Research progress of on-line automatic monitoring of chemical oxygen demand (COD) of water

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Abstract. With the increasingly stricter control of pollutant emission in China, the on-line automatic monitoring of water quality is particularly urgent. The chemical oxygen demand (COD) is a comprehensive index to measure the contamination caused by organic matters, and thus it is taken as one important index of energy-saving and emission reduction in China's "Twelve-Five" program. So far, the COD on-line automatic monitoring instrument has played an important role in the field of sewage monitoring. This paper reviews the existing methods to achieve on-line automatic monitoring of COD, and on the basis, points out the future trend of the COD on-line automatic monitoring instruments.

1. Introduction

Mainly depending on on-site manual sampling and laboratory analysis, the traditional water quality monitoring is faulted for its large sampling error, high labor intensity, low monitoring frequency and insensitivity to the change of water. It is thus hard to meet the demands of the governments and enterprises to manage the environmental water quality effectively. So the on-line automatic monitoring of water quality is in urgent need, particularly with the deepening of the control of the pollutant emission in China.

The chemical oxygen demand (COD) refers to the amount of oxidant consumed when the water is digested with a strong oxidizing agent under certain conditions. It is commonly expressed in oxygen concentration (mg/L). It is one of the important energy-saving and emission reduction targets in China's "Twelve-Five" program [1], as it is an important indication of the organic substance in water and it reflects the situation of the water pollution. The greater the COD value is, the more serious the water pollution is. The COD is often used to monitor and analyze the quality of the surface water, industrial wastewater and domestic wastewater [2]. However, it can only reflect the pollution caused by the oxidized organic matters while cannot reflect the pollution degree caused by the polycyclic aromatic hydrocarbons, PCBs and dioxins [3].

The COD on-line automatic monitor is a fully automated instrument, integrating the modern sensor technology, automatic measurement technology, automatic control technology and computer application technology. The COD on-line automatic monitor has played an important role in the field of sewage monitoring since China's first batch of the COD on-line automatic monitoring instruments
with the independent intellectual property rights were developed and granted accreditation in 1996 by the National Environmental Protection Bureau of China [4].

2. COD on-line automatic monitoring instrument

At present, many domestic and foreign manufacturers have developed the COD on-line automatic monitoring instruments. Great differences exist among them in terms of the application scope and measurement range, as they may adopt different principles and methods [5]. But, generally speaking, a COD on-line automatic monitoring instrument consists of injection system, reaction system, detection and control system, as is shown in figure 1. In the injection system, the water sample is collected, transported and mixed with the reagent, and then the wastewater is discharged and the reaction chamber is cleaned. The reaction system is responsible for the digestion and reaction of the water sample. While the detection-control system is the system for on-line analysis. It includes the monitoring, data acquisition, data processing, display, storage, printout and transmission. The COD on-line automatic monitoring instruments generally have the following functions and features: (1) They cover a wide measuring range in a comparatively short time; (2) They can activate alarms when an excessive concentration occurs and collect the water sample correspondingly; (3) They provide accurate measurements. The measurement frequency can be adjusted and the measurement data can be uploaded in real time; (4) They have the functions of intelligent self-diagnosis and alarm prompt; (5) They can automatically clean the sampling pipeline and are easy to be maintained; (6) They are open to other instruments; (7) They are fully compatible with Chinese environmental information system software, and have a variety of adaptation functions; (8) They are equipped with abnormal reset and power protection to ensure automatic restore when reenergized.

3. Principle and classification of COD automatic monitoring instrument

Based on the different detection principles, such as chemical method, electrochemical method, physical method, biological method, correlation coefficient method, soft measurement method and so on, the COD automatic monitoring instruments can be divided into different types.

