous samples, based on published literature since 2000. The features of principal methods are critically reviewed, focusing on their practical applicability. This review includes an overview of: 1) standard methods; 2) novel digestion techniques; 3) varying detection methods, such as chemiluminescence, spectrophotometry and others; 4) and future trends in COD measurements. Electrochemical techniques are excluded, as despite their importance as an environmental friendly alternative for COD measurement, these methods have only recently been developed and require a full and separate review.

1. Introduction

With rapid industrial development and rising global populations, water quality issues are an increasing challenge world-wide. Organic pollutants are one of the main groups of environmental contaminants, causing significant effects on both human health and aquatic ecosystems [1]. The concentration of “oxygen-demanding” substances, is an important parameter for assessing the level of organic contaminants in a water source. There are three widely used indices for assessing the oxygen demand of organic pollutants in an aqueous system: total organic carbon (TOC), biochemical oxygen demand (BOD) and chemical oxygen demand (COD) [2]. TOC analysis is utilized to assess soluble organic compounds, but does not express the oxidizable fraction of organic matter, which is responsible for eutrophication in aquatic systems. In addition, the application of TOC analysis is limited as measurements requires expensive equipment; BOD analysis directly measures the amount of oxygen consumed by microorganisms over a specified time-period (typically 5 days), during the biodegradation period of wastewater [3]; and COD analysis measures consumed oxygen correlating to the reduction of strong oxidizing agents under highly acidic conditions at high temperatures.

It is of note, that BOD analysis most closely models the conditions of aerobic wastewater treatment and aquatic ecosystems, although its

application is limited as methods are time consuming, not suitable for heavily polluted water bodies and results can be highly variable [3]. COD analysis has several advantages over BOD analysis, such as having rapid and simple experimental methods, which generate reproducible results. Therefore, COD values are often used as a principal water quality parameter in wastewater treatment facilities [4,5]. A significant increase can be observed in the number of publications between 2000 and 2016 using “chemical oxygen demand” as keywords on the “Web of Science” database (Fig. S1 in Supplementary material).

COD is defined as the amount of an oxidant (expressed in terms of oxygen equivalence), that is consumed during the oxidation of organic compounds by strong oxidizing agents, such as dichromate ($E^0 = 1.36$ V); permanganate ($E^0 = 1.51$ V); or cerium ($E^0 = 1.44$ V); where E^0 is the standard reduction potential (25 °C vs. Normal Hydrogen Electrode, pH = 0) [6]. Based on the specific oxidizing agents used, COD can be classified into either dichromate COD (COD_{Cr}) or permanganate COD (COD_{Mn}), although generally COD refers to COD_{Cr} , while COD_{Mn} is known as the permanganate index. COD values or the permanganate index, are widely used as a critical measurable parameter for water quality testing [4]. For example, in China there are several national standards regulating COD or permanganate index concentrations, in surface, ground and wastewaters, with the real-time data available on the website (National surface water quality on-line

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monitoring system, <http://58.68.130.147/>).

Reliable determination of accurate COD values is urgently required for both environmental and analytical research, with a comparison of available published methods for COD determination briefly summarized in various research studies [4,7]. The standard methods for COD determination have also been described in detail in commercial publications [5] and some comprehensive reviews [8], with a recent review by Geerdink et al., [9] presenting a historical overview of the development of COD determination methods.

In recent years, much research effort has been devoted to the development of rapid, sensitive and environmentally friendly methods for the determination of COD levels in aquatic systems [9]. For the purposes of this paper we have limited our review to studies published since 2000, with specific pre-2000 papers cited where required to illustrate a specific point, as well as describing international and national standard methods and reports of method optimization and improvements. In addition, techniques for sample pre-treatment and detection are critically reviewed, with conclusions and future trends for the determination of COD discussed. Electrochemical techniques are excluded, as despite their importance as an environmental friendly alternative for COD measurement, these methods have only recently been developed and require a full and separate review. A list of recent publications using electrochemical methods can be found in the Supplementary material.

