American Journal of Biochemistry and Biotechnology

Original Research Paper

A Review of Detection Techniques for Chemical Oxygen Demand in Wastewater

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Article history
Received: 04-10-2021
Revised: 29-11-2021
Accepted: 04-12-2021

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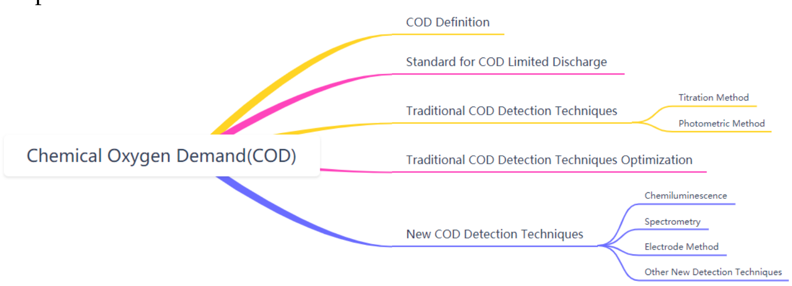
Abstract: Water pollution is a major problem all over the world, the detection techniques of water play an important role in the evaluation of water pollution. Chemical Oxygen Demand (COD) is an important index for the evaluation of water pollution. The paper reviews the detection methods of chemical oxygen demand in wastewater, introduces the standard of chemical oxygen demand emission limit in different countries, the traditional detection methods and their optimization, and the new detection techniques which include chemiluminescence, spectrometry, electrode, microbial fuel cells, silver nanoparticles sensor and so on. It's important to establish a new environmentally friendly chemical oxygen demand detection method with safe and high efficiency in the further.

Graphical Abstract:



Keywords: Chemical Oxygen Demand, Waster Water, Detection, Review

Introduction

Water pollution and water shortage are important factors affecting regional economic development and social construction in different countries. Water pollution not only destroys the ecological environment but also affects people's daily life and production. Water quality detection plays an important role in the evaluation of water environmental pollution. Therefore, the rapid development of water quality detection technology is very important to social-ecological development. Chemical Oxygen Demand (COD) is a constant indicator, it reflects the degree of water pollution by reducing substances. Its value is equivalent to the amount of dichromate consumed by dissolving in a water sample which treated under defined conditions (ISO, 1989). There is a lot of reducing substances in domestic sewage or some industrial wastewater, including organic matter, nitrate, ferric salt, sulfide, and so on. If the high COD wastewater is directly discharged into the environment, it will threaten aquatic organisms, directly or indirectly affecting human life and health. Therefore, the detection of COD in water is very important. It has great significance in the prevention and control of environmental and ecological pollution.

The COD detection technology is discussed here, including the COD emission limit standard, traditional COD detection techniques, their improvement, and new COD detection techniques.

The standard for COD Limited Discharge

The standard of COD discharge is different for different water bodies in different countries. For an example of the cleaner water sample in China, surface water quality standard requirements COD ≤40 mg/L, the class I and class II water for COD ≤15 mg/L (SEPA, 2002): The limit standard of farmland irrigation water is also different for different corps, the irrigation water for paddy field crops should be ≤150 mg/L that for dry land crops should be ≤200 mg/L (MEE, 2021). For industrial wastewater, the allowable COD discharge value is between 60 mg/L-1000 mg/L (SEPA, 1996).

In 2000, the EU issued the EU water framework directive (European Commission, 2000), which provided its member states with agreed water quality objectives and guided the realization of sustainable environmental development (Voulvoulis *et al*., 2017). Its Integrated Pollution Prevention and Control (IPPC) directive 2010/75/EU also set out the best feasible technical reference documents for controlling water pollution in different industries. For example, the COD of food, beverage, diary industry, urban sewage plant, slaughtering and livestock by-product processing industry requirements ≤125 mg/L, the COD of metal and plastic surface processing industry ≤500 mg/L, the COD of organic fine chemical and pharmaceutical manufacturing industry ≤250 mg/L (European Commission, 2005; 2006a, b, c; Directive, 1991). The United States has Clean Water Act Programs, but there is no COD limit requirement in the conventional index (USEPA, 2010). According to The Water Pollution Prevention and Control Law of Japan, the limit standard of COD discharge for specific factories with displacement ≥50 m^3/d is ≤160 mg/L (Ichiro Ishii, 1992).