3.1. Chemical method

Those adopting the chemical method use the strong oxidant to oxidate the organic matters. The corresponding relationship between the amount of the oxidant used and the COD value of the water samples is established, which helps to achieve the COD value by measuring the amount of the oxidant. Based on different oxidants, chemical method can be further divided into the potassium dichromate digestion method, permanganate index method and O₃ oxidation method.
3.1.1. Potassium dichromate digestion method The potassium dichromate digestion method [6] refers to the mass concentration of the oxygen, equivalent to the amount of dichromate consumed by the dissolved and suspended matters when a water sample is treated with potassium dichromate oxidation under defined conditions. Basically, it works in this way: to begin with a known amount of potassium dichromate solution added to the water sample, then the silver salt is taken as a catalyst in the strong acid medium. After boiling reflux, the COD value of the water sample is calculated. Based on the test methods, the potassium dichromate digestion method can be further divided into the potassium dichromate digestion-photometric method, potassium dichromate digestion-coulometric titration and potassium dichromate digestion-redox titration [4]. The potassium dichromate digestion method is the most widely used method. It is applicable to all types of water samples whose COD is more than 30 mg/L, and to the undiluted sample whose detection limit is no more than 700 mg/L. But meanwhile, it cannot be applied to the sample whose chloride concentration is greater than 1,000 mg/L (diluted).

The potassium dichromate digestion method has high accuracy and good reproducibility, but its digestion takes too much time, which is about two hours. It consumes a lot of concentrated sulfuric acid and silver sulfate during the reaction, and it tends to cause serious secondary pollution. What is more, it could be easily affected by chloride concentration and is always blamed for the high cost [7-9]. To solve the problems above, the researchers both at home and abroad have conducted lots of researches on the rapid digestion methods (such as sealed digestion method, open tube digestion method, microwave digestion method and other catalytic digestion method [8,10]), measurement methods (such as Coulomb method, spectrophotometry, potentiometry, continuous flow analysis, polarography, atomic absorption spectrometry, chemiluminescence and plasma emission spectroscopy (ICP-AES) [2,15]), silver catalyst replacement [7-8,10], elimination of chloride ion interference [7-8,10] and so on. Significant findings have been achieved, which partially make up for the deficiencies and shortcomings of the potassium dichromate digestion method. For example, Shen Yuhang et al. proposed the open tube method and reduced the digestion time from 2 hours to 12 minutes. Wang Hui et al. replaced H2SO4 with H2SO4-H3PO4 without using the masking agent HgSO4 and catalyst Ag2SO4, and then accurately determined the COD value of the high chlorine fluoride wastewater by subtracting the COD value of the chloride ion itself from the gross COD value of the sample water [8]. Vaidya proposed a mercury-free sealed COD value measurement method. In the method, firstly, the chlorine ions were converted into HCl, and then HCl was adsorbed by the bismuth adsorbent. Such method helped to get rid of the interference of chloride ion [10]. However, all these methods failed to avoid the secondary pollution.

In China, most of the COD on-line automatic monitoring instruments are based on the potassium dichromate digestion method. High temperature (175℃) or high temperature and pressure is used to speed up the digestion and colorimetry is used to measure the sample. Most of the measurement ranges are around 10~2,000 mg/L, the measurement period is about 30 minutes and the measurement error generally is less than 10%. For example, the CH1-TL-1A sewage COD quick measurement instrument has a range of 60~1,000 mg/L and the secondary pollution of 0.5 g per time (according to the consumed HgSO4). US HACH CODmax potassium dichromate on-line monitor has three test levels of 0~100 mg/L, 100~1,000 mg/L and 1,000~5,000 mg/L and its resolution is less than 1 mg/L. When the COD of sewage is greater than 100 mg/L, the measuring error is less than 10%. While its error is less than 6 mg/L with the COD being less than 100 mg/L.

3.1.2. Permanganate index method The permanganate index method [11] refers to the mass concentration of the oxygen, equivalent to the permanganate consumed by certain organic matters and inorganic reductive substances when the water sample is treated with permanganate oxidation under defined conditions. Basically, it works in this way: to begin with, a known amount of potassium permanganate and sulfuric acid are added to the sample. Then, after the potassium permanganate oxidizes the organic matters and inorganic reductive substances in the heating digestion, the remaining Mn5+ is measured. In this way, the permanganate index value of the water sample, that is, CODMn, is obtained. At present, the permanganate index on-line automatic monitoring instrument is mainly based
on the following three principles: permanganate oxidation-chemical measurement, permanganate oxidation-potentiometric titration and UV spectroscopy [13]. Generally speaking, the oxidation ratio of potassium dichromate digestion is above 90%, while that of permanganate index is about 50% [12]. According to the International Organization for Standardization (ISO), the permanganate index method could only be applied to the measurement of the surface water, drinking water and domestic sewage.