2. Standard method and its improvements

2.1. Standard methods

Various international standard methods exist for the determination of COD, such as ISO 6060:1989, ISO 15705:2002, ASTM D 1252-06, Standard Methods for the Examination of Water and Wastewater 5220-COD₂ and EPA Method 410.1/410.2/410.3/410.4, among others. Based on these international standard methods, various countries have released national standards, such as China (GB11914-89, GB 17378.4-2007, and HJ/T399-2007; among others).

In addition, industrial technical notes exist relevant to specific commercial instruments, such as the “Thermo Orion Methods CODL00 and CODH00” and “Method 8000 and Method 10212 from HACH”. As shown in Fig. 1, COD determination typically includes two steps [5]:

- (1) Digestion or oxidation of samples in water using a strong oxidant such as dichromate or permanganate. Both open and closed reflux can be used, with closed reflux methods requiring lower sample volumes and levels of chemical usage as compared with open reflux methods.
- (2) Determining the amount of consumed or residual oxidant by titration or spectrophotometry. In titration assays, where excess dichromate is monitored either with a standard ferrous ammonium sulfate solution using *ortho*-phenanthroline ferrous complex as an indicator, or using oxidation-reduction potential (ORP) electrode analysis. Alternatively, spectrophotometric procedures are based on the loss of hexavalent chromium (Cr(VI)) ions at 420 nm or the increase in trivalent chromium (Cr(III)) ions at 600 nm.

Standard methods for COD determination are accurate, reliable and reproducible, although procedural limitations still exist with conventional open reflux-titration methods, such as long digestion and titration times, high digestion temperatures, high consumption of expensive (Ag_2SO_4), highly corrosive (concentrated H_2SO_4) and toxic (HgSO_4 and $\text{Cr}_2\text{O}_7^{2-}$) chemicals required, interference from inorganic species (such as chloride and nitrite), and incomplete oxidation of volatile compounds, among others [5].

Closed reflux with spectrophotometric detection overcomes some of the drawbacks observed with open reflux-titration methods, with shorter heating times; lower consumption of energy and reagents; lower levels of secondary pollutant production; and lower experimental costs. However, some inherent problems also exist with spectrophotometric detection methods, such as bubble formation, turbidity, or color interfering with optical signals and the narrow linear range of spectrophotometric systems [10].

The determination of permanganate index values in aquatic samples, is performed via the oxidation of organic compounds by KMnO_4 , with subsequent titration of excess added $\text{Na}_2\text{C}_2\text{O}_4$. During the digestion step for COD measurement, all organic compounds should be oxidized with a degradation efficiency of above 90%, due to the highly oxidative reagents, long digestion time and high digestion temperatures or pressures. Conversely, the digestion conditions applied for permanganate index measurements are relatively mild (e.g. digestion at 100 °C for 30 min) and compared with dichromate COD measurements, the permanganate index can be considered a more relevant criteria for describing organic pollutants. It should be noted, that significant