Traditional COD Detection Techniques

The traditional method of COD detection in wastewater is the dichromate oxidation method, it also is divided into spectrophotometry and titration methods. The difference between titration and photometric methods is that after the sample is treated with potassium dichromate, the remaining potassium dichromate is determined by the colorimetric method or titrated with ammonium ferrous sulfate (Rohyami *et al*., 2021). The chemical reaction equations of these two methods are shown as follows (Mónica Gisel *et al*., 2021; Rohyami *et al*., 2021; Gao *et al*., 2016);

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow \mathbf{2}Cr^{3+} + 7H_2O \quad (1)$$

$$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow \mathbf{2}Cr^{3+} + 6Fe^{3+} + 7H_2O \quad (2)$$

Table 1 compares national standard COD measurement methods in China. There is a little difference in masking agents and digestion methods in different determination standards.

The spectrophotometry is different according to the measurement range. China national standard HJ399 (SEPA, 2007) recommended, that when the COD value of the sample is between 100 and 1000 mg/L, it is proportional to the increase of the absorbance of trivalent chromium [Cr^{3+}] in a sample and is calculated by measuring the absorbance of trivalent chromium [Cr^{3+}] produced by the reduction of potassium dichromate [$KCr_2O_{7(aq)}$] at 600 nm. When the COD value of the sample ranges from 15 mg/L to 250 mg/L, it is proportional to the absorbance reduction value of hexavalent chromium [Cr^{6+}] and the absorbance increase value of trivalent chromium [Cr^{3+}], it is also proportional to the total absorbance reduction value of a sample. At this time, the detection standard state that it is calculated by measuring the total absorbance reduction at 440 nm. The difference in measuring wavelength lies in the transformation of hexavalent chromium [Cr^{6+}] into trivalent chromium [Cr^{3+}] after reduction, the maximum absorption peak of hexavalent chromium [Cr^{6+}] is about 440 nm that of trivalent chromium [Cr^{3+}] is about 600 nm, the solution color changes from yellow to blue-green (Rohyami *et al*., 2021). In ISO 15705-2002, if COD ≤150 mg/L, the residual hexavalent chromium content is detected at 440 nm; if COD ≦50 mg/L, the remaining hexavalent chromium content is detected at 348 nm (ISO, 2002).

Chloride ion is the main disturbance in COD testing. The traditional method of COD detection focuses on the influence of chloride ions in water samples to determine how to eliminate this interference. In some industrial wastewater, the concentration of chloride ions can reach 10000 mg/L, which seriously affects the accuracy of COD testing. Mercury sulfate [Hg_2SO_4], silver sulfate [Ag_2SO_4], silver nitrate [$AgNO_3$], bismuth nitrate [$BiNO_3$] antimony (III) sulfate [$Sb_2(SO_4)_3$] is used to eliminate the interference caused by chloride ions (Ballinger *et al*., 1982; Geerdink, *et al*., 2017; GAQS, 2013, 2017a; Rohyami *et al*., 2021; SEPA, 2007; 2002). Nonetheless, mercury sulfate is the most commonly used which reaction with chloride ions is proposed to occur as follows (Rohyami *et al*., 2021):

$$Hg^{2+} + 2Cl^- \rightarrow HgCl_2 \quad (3)$$

However, the effect of some of these transition ions is limited and only suitable for water with chloride content ≤1000 mg/L (GAQS, 2017a; 2017b; SEPA, 2001). For high-chloride and high-ammonia wastewater contaminants, it is necessary to remove the ammonium ion by nitrogen under strongly alkaline conditions and calculate the chloride ion calibration value (GAQS, 2014).