COD (permanganate index) on-line automatic analyzer of Shanghai Qing Miao Optoelectronics Technology Co., Ltd. has the resolution of less than 0.001 mg/L, the measurement range is 0–50 mg/L, and the measurement period is about 45 minutes. It adopts colorimetric measurement and can be used for surface water COD test. US HACH COD203A COD\textsubscript{Mn} analyzer uses acid potassium permanganate at 100°C to oxidate the organic matters and uses redox potential titration to measure the COD. It is developed for the surface water, drinking water or raw water with low concentration.

3.1.3. \textit{O}_3 oxidation \textit{O}_3 is a strong oxidant with high efficiency while without secondary pollution. It can directly oxidate the organic matters of the water by cycloaddition, electrophilic addition and nucleophilic addition, and indirectly oxidate partial organic matters by the hydroxyl ·OH, which is produced by the reaction between \textit{O}_3 and H\textsubscript{2}O. However, as \textit{O}_3 itself is selective for the oxidation of the organic matters, its application to monitor the refractory organic wastewater is limited [14]. \textit{O}_3/UV is a high-level oxidation technology that combines \textit{O}_3 and ultraviolet radiation to enhance the oxidability. Prengle et al. found that the decomposition process of \textit{O}_3 to generate free hydroxyl radicals can be accelerated in the ultraviolet light, thus significantly accelerating the degradation rate of organic matters in the wastewater [14]. Xue Peijiao et al. [1] built a relationship model between the oxygen consumed and the amount of \textit{O}_3, with a COD on-line detection system that integrated the \textit{O}_3-synergetic UV digestion technology and the multi-sensor data fusion technology. The results demonstrated a high accuracy of the correlation coefficient of the model between the measured value and the theoretical value, being 0.96. Its relative standard deviation was within 7%. With the similar method, Zhang Long et al. [9] built a model whose relative standard deviation was less than 5% and whose recovery rate was about 90–110% when the COD of water sample was 50–1,000 mg/L. Liu Yan et al. measured the residual \textit{O}_3 after oxidation with chemiluminescence and determined the COD of sea water through quick measurement by using flow injection method. The results showed high sensitivity, with a detection limit of 0.03 mg/L and salinity within 0–50%. The test results of COD were not affected by salinity, and they were in a good correlation with the results obtained by the standard KMnO\textsubscript{4} method [14].

3.2. Electrochemical method

Electrochemical method measures the COD by oxidating organic matters in water by the electrolysis or photoelectron-catalysis method and then calculating the amount of organic matters in the water sample based on the current (ampere) or the electricity (coulomb) consumption during oxidation process. Such method is also known as electrochemical oxygen demand (EOD) [3]. The electrochemical method is simple to operate and free of pollution, but the electrode life and reproducibility are limited to a certain degree. To extend the working electrode fatigue and ensure long-term stable measurement, Na\textsubscript{2}SO\textsubscript{4} solution will be used, which nonetheless leads to the unavoidable use of reagents [9].

3.2.1. Electro-catalytic oxidation method [14-16] Nowadays, electro-catalytic oxidation method is widely used in practice, and the use of PbO\textsubscript{2} electrode oxidation method has a breakthrough progress in the field of electrochemical COD measurement method. As PbO\textsubscript{2} electrode has high conductivity, high oxygen potential, and good inertia to strong acid and alkali, the hydroxyl radicals can be generated by the anode during electro-catalysis process to thoroughly degrade organic matters. Westbroek et al. measured the COD with Pt/PbO\textsubscript{2} rotating disc electrode and the working range was 20–25,000 mg/L. However, due to the effect of Langmuir and other temperature adsorption
characteristics, the linear factors of the COD with the low concentration and high concentration were different and thus needed to be regulated [14]. Xie Zhenwei et al. developed Platinum-based α-PbO2 and β-PbO2 double plating electrodes with large oxygen evolution potential and used them to produce hydroxyl radicals, which could directly oxidate organic matters in wastewater. Li Luoping et al. developed F-PbO2 electrode for electrochemical oxidation of organic matters in water and used amperometry to measure COD [3]. Li et al. studied the COD measurement method with fluorine-doped nano-PbO2 electrode, and confirmed the correlation between response current and COD [14]. However, PbO2 electrode is faulted for its complex preparation, narrow use range, short service life, tricky electrode repair, potential of pollution by the toxic heavy metal lead and other issues that may be caused by the electrode waste processing. Because of these reasons, the methods mentioned above could hardly gain wide promotion and application [3,15].