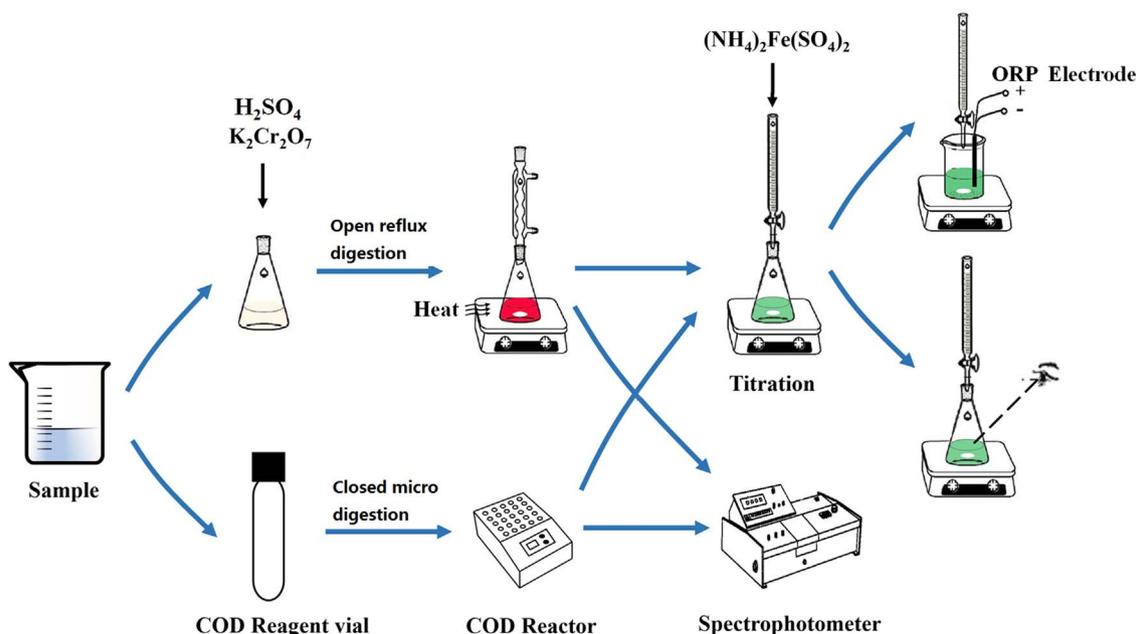


Fig. 1. Manifold of the standard dichromate COD detection method.

differences exist between different standard methods (e.g. international standard ISO 8467-1993, local standard GB 11892-89 (China), or K0102-2013 (Japan)), such as reagent concentrations, reaction times, and sample/reagent ratio, among others. Therefore, operators should follow standard protocols in detail to ensure valid “permanganate index” measurements.

Various efforts have been made to improve the efficiency of these standard methods, such as Raposo et al., [11] who reviewed how to improve the quality of COD analysis, particularly in samples with difficult and complex matrices. This review focuses on anaerobic-reactor samples, including solid samples and liquid samples with high concentrations of suspended solids. Even standard laboratories utilize slightly different digestion equipment, reagents and detection modes and that inter-laboratory comparative studies would be highly useful for proficiency testing of COD analysis methods [12].

2.2. General improvements of the standard methods

In recent years there have been several published reports evaluating and improving standard methods for COD analysis, particularly focussing on removing uncertainties added by the numerous experimental steps required. Da Silva et al., [13] published a detailed assessment model for the performance of COD determination in wastewater samples, aiding a reduction in both measurement uncertainties and cost of analysis.

Dedkov et al., [14] investigated the ability to oxidize different classes of organic substances under the conditions required for standard COD analysis, with or without the use of Ag_2SO_4 as a catalyst. Three groups were classified according to the percentage of oxidation, classed as easily oxidizable, medium oxidizable, or hardly oxidizable compounds. These findings show that a single reference material using easily oxidizable substances such as potassium hydrophthalate or glucose, may not be relevant when representing medium or hardly oxidizable substances. Dedkov et al., recommend the use of a standard mixture containing ethylene glycol, acetic acid, dimethylformamide and nitrobenzene for verification of COD analysis results in different water types.

The Hach company (USA) have produced commercial code-labeled digest tubes with pre-added reagents, resulting in highly efficient analysis with traceable results, with only one-tenth of the consumption of reagents required for conventional analytical procedures. Unfortunately, the high costs of the Hach assay method are a significant limitation, although Li et al., [15] reported having replicated the method using in-lab prepared reagents with the same method and instruments (Hach DR/5000U spectrophotometer and Hach DRB200 COD digester), significantly reducing the costs of routine COD analysis.

Ma et al., [16] combined the advantages of using alkaline potassium permanganate and acidic potassium dichromate digestion modes, to improve digestion efficiency, with improved automatic potentiometric titration and less interference from chloride. Both standard materials and real samples were analyzed, showing good precision and high recovery; however no data is available comparing this method with the standard method under the same experimental condition. It is of note, that if the degradation efficiency in the standard method is lower than in the method by Ma et al., this may suggest some bias for specific substances within samples.