Traditional COD Detection Techniques Optimization

In traditional COD detection methods, there are some problems, such as the serious interference of chloride ions, the toxic masking agent the incomplete oxidation reaction. Many scholars had explored and optimized the traditional methods (Dan *et al*., 2000; Dharmadhikari *et al*., 2005; Domini *et al*., 2009; Li *et al*., 2009; Rohyami *et al*., 2021; Xu, *et al*., 2019). In the traditional method, potassium dichromate needs to reflux and boil for 2h in a sulfuric acid medium to fully decompose organic matter. Microwave and ultrasonic technologies are used as digestion methods for COD detection, which can effectively reduce the digestion time. Feng *et al.* (2017) reported that the COD (≤500 mg/L) of water sample could be accurately detected by synergistic treatments of pressure and microwave under 1350 W power with mercury sulfate as the shielding agent in a short time. The interference of chloride ions was effectively reduced in this method the maximum allowable coexisting concentration was up to 30,000 mg/L. Domini *et al.* (2006) utilized three microwave digestion methods to obtain COD values which include "closed microwave-assisted", "open microwave-assisted" and "ultrasound-assisted" methods. The result showed that the COD values for 10 real wastewater samples ranged between 88 and 104% compared with the classical method, the "ultrasound-assisted" digestion method showed better applicability. Combined microwave digestion with a mixed acid reagent (H_2SO_4- H_3PO_4) technology. It only took 1 min to determine the COD the recovery rate reaches 96%. Bo *et al.* (2017) found that the ultrasound-assisted method could determine the concentration of COD of samples rapidly when its value was ≤400 mg/L, the recoveries of the COD of samples were higher than 94%.

The potassium dichromate oxidation method inevitably used toxic reagents, so many scholars also tried to find more green oxidants or catalysts. For example, Almeida *et al.* (2013) used green manganese as an oxidant [$KMnO_4$] to detect the COD of several organic compounds and actual samples, which were treated by an activated carbon microwave solid-phase extraction system at first. The method showed better resistance to chloride ion interference than the standard method, the detection limit was 1.25 mg/L, and the linear range was 2.6-850 mg/L. Using [$Mn(H_2PO_4)$] instead of [Ag] as the catalyst to rapidly oxidize organic compounds in wastewater, the digestion time could be reduced to 20 min. Esteves *et al.* (2015) adopted heterogeneous Fenton oxidant ($H_2O_2/Fe_{3-x}Co_xO_4$ nanoparticles) to achieve rapid and environmentally friendly determination of COD, COD was quantified by the amount of [H_2O_2] consumed. The detection limit of the method was 2.0 mg/L. The oxidant in the method could be recycled. Pisutpaisal and Sirisukpoca (2014) proposed to use of ozone as an oxidant to measure the COD content in the wastewater. Under the condition of 31℃, an ozone probe (WISCO AI210, Thailand) was used to monitor the concentration of dissolved ozone in water for 60 sec. There was a good linear relationship between the degradation rate of ozone and the COD value in the range of 0-80 mg/L (R^2>0.96), The Schematic of the ozone monitoring system as COD prediction is shown in Fig. 1.

New COD Detection Techniques

Along with the development of the industry, all kinds of new organic pollutants in water appear ceaselessly, and the accuracy of traditional COD detection technology is affected. On the other hand, there are some problems with the traditional method, such as the toxic reagent usage, complicated operation, the long testing time the chlorine ion disruption, and so on. Therefore, to develop a new type of COD detection technology, promote environmental protection, high precision, short time consuming, online detection will become a trend.

Chemiluminescence

Most chemiluminescence mainly uses Lumimol for the indirect determination of COD. Luminol is a common luminescent agent and is widely used in bioengineering, chemical tracer, and other fields (Pu *et al*., 2020; Deepa and Rajendrakumar, 2019; Riaz *et al*. (2018). Silvestre *et al.* (2011) combined quantum dot luminol-H_2O_2 system, CdTe nanocrystals, and UV light as an oxidation system to catalyze the degradation of organic compounds. Meanwhile, oxidized Luminol emitted strong fluorescence quenching occurred when organic matter existed. The COD concentration of 1-35 mg/L could be detected by this method.

Ozonation chemiluminescence is a novel determination technique developed in recent years. Its principle is that ozonation produces free radicals in water, oxidizes organic matter, and produces chemiluminescence. Established seawater COD analysis system with the help of a microfluidic chip. As shown in Fig. 2. The ozone generator generated ozone, the ozone went through a peristaltic pump, flow meter, and pressure gauge, and reached into the analysis chip. The water sample entered the analysis chip through the peristaltic pump. Water samples and ozone were mixed in the chip to generate chemiluminescence signals, which were measured by photomultiplier tubes. By optimizing the reaction conditions, the linear range of detection was 0.1-10 mg/L the detection limit was 0.08 mg/L. There was no significant difference compared with the national standard method.