In addition to PbO2 electrode oxidation, Cu electrode oxidation and boron-doped diamond (BDD) electrode oxidation have been developed rapidly in recent years. Ibrahim et al. [17] used an optimized nano-Cu/GCE thin film electrode to achieve a linear operating range of 15–629.3 ppm with 7 ppm detection limit and 0.35 mol/L chloride ion concentration, and the chloride ion concentration has little effect on the measurement results. Silva et al. studied the cyclic voltammetric behavior of Cu electrode in 0.1mol/L NaOH electrolyte, and obtained the linear range of 53–2,801.4 mg/L with the lowest detection limit of 20.3 mg/L. Kim et al. developed a new type of COD monitor based on Cu electrode electrochemical oxidation. The linear working range of the instrument was within 10–10,000 mg/L and it could work continuously for more than 3 months. Meanwhile, the passivation of the copper electrode surface during monitoring process was activated through the rotary grinding [14].

Bogdanowicz et al. [18] developed the BDD thin film electrode deposited on silicon wafers and glassy carbon substrates, which was prepared by microwave plasma enhanced chemical vapor deposition. The BDD electrode of this structure was able to greatly reduce the background noise and realize 0.3 mg/L detection limit. Wang et al. used both BDD electrode and BDD electrode-ultrasonic electrochemical method for the COD measurement. Compared with BDD electrode method, BDD electrode-ultrasonic electrochemical method could extend the linear range of COD detection from 19.2–11,600 mg/L to 0–23,200 mg/L, while without changing the detection limit because of the promotion of organics’ degradation rate and detection range due to ultrasonic digestion. It was suitable for clean water and sewage [15]. A new system combined with the flow injection analysis technology was established by Liu Meichuan et al. to achieve a rapid and direct measurement of COD. In the system, the boron-doped diamond film electrode was taken as the working electrode and the electrochemical amperometric method was used to measure COD. Besides, Potassium dichromate, mercury sulfate and other toxic reagents were not used in the system, so no secondary pollution would be produced and no pretreatment of water samples would be needed [3]. Zhao Guohua et al. adopted Si/BDD electrochemical oxidation-flow injection method to obtain the linear relationship between the response current and COD value. In the study of cyclic voltammetry, the selective characteristic of electrode catalytic oxidation, which had strong oxidizability for aromatic compound such as phenol, nitrobenzene and benzene, had also been found [14]. Based on boron-doped diamond electrode, the limit currents of glucose, potassium hydrogen phthalate and other solutions were measured through the detection of current-time curves and the good linear relationships between limit current and COD value were found by Yu H B et al. The linear working range was 20–9,000 mg/L, the minimum detection limit was 7.5 mg/L, and the standard deviation was less than 6%. At the same time, pH, anode bias and other Ti/BDD composite electrode current response were also studied [19].

3.2.2. Photo-catalytic oxidation method [14-15] Photo-catalytic technology is a high-level oxidation technology, which can use the wide band gap N-type semiconductor to prepare dye-sensitized solar cells and use the photo-catalytic method to degrade organics. With the development of science and technology, semiconductor nano-materials such as ZnO, SnO2 and TiO2 have been widely used in photo-catalytic measurement of COD. Compared with nano-ZnO and SnO2, TiO2 is a kind of photo-catalyst with good application prospect because of its high sensitivity, rich source, low cost, good
corrosion resistance and good photochemical stability [14]. However, the main problem of the photo-catalytic technology is that photo-generated electrons and holes are easily compounded, which greatly reduces the degradation efficiency of the catalyst to organic matters [3, 14].