Zenki et al., [17] developed a single-line cyclic flow injection system using on-line regeneration of consumed KMnO_4 , where after oxidation of organic substances, KMnO_4 is reduced to Mn(II) , which can subsequently be oxidized by HIO_4 . KMnO_4 is then regenerated to its original concentration level allowing repeated reuse, resulting in significantly lower levels of both consumption of reagents and production of hazardous waste, with only 50 mL of reagent carrier solution circulated through the system, with an analytical frequency of 30 h^{-1} .

2.3. Improvements focused on eliminating interferences

There are different types of interference to the determination of COD, such as high levels of chloride, suspended solids and hydrogen peroxide (H_2O_2), among others. Chloride is a well-known interference in COD analysis, as it can be oxidized to chlorine by strong oxidizing agents, resulting in a positive analytical error. Additionally, chloride also depletes the Ag_2SO_4 catalyst by forming an AgCl precipitate, which causes a negative analytical error. One method of eliminating its interference is the addition of highly toxic HgSO_4 to complex chloride [18,19], although in samples with high salinity and low organic compound levels, the Hg:Cl ratio and strength of the digestion solution should be carefully optimized for the correct determination of COD [20,21].

The assessment of COD concentrations in samples with high suspended solid concentrations, such as cattle dung slurry or anaerobic digester treated brewery wastewater, is of high importance, however traditional methods are not applicable to these samples with low levels of recovery reported. Sample preparation techniques, quantities of reagents and reflux time should be modified accordingly, with solid reference materials also used [22,23].

For samples such as bleached textile mill effluents, the inherent color and other materials present in samples, may significantly interfere with spectrophotometric detection. Torrades and Cecilia [24] utilized the Youden blank to eliminate this error, evaluating the matrix effect and avoiding interactive interference, showing this methodology to be useful for validating analytical processes as no standard reference material is available.

Hydrogen peroxide is added in many advanced oxidation processes, generating hydroxyl radicals required to oxidize organic pollutants in aquatic samples. However, residual H_2O_2 present in treated water can interfere with COD determination, with Wu and Englehardt [25] proposing a novel method to address this problem, involving catalytic decomposition of H_2O_2 in the presence of heat and sodium carbonate. The development of this method was conducted in both pure water and treated municipal wastewater matrices, with further pilot scale tests needed before routine application to remove H_2O_2 from water or wastewater.

3. Digestion techniques

The main purpose of digestion is to oxidize all possible substances present in aqueous samples, to their highest potential oxidative state, for example hydrocarbon compounds are oxidized completely into carbon dioxide and water. Therefore, the chemical oxidation efficiency of different digestion techniques, depends on both the method of digestion and the oxidants used, which play a key role in accurate COD determination [16]. In addition to conventional standard methods, various alternative oxidation methods have been investigated, including microwave-assisted oxidation; ultrasound-assisted oxidation; UV-O_3 oxidation; electro-catalytic oxidation; and TiO_2 photo-catalytic oxidation, with a comparative study of digestion techniques reported in the literature [26].

3.1. Microwave-assisted digestion

Microwave-assisted sample pre-treatment techniques have been well developed [27] and show high efficiency, rapidly heating sample and oxidant mixtures to a high temperature, with losses of volatilizable compounds prevented due to closed sample vessels. The overall advantages of microwave digestion include good recoveries; reduced digestion time and contamination; lower consumption of reagents and sample; with straightforward non-hazardous processes. However, microwave oven technology expensive and requires careful operation due to high internal pressure and temperature [28].

Chen et al., [29] presented a focused microwave system, digesting

samples at 150 °C for 8 min, with excess dichromate in the digestion solution titrated with ferrous ammonium sulfate solution. Ramon et al., [30] optimized a similar focused microwave system using a constant power strategy and temperature control system, where samples were digested at 170 °C for between 1 and 15 min, with digestion tubes connected to a condenser using cooling water. While this method resolves problems arising from abrupt sample heating and potential thermal decomposition of potassium dichromate, a significant limitation is that only one sample can be processed per batch [29,30]. In contrast, Dharmadhikari et al., [31] developed a closed microwave system for the digestion of small sample volumes (3 mL). In this method up to 10 samples can be digested per batch lasting 15 min, with a working range of 5–1000 mg/L COD and with no reported interference from chloride at concentrations of up to 6000 mg/L.