Spectrometry

Spectrometry is divided into ultraviolet spectroscopy, fluorescence spectroscopy, near-infrared spectroscopy the fusion of multi-source spectroscopy. The development of ultraviolet has gone through three stages: Single wavelength, double wavelength, and full wavelength (Albrektienė *et al*., 2012; Roudi *et al*., 2019; Li and Hur, 2017), these methods applied different algorithms and models, such as LSSVMs (Least Squares Support Vector Machine) (Mu *et al*., 2019), PLS (partial least squares) (Chen *et al*., 2021), MLR (Multiple Regression) (Hu *et al.,* 2016) so on. Liu *et al.* (2017) compared the determination of COD by ultraviolet absorption spectrum and near-infrared spectrum. The COD prediction model established based on ultraviolet spectroscopy has a better prediction effect in the 280-310 nm spectrum region the COD model established based on infrared spectroscopy has a better prediction effect with COD in the 7250-6870 cm^{-1}

spectrum region. Wu and Bi (2014) reported that a more accurate prediction model can be obtained by combining the ultraviolet spectrum and near-infrared spectrum. Since the turbidity of natural water samples would affect the determination of COD, Wu *et al.* (2013) and Li *et al.* (2019); studied the turbidity compensation technology, which would effectively improve the accuracy of COD determination by UV-vis spectroscopy. However, it was difficult to obtain the turbidity interference baseline because of the different size distribution of titrated suspended particles in the actual water environment. Hu *et al.* (2020) proposed a direct derivative method without a standard baseline, which could effectively eliminate the bias caused by turbidity particles. In addition to turbidity, the temperature was also one of the factors affecting the accuracy of COD determination by spectrometry. Xin *et al.* (2019) found that the UV absorption spectrum of COD standard solution increased with temperature in the range of 0-30°C. they established a temperature compensation model by using the least square method and obtained good results.

Table 1: Comparison of national standard COD measurement methods in China

Methods	Masking agent	Digestion methods	National standard no.
Spectrophotometry	Silver nitrate	Digestion at 165°C for 40 min	GB/T29599-2013 (GAQS, 2013)
Titration	Mercury sulfate	Boiling reflux 2h	
Titration	of Silver nitrate and bismuth nitrate	Reflux at 180°C for 10 min	GB/T34500.2-2017 (General Administration of Quality Supervision, 2017a)
Titration	Mercury sulfate	Reflux at 148°C for 110 min	SN/T2835-2011 (The State Administration of Quality Supervision, 2011)
Titration	Mercury sulfate and silver sulfate	Boiling reflux 2 h	CJ/T428-2013(Ministry of Urban-rural Development of People's Republic of China,2013)
Titration	Mercury sulfate in combination with chlorine calibration method	Nitrogen boiled and refluxed for 2 h	HJ/T70-2001 (State Environmental Protection Administration, 2001)
Titration	Chlorine calibration method	Boiling reflux 2 h	GB/T31195-2014(General Administration of Quality Supervision, 2014)
Spectrophotometry	Mercury sulfate	Digestion at 165°C for 40 min	HJ/T399 (State Environmental Protection Administration, 2007)
Titration	Mercury sulfate	Boiling reflux 2 h	HJ/T828-2017(State Environmental Protection Administration, 2017)

Table 2: Summary of COD measurement methods

Methods		Case	Detection range mg/L	Precision	Advantages	Disadvantages
Traditional COD analysis	Spectrop hotometry	HJ/T 399(State Environmental Protection Administration, 2007)	100-1000 15-150	RSD<5.4% RSD<8.8%	Spectrophotometric method is simple to operate, use less drug quantity, environmental protection and convenient than titration method	Chloride ion interference, mercury salt or silver salt masking, Ag+/Ag+/ Cr6+ pollution
	Titration	HJ 828-2017 (State Environmental Protection Administration, 2017)	16-700 1-35	RSD<11% RSD<1.1%	Avoid the use of Cr^{6+}, reduce the burden of the environment	Low concentration and narrow range
New COD Detection Techniques	Chemilu minescence	Lumimol method (Silvestre *et al*., 2011) Ozonation method	0.1-10	RSD<5%		
	Spectrometry	Ultraviolet (Bi *et al*., 2014)	1-800	RSD<7%	Fast, no secondary contamination	Need the assistance of instruments, some of which are expensive, and their accuracy needs to be improved
		Fluorescence (Zhou, *et al*., 2019a)	1-55	RSD<22%		
		Near infrare (Wu and Zhao, 2019)	0.5-100	RMSEP: ±0.79 mg/L		
		Multi-source spectroscopy (Wu and Bi, 2014)	1-800	RMSEP: ±3.26 mg/L		
	Electrode	AuNP-TiO_2NA sensor (Liang *et al*.,2019)	5-100	RSD<3.9%	Fast, portable, no secondary	Chloride ion interference, the electrode is easily contaminated, resulting in unstable measurement
	Other new detection techniques	CW-MFC system, paper-based nano-silver functional colorimetric sensor, TOC analyzer *et al*. (Xu *et al*., 2017; Nóbrega *et al*., 2019; Long *et al*., 2019)	-	-		The new methods need to do more exploration in practical application and it needs researchers' efforts to promote and apply it in the market