In the photo-catalytic technology, DO and some other efficient oxidants such as Cr$^{6+}$, Mn$^{7+}$, Ce$^{4+}$ and S$_2$O$_8^{2-}$ are the main things used to remove the photoelectron and the indicating signal. Li Chengfang et al. reported a rapid measurement technique of COD by adopting nano-TiO$_2$-K$_2$Cr$_2$O$_7$ system, whose linear range was 0.0~150.0 mg/L and detection limit was 0.4 mg/L.

Because the doping could improve the semiconductor’s quantum efficiency, Li et al. produced an electron acceptor by adding Ce$^{4+}$, and measured COD synergistically in the TiO$_2$-Ce (SO$_4$)$_2$ coexistence system. Ce$^{4+}$ and photo-generated electron could produce Ce$^{3+}$, whose concentration could be detected by fluorescence, and thus helped to measure COD indirectly. The linear range of the method was 0.0~100.0 mg/L, while the detection limit was 0.9 mg/L. It was suitable for COD determination of lake water or mildly polluted wastewater. When the Cl$^-$ concentration was less than 2,000.0 mg/L, it would not affect the measurement. There was no need to add mercury salt, thus mercury and other environmental pollution could be reduced. Zhang et al. reported a system which measured COD by combining photon-efficient photo-generated method with photo-catalytic under the coexistence of KMnO$_4$-organic matters and adopted the rotating plate photo-catalytic detector (RDPD) to indicate the detection signal. As the system had a high photon utilization ratio and automatic mixing function, it was suitable for the detection of the COD of water sample whose concentration was 0~260 mg/L. At the same time, there was no interference when Cl$^-$ concentration was less than 2,000 mg/L. The molecular sieve had superior adsorption capacity and special ion exchange capacity. Moreover, no polarity molecular sieve could also prevent light attenuation. Wang et al. reported a coexistence system of molecular sieves 4A-TiO$_2$-K$_2$Cr$_2$O$_7$, which overcame the problem of light attenuation and recycling difficulties by the direct use of TiO$_2$ as photo-catalyst. The linear range of this method was only 3~15 mg/L, the detection limit was 0.24 mg/L, and it could be used as a promising method of environmental assessment for surface water. Silvestre et al. reported a photo-catalytic technique combining a fully automated single interface flow system, an on-line UV-catalyzed unit and a quantum dot nanotechnology. In this method, CdTe quantum dots was used to catalyze the degradation of organic compounds in water under UV light source, and could detect slightly polluted water with COD concentration within 1~35 mg/L. The photo-catalytic equipment is complex and costly, but as a new detection technology, it is promising [15].

3.2.3. Photoelectro-catalytic oxidation method [14-16] Photoelectro-catalytic oxidation is to use the holes and hydroxyl radicals, which are generated during the photo-catalytic process with nano-TiO$_2$, to oxidate almost all organic pollutants to produce the final product CO$_2$ and H$_2$O. In the photoelectric catalytic oxidation method, photo-catalyst is taken as the light anode. If a certain bias voltage is imposed on it, photo-generated electrons will migrate to the external circuit, and then the compound of photo-generated electrons and holes is inhibited [3].

TiO$_2$ electrode is a key factor in the method. The modification of TiO$_2$ can improve its photo-catalytic efficiency. Zhang et al. [20] studied the COD measurement of various industrial wastes by using a thin-layer anode with a high-performance nano-TiO$_2$ and a flow injection technique. The detection time range was 1~5 minutes, the linear range under the best condition was 1~100 mg/L and the detection limit was 1 mg/L. Tian Yuhua et al. fabricated the TiO$_2$ thin film electrode with the manganese ion non-uniformly being doped by Sol-Gel method. Yuan et al. packaged the layer-layer TiO$_2$ thin film electrode with anatase TiO$_2$ nano sol. Compared with pure TiO$_2$ thin film electrode, the degradation rates of organic pollutants by manganese ion non-uniformly doped TiO$_2$ thin film electrode and layer-layer TiO$_2$ thin film electrode were better, so the COD could be detected more rapidly in water. TiO$_2$ nanotube array (TNAs) and thin-layer reactor (TCR) proposed by Dong Chaoping et al. were used to measure the COD of the surface water. Because of short reaction time, fast medium transfer and small volume, the method was suitable for surface water COD detection within the range of 3~15 mg/L and its detection limit was 0.30 mg/L. The Cl$^-$ concentration less than
50 mg/L would not interfere with the determination and so it could make up for the lack of oxidation capacity in the traditional method. Mu et al. fixed TiO$_2$ nano-fibers (TNFs) on poly-dimethyl-siloxane (PDMS) microfluidic devices for rapid determination of COD. Because of TNFs’ excellent response to the excitation light source and the applied electric field and the efficient separation of photo-generated electrons and holes, the method could detect the surface water and mild effluent with COD in the range of 0–250 mg/L in a few minutes and its detection limit was up to 0.95 mg/L. Wang et al. studied the method of COD determination with TiO$_2$ nano-rod array. After the optimization of parameters such as potential, light intensity and pH value, this method could be used to detect water with COD within 20–280 mg/L, but it would not be suitable for the relatively clean surface water when the detection limit arrived at 18.3 mg/L. However, the method had the advantages of simple operation, long-term stability and little pollution. The research group further used Cu$_2$O-loaded TiO$_2$ nanotube array electrode to measure COD by the photocatalytic oxidation. The composite electrode’s response had been significantly enhanced in the visible range compared to using single TiO$_2$ nanotube array electrode (TNTAs) method [15].