In variation from manual digestion modes using scientific microwave digestion and titrimetric detection, Almeida et al., [32,33] combined flow injection and domestic microwave digestion methods for automated sample loading and digestion, with inductively coupled plasma optical emission spectrometry for chromium/manganese detection. The speciation of Cr(VI)/Cr(III) and Mn(VII)/Mn(II) are based on the selective extraction of Cr(III) and Mn(II) using solid phase extraction columns filled with activated carbon. This system provides a sample throughput of 18 and 22 h⁻¹, with matrix interferences avoided due to the selectivity of both extraction and detection. A significant limitation is that these systems may be too costly and time-consuming for routine laboratory analysis.

3.2. Ultrasonic digestion

Ultrasonic technology is highly useful in analytical chemistry, with its applications in environmental and other research fields having been comprehensively reviewed by Seidi and Yamini [34]. Canals et al., [35,36] used ultrasound to promote the oxidation of organic compounds using dichromate in the presence of concentrated sulfuric acid, resulting in a highly rapid digestion, complete within 2 min. Kim et al., [37] used a similar ultrasonic digestion, although residual dichromate concentration was determined using automated ORP-based titration, allowing the potential to combine this method with an online COD analyser. Zhang et al., [38] proposed a flame atomic absorption spectrometry method, based on the use of ultrasonic advancement of sample digestion by KMnO₄ and flow injection on-line speciation of manganese. It should be noted that while ultrasonic digestion is highly effective for easily digested organic compounds, in the case of more refractory organic substances, measured values might be lower than the true values.

3.3. Photocatalytic oxidation

Photocatalytic oxidation is an efficient alternative to wet digestion methods for the degradation of organic compounds, with the advantages of high efficiency; mild reaction conditions; low energy consumption; simple operation procedures; and low levels of secondary pollution [39]. TiO₂ can be used as a heterogeneous photo-catalyst because it has high photo-oxidative efficiency and is neither toxic, nor photo-corrosive. Photocatalytic degradation reactions using UV illuminated TiO₂ was initially utilized for the determination of COD in 2000 [40]. Since then, flow methods have been reported for the measurement of COD, showing the advantages of automation; lower costs; shorter analysis time; increased reproducibility; and the ability for unattended operation [41,42]. Nano-TiO₂-based photocatalytic oxidation has been reported for the digestion of samples for COD analysis [43]. This method has since been further optimized in various reports, showing increased oxidation efficiency and ease of operation, such as the addition of Ce(VI) as an electron scavenger [44]; the use of nano-TiO₂ film instead of powder [45]; the fabrication of composite nano-ZnO/TiO₂ film [46]; the combination of ion chromatography for post-

oxidation measurements [47]; the combination of photo-efficient thin-layer photocatalytic oxidation, conventional bulk-phase photocatalytic oxidation and photocarrier-efficient high-activity photocatalytic reduction in one single photo-digestion system [48]; *in situ* surface modification of TiO₂ with 5-sulfosalicylic acid and KMnO₄ [49], and modification of photo-reactor and reaction parameters [50], among others.

Quantum dots are nano-scale semiconductor crystals, which unlike TiO₂, can be directly prepared in aqueous media or be water-soluble following appropriate capping with hydrophilic ligands. Silvestre et al. [51] first utilized CdTe quantum dots to generate strong oxidizing species upon irradiation with UV light, resulting in rapid photocatalytic degradation of organic compounds. This method applied a luminol chemiluminescence probe for detection and solenoid micro-pumps to propel liquids, resulting in a high sample analysis frequency of 33 h⁻¹.