RSD: Relative Standard Deviation; RMSEP: Root Mean Square Error

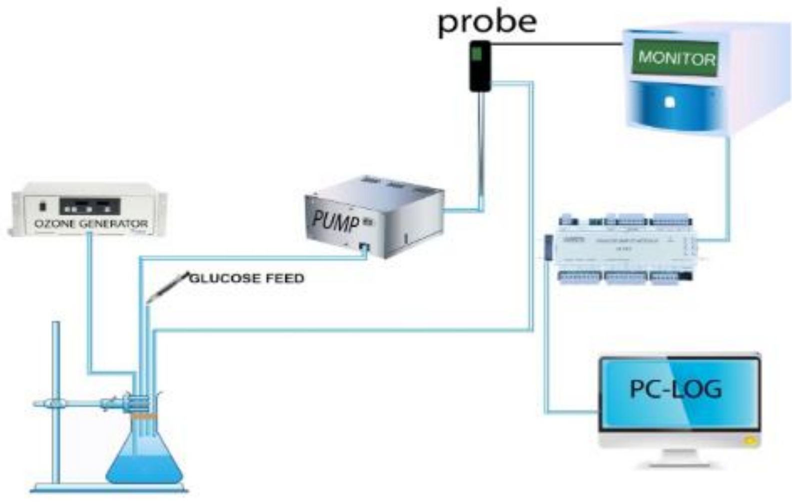


Fig.1: Schematic of the ozone monitoring system as COD prediction (Pisutpaisal *et al*., 2014)

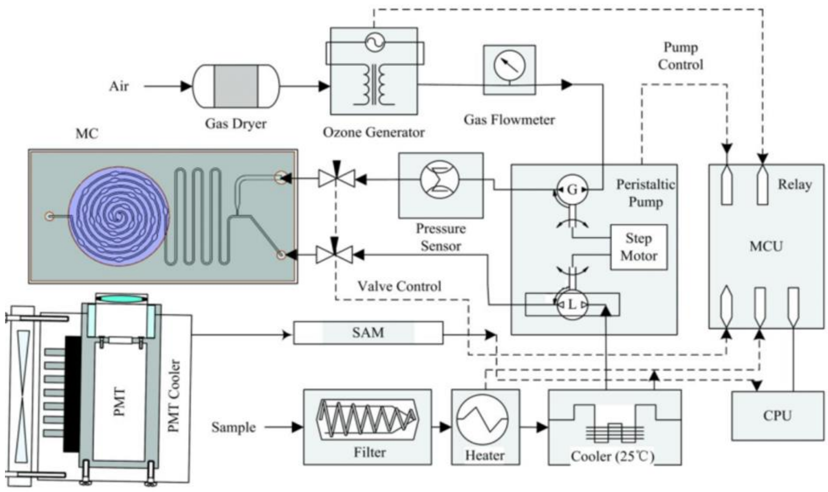


Fig. 2: Analysis system structure (MC: Microfluidic Chip; MCU: Microcontroller Unit; CPU: Centre Processing Unit; G: Gas; L: Liquid; SAM: Signal Acquisition Module; PMT: Photomultiplier)

Zhou *et al*. (2019a; 2019b) compared the COD value of water quality with the fluorescence emission spectrum data at specific excitation wavelengths and at multiple excitation wavelengths, the result showed that it was an effective method to analyze COD in the multi-spectral feature-level fusion model was more accurate and more effective for predicting COD of water quality.