Dan et al., [52] combined UV-photocatalytic oxidation and flow injection for on-line COD determination, using acidified potassium permanganate as an oxidant. This analytical system has been comprehensively optimized, resulting in a sample throughput of 30 h⁻¹, with results showing good agreement with certified reference material values. However, one limitation of this method is that different calibration curves exist for different COD standards (sodium oxalate, D-glucose and potassium hydrogen phthalate), suggesting total oxidation efficiencies may vary for different substances in an environmental matrix.

Recently, the combination of nano-particle-based photocatalytic/ photoelectrocatalytic digestion and electrochemical detection methods have been widely developed and applied to the determination of COD. A specific review on this topic would be of value, as it is not possible within the scope of this review.

3.4. Other digestion techniques

Han et al., [53] incorporated electromagnetic induction heating to a flow injection system for COD determination, resulting in on-line sample oxidation at 145 °C and 0.44 MPa manifold pressure, within 8 min. Benefits of this system are lower levels of reagent consumption, reduced potential external contamination and lower costs compared with the conventional techniques, although overall efficiency is only ~70% of the standard methods.

Normally, for the determination of COD, dichromate solution acts as both an oxidizing agent and a reagent to aid quantification, allowing measurement by titration or spectrophotometry. Several new digestion and detection techniques without the use of dichromate have been reported. For example, Akhoundzadeh et al., [54] presented a method based on the combination of UV-induced H₂O₂ oxidation, with head-space single-drop micro-extraction, in-drop precipitation and micro-turbidimetry. In this method, organic matter is oxidized to CO₂, which is then sequestered by a micro-drop of Ba(OH)₂, forming a BaCO₃ precipitate which can be quantified by turbidimetry. Pisutpaisal and Sirisukpoca [55] utilized ozone as an oxidizing agent, with the resulting dissolved ozone monitored using an ozone sensor. This method has the benefit of being highly rapid, with reaction times of under 1 min, although to maintain experimental conditions, samples must be diluted 40-fold prior to ozone oxidation, limited the sensitivity of this method. Both Fenton reagents (H₂O₂ and FeSO₄) [56] and heterogeneous Fenton-like process (H₂O₂/Fe_{3-x}Co_xO₄ nanoparticles) [57], have been used as rapid and environmentally-friendly oxidants for digesting samples for COD analysis. FeSO₄ or Fe_{3-x}Co_xO₄ nanoparticles activate H₂O₂ molecules to produce hydroxyl radicals, which are highly reactive and efficient in the oxidization of organic matter, allowing quantification using malachite green or levels of consumed H₂O₂ with spectrophotometry. Yu et al., [58] modified a drinking water purification and wastewater treatment technique based on UV/O₃ processes for COD measurement. In this method, hydroxyl radicals generated by UV photolysis of O₃ oxidize organic species, allowing residual O₃ dissolved in solution post digestion to be quantified using the indigo method,

which has linear relationship with COD values. A similar UV/O₃ oxidation method was also utilized by Jin et al., [59] developing a flow injection ozonation chemiluminescence method.

4. Chemiluminescence

Chemiluminescence detection has many advantages such as high sensitivity, fast response times, extensive dynamic range and relatively inexpensive instrumentation costs. Combination of this method with flow injection analysis has been proven to be a powerful analytical technique for successful determination of many environmental pollutants [60].

For the determination of COD levels during the oxidation of organic matter, pre-added Cr(VI) is reduced to Cr(III), which can then be measured based on the chemiluminescent reaction of the luminol-H₂O₂-Cr(III) system. Hu et al., [61] evaluated two different digestion procedures, replacing the use of expensive photomultiplier tubes with photodiodes, allowing the cost of instrumentation to be further reduced. Liu et al., [62] designed a micro-flow chemiluminescence system where a single determination requires only 33 µL oxidant and 40 s per reaction, resulting in the consumption of toxic and expensive reagents being significantly reduced.