Electrode

The electrode has the advantages of less sample preparation, strong continuous detection ability, and low cost. The electrode film sensor is the key component. Finding a good working electrode to determine the amount of OH· production is the challenge of the electrode method. A variety of new membrane electrode studies had been reported, including metal alloy electrodes, bismuth-based semiconductor electrodes (Fang *et al.*, 2021; Alves *et al.*, 2020), graphene-based electrodes (Li *et al.*, 2020), [TiO_2] photocatalytic electrode (Liang *et al.*, 2019) so on. Fang *et al.* (2021) prepared a new Ni/ZnO/Cu composite electrode as an electrocatalytic sensor. They found that the electrode with zinc oxide had a better electrochemical performance the detection limit and sensitivity of COD could reach 0.6036 and 2.403×10^{-2} mg/L. It was in good agreement with the traditional potassium dichromate method in the actual water sample, but it was easy to lose activity due to the influence of chloride ions. [TiO_2] photodegradable nanomaterials were non-toxic and cheap and a photos table could be used for COD determination, but photoelectron/hole pairs were easy to recombine, resulting in poor reproducibility. Liang *et al.* (2019) electrodeposited Au nanoparticles (AuNPs) on anatase

DOI: 10.3844/ajbbsp.2022.23.32

[TiO_2] nanotube (TiO_2NA) array electrode under ultrasound (Fig. 3a and 3b) for COD test, there was a linear relationship between photocurrent and COD value from 5 mg/L to 100 mg/L. it was compared with pure TiO_2 sensor (Fig.3c), Au nanoparticles modified [TiO_2] nanotube (AuNP-TiO_2NA) array sensor had lower photoelectric resistance. It had higher photocatalytic activity and stability, which was consistent with the determination result of the potassium dichromate method in actual COD determination.

Although the electrode is simple and convenient, it also has obvious shortcomings. The electrode is easy to corrode in the process of organic oxidation the electrode surface is easy to be polluted, resulting in unstable measurement and a narrow linear range. Kabir *et al.* (2019) studied the applicability of the corrosion-resistant graphite-like carbon electrode produced by pyrolysis asphalt reaction as a COD detection electrode. The surface of the electrode was modified with quinone functional groups to make it more hydrophilic. The linear range of COD detection for glucose solution could reach 0-10000 mg/L the detection limit was 40 mg/L, but the resistance to chloride ion interference was still insufficient.

Other New Detection Techniques

In recent years, a new constructed wetland-based microbial fuel cell (CW-MFC) integrated platform has come into view. Although it is still in its infancy, it has the dual role of sewage treatment and power generation (Liu *et al*., 2014; Sruvastava *et al*. (2015). In a typical CW-MFC, the cathode of the MFC is used to receive oxygen from the open-air the anode is involved in the oxidation of organic matter at the bottom of the wetland. The bioelectricity generated by the MFC can be used to reflect the COD concentration in the wastewater, providing a potential method for COD monitoring in the CW-MFC system. Xu *et al.* (2017) discussed the feasibility of applying CW-MFC to COD monitoring in constructed wetlands and fitted the linear relationship between the electrical signals generated in the CW-MFC system and COD concentration within the range of 0-500 and 500-1000 mg/L. This method could be performed online for COD monitoring without the participation of chemicals the system had the ability of self-sufficiency and even energy output, which showed its application in the further. However, the linear relationship was obtained by the input of specific COD components, the actual wastewater had different COD components, such as biodegradable compounds, polycyclic aromatic hydrocarbons, or multi-organic components, and the standard curve needed to be calibrated. On the other side, other substances in the wastewater, such as nitrogen or sulfur, interfered with the output of anode potential, so more detailed component interaction studies would be needed in the future.

Nóbrega *et al.* (2019) proposed a paper-based nano-silver functional colorimetric sensor. Glycerol was used as a reducing agent to prepare nanoparticles (AgNPs) then the colloidal solution containing AgNPs is coated on the paper and the paper presented yellow color. When the paper was exposed to the actual wastewater, the sensor changes from yellow to gray due to vulcanization (Fig. 4a and 4b). A linear curve (Fig. 4c) was established through RGB image processing combined with Principal Component Analysis (PCA). Five wastewater was detected the COD values were between 66-1160 mg/L. The detection limit of the method was 46.6 mg/L. Although this method was superior to the standard method, it was not suitable for all organic matter.

Long *et al.* (2021) proposed that Total Organic Carbon (TOC) analyzer could be used to detect COD. High-temperature TOC analyzer was firstly used to detect TOC in the simulated wastewater, the linear conversion relationship between TOC and COD has established then the COD value in oilfield wastewater was predicted by the conversion model. This method could avoid the interference of dangerous chemicals and chloride ions in conventional testing. However, this method required that the COD components in the tested sample must be the same or similar to those in the simulated wastewater used in the conversion model. In reality, the composition of wastewater was complex and unpredictable, this situation would limit its application in detection.

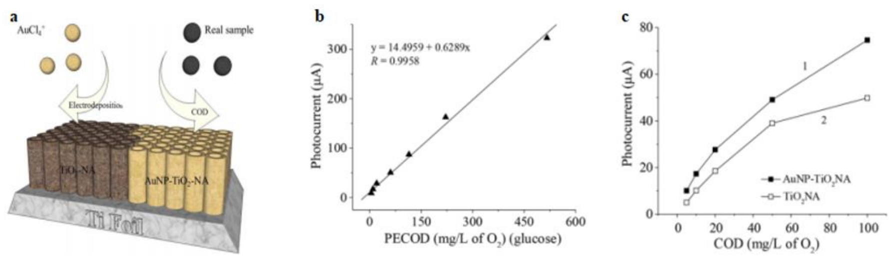


Fig. 3: Preparation of AuNP-TiO2NA sensor and its application for COD analysis. (a) The sketch of the whole process from facile preparation to effective application for AuNP-TiO2NA sensor. (b) The calibration curve of photocurrent was obtained from glucose standard solutions of different COD values at the AuNP-TiO2NA sensor. (c) Comparison of TiO2NA and AuNP-TiO_2NA sensors (Liang *et al*., 2019)

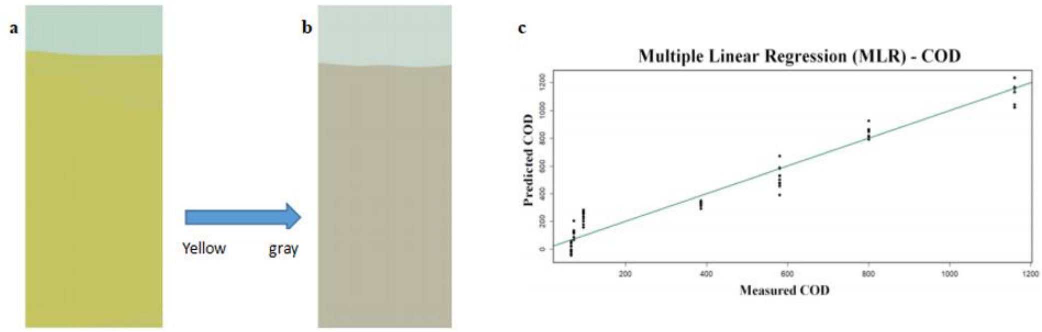


Fig. 4: Schematic diagram of nanometer silver functional colorimetric sensor for determination of COD. (a) Sensor unused. (b) Sensor after exposure to the wastewater sample (COD 1160 mg/L) for 20 sec. (c) Calibration curve for COD analysis showing the predicted COD (RGB) vs. COD concentration. Adjusted $R^2 = 0.96$. (Nóbrega *et al*., 2019)

Conclusion

Water resource is closely related to human activities. With the development of industry, water pollution is becoming more and more serious. It is very important to monitor water in time to control water pollution. COD is an important parameter to reflect water quality. The COD detection method in wastewater is mainly the potassium dichromate oxidation method. Traditional analytical methods are mainly divided into titration and spectrophotometry. Due to the disadvantages of the traditional COD detection methods, such as large drug consumption, toxic reagent, cumbersome operation, long detection time serious chloride ion interference. A lot of researchers have made a lot of exploration on the optimization of this method and developed a series of new COD detection technologies, including chemiluminescence, spectrometry, electrode, microbial fuel cell, paper nano silver colorimetric sensor TOC indirect determination methods, which are summarized in Table 2. With the development of the times, people's requirements for sustainable development of the environment will be higher and higher. Green online detection technology with safe and high efficiency will become a trend.

Acknowledgment

This research was supported by the Provincial Natural Science Fund (LGN21C200017), the National High Technology Research and Development Program of China (2016YFD0400405) Provincial Key R and D Program（2015C02036).

Author’s Contributions

Dan Wu and Yinglu Hu: Contributed to the writing of the manuscript.

Ying Liu: Grammar checking and modification.

Ethics

This article is original and contains unpublished material. The corresponding author confirms that all of the other authors have read and approved the manuscript and that no ethical issues are involved.

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