Several chemiluminescence detection methods utilize KMnO₄ as an oxidant. Li et al., [63] proposed an in-line pre-concentration-flow injection system based on the luminol-H₂O₂-Mn(II) chemiluminescence reaction. In this system, during the chemical oxidation of organic compounds at ambient temperatures, KMnO₄ is reduced to Mn(II), with Mn(II) absorbed onto mini-columns filled with strongly acidic cation-exchange resins, allowing the concentrated Mn(II) solution to be eluted reversely and measured by luminol-H₂O₂ chemiluminescence, at a sample throughput of 40 h⁻¹. Tian et al., [64] and Fujimori et al., [65] simplified the Li et al., [63] system, removing the use of mini-columns and the indirect luminol-H₂O₂-Mn(II) reaction. These optimized methods utilize the chemiluminescent reaction of luminol and KMnO₄, resulting in the detected signal being inversely proportional to COD values, with interference from chloride in seawater evaluated and minimized via the optimization of experimental parameters [65]. Yao et al., [66] combined off-line digestion and automated KMnO₄-glutaraldehyde chemiluminescence detection on a movable 96-well plate, reporting complete analysis in 40 min including digestion and detection, resulting in a high throughput rate of 3 readings of 96 samples in 60 min. However, a significant limitation is the time-consuming experimental procedure of adding reagents and transferring samples from digestion tubes to the 96-well plate, which presents a significant rate determining step.

Without using chemical oxidants, Su et al., [67] established a on-line method based on the combination of UV photolysis and chemiluminescence detection for COD determination, using a specially designed photo-reactor, where organic substances are decomposed by UV light using a high-pressure mercury lamp. The radicals produced oxidize luminol and result in luminescence, resulting in a method that is environmentally friendly, automated and highly sensitive with a low limit of detection at 0.08 mg/L. Unlike most photocatalytic techniques as discussed in Section 3.3, neither TiO₂ or any other catalyst are required, however, different light sources with different wavelengths and intensities may have variable oxidation abilities, which requires further investigation in different sample matrices.

5. Thermal biosensor

Yao et al., [68] developed a thermal biosensor for potentially long-term in-line COD monitoring in natural water samples, where biosensors measure the amount of heat generated during organic compound oxidation as samples are passed through a column containing periodic acid (H₃IO₆). The thermometric signal generated in this system is proportional to the change in the enthalpy of the organic content of the

sample. Compared with other detectors, the thermistor is more tolerant to interference because it is less sensitive to optical, electrochemical, or other material properties of the samples. This system shows robustness and long-term stability with sequentially analysis of more than 70 sample in 20 days, however accuracy was variable as the measured value of 34 samples were only one third of the values measured using the standard dichromate method. In addition, while periodic acid can oxidize polysaccharides, its oxidative ability is not enough for the digestion of a variety of organic compounds in real samples, limiting the potential application of this biosensor system.

6. Chemical-free methods based on absorption spectra

Most of the aforementioned methods and techniques are based on chemical or physical digestion of organic compounds, with detection of residual oxidants or other indirect indices. Consequently, these methods are inevitably complicated and generally not viable for long-term on-line or *in situ* applications. In recent years, chemical-free methods for COD determination have been developed based on the relationship between absorption spectra and organic matter, with different algorithms and models reported for application of these methods in natural environments.

UV-visible (UV-vis) spectroscopy is an indirect method for COD measurement, which relies on the use of regression model standards or measured data using chemical methods. The selectivity and accuracy of UV-vis spectroscopic methods are limited by its co-sensitivity to different chemical substances, as well as physical interference, such as turbidity. Therefore, Hu et al., [69] used a normalization technique to both estimate turbidity and dynamically simulate the absorption spectra of turbidity. In this system, after the process of turbidity compensation the root mean square error of predictions were minor, based on comparison with the standard turbidity formazine solution. Further research is required to optimize this method for natural water sample matrices, as the issue of turbidity involves a wide range of substances, the particle size distributions of which may significantly affect scattering models. Torres and Bertrand-Krajewski [70] identified the variables of partial least squares (PLS) regression of UV-vis spectra and COD values, although no real samples were analyzed, meaning further investigation of matrix effects are required.

Several methods have been established to resolve the problems associated with complex sample matrices. For example, print and dye industry wastewaters are composed of dye molecules with color or polar radicals generated from aromatic hydrocarbons or heterocyclic compounds, which present a significant challenge for accurate COD measurements. A study by Kong and Wu [71] correlated COD values measured using the dichromate method with UV absorbance at 254 nm in a range of sample matrices. Following evaluation of the effects of suspended solids, temperature, pH and dilution factor, 14 samples were successfully analysed and results corroborated by measured data using the dichromate method, showing that using regression, the COD of samples can be easily calculated. To optimize the model for rapid determination of COD in aquaculture wastewaters, Cao et al., [72] investigated four calibration methods and six spectral pre-treatment methods, with a variable selection method of successive projections algorithm used to select efficient wavelengths. Following optimization, the COD value of 45 samples were successfully predicted and compared to data from standard methods. Chen et al., [73] developed a chemometrics-assisted spectrophotometric method for determining COD values in pulping effluent, a complex multi-component system where calibration modes based on both inducing UV-vis spectroscopy and derivative spectroscopy, showed satisfactory results with reasonable detection limits and low relative error.

Near-infrared reflectance (NIRR) spectrometry has also been successfully combined with multivariate analysis to measure COD values in domestic wastewater samples [74], with inherent baseline noise features associated with NIRR spectra removed using the Savitzky-

Golay derivative procedure followed by wavelet de-noising. The resulting wavelet approximation coefficients can be used for PLS modelling and subsequent prediction of COD values and has been successfully applied to the analysis of effluent samples from anaerobic ponds of municipal wastewater treatment plants.

These chemometrics-assisted spectrometry methods do not require chemical reagents or digestion steps, resulting in simple and fast methods which are free from secondary pollution. However, as noted in literature [72], it is important to compare predicted results under different environments to verify the applicability of algorithms and models.

7. Conclusion

This review identified and discusses the main non-electrochemical technological strategies designed to measure COD in aqueous samples. Although many new methods have developed, demonstrating a range of advantages over standard methods, the applicability of these methods may be limited for routine analysis. The choice of a suitable method for COD determination should consider aspects such as sample matrices; samples numbers for routine analysis; measurement frequency; the type of considered applications (laboratory, on-line, *in situ*, etc.); the cost of both instruments and labour; tolerable error rate; among other factors. For further optimization of COD determination methods, aspects to be considered in the future include:

- (1) Various factors can affect measured COD values, such as the type and concentration of oxidant used, the pH of reagents, reaction temperature and time, as well as the use of catalysts. Therefore, COD is an index that must be measured under strictly controlled conditions following defined procedures. The values measured using newly developed methods should be compared carefully with standard protocols, particularly when being used for “permanganate index” assessment.
- (2) It is essential to evaluate the riverine organic pollutants input flux into oceans, using accurate COD data from coastal waters with varying salinity. However, the measured COD values in coastal waters have not been found to be consistent using different standard methods [75]. Therefore, to overcome problems in comparisons between marine quality standard data and surface water quality standard data, a special coastal water quality measurement standard requires development.
- (3) Different model compounds (D-glucose; potassium hydrogen phthalate; lactic acid; phenol; acetic acid; etc.) have been used for the evaluation of digestion efficiency, however most methods utilize only one of these compounds, with a general focus on potassium hydrogen phthalate. Both refractory and labile compounds should be used to evaluate the reliability and limitations of digestion methods and suitable reference materials containing mixed organic compounds are therefore needed [14,76].
- (4) There is the requirement in some laboratories to routinely measure large sample numbers daily, ensuring high repeatability and accuracy is maintained. Therefore, it is necessary to automate most or all sample handling steps [77], in the case of COD measurement, these steps include (but are not limited to) sample transfer, pre-evaluation of COD and chloride concentrations, dilution, addition of reagents, digestion, titration, calculation, and reactor cleaning.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [10.1016/j.teac.2017.05.002](https://doi.org/10.1016/j.teac.2017.05.002).

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