SJC COD on-line automatic monitor instrument adopts the electrochemical principle of hydroxyl radical oxidation. The measurement range of the instrument is 10–10,000 mg/L. The measurement error is less than or equal to ±10%. The repeatability is less than ±10%. The zero drift is less than or equal to 5 mg/L. The measuring period is 5 minutes and measurement interval can be freely set, ranging from 10 minutes to 24 hours.

### 3.3. Physical method

The physical method is based on the spectral analysis method [21]. The basis process is: Firstly, a relationship model between absorption spectrum and COD value is established, and then a specific light is used to irradiate the water samples. After that, absorption spectrum is transmitted to the computer by the sensor and the absorption spectrum is analyzed by software. According to the spectral range used, the physical methods mainly include UV spectroscopy and near infrared spectroscopy.

UV spectroscopy measurement is based on the fact that all kinds of organics in water samples have good absorption effect in the ultraviolet spectrum. When UV meter is used to calculate COD, the water sample needs to be divided into two groups. For one group, the national standard method is used to measure COD. For another group, UV spectral absorbance curve is collected. Then by the least squares method or the intelligent algorithm such as neural network algorithm, the COD prediction model of the water sample, which reflects the relationship between the UV spectrum and COD, is built up, so COD can be achieved quickly if the UV absorbance situation is known. Compared with the longer detection time consumed by potassium dichromate digestion, the COD of water samples can be calculated immediately after 2 minutes optical scanning, which means that the detection efficiency is greatly improved.

Li Dan et al. [22] designed a dual optical system by combining xenon light source with Ocean Optics USB2000+ spectrometer. In the system, they took variable optical path flow to meet the requirements of different water testing. The water absorption range of the measured water sample was about 200 to 300 nm in the ultraviolet band and there was a maximum absorption peak around 250 nm and a small absorption peak around 285 nm, respectively. The experimental results showed that the average relative error of the test results was 6.72% and the standard deviation was 4.66. Zhang Guoqiang et al. [23] took the potassium hydrogen phthalate standard solution as a water sample, and utilized the ultraviolet spectrophotometry to verify the good linear relationship between COD of water
sample and 254 nm UV absorbance within a certain range, the linear regression equation achieved as \( y = 125.33x - 2.3605 \) and the correlation coefficient as \( r = 0.9945 \). COD detection system designed by Liu Shuang et al. [24] was based on the UV absorption principle. Its range was within 0–1,000 mg/L and resolution was 0.01 mg/L. Compared with the spectrophotometer test results of American HACH DR6000, the maximum indication error of the system was 1.4%. Zhao Youquan et al. [25] designed a new type of scanning water COD detection instrument based on the UV spectroscopy. The equipment could measure from 5 to 10 datum per second and it was adaptive for long and real time on-line monitoring of water parameters. The deionized water was taken as the reference water sample, and then the UV spectrum of the standard solution of sodium hydrogen phthalate was obtained. The results showed that the equipment had obvious absorption of UV in the region of 200–320 nm, and the larger COD was, the lower the energy of the spectrum was, which verified the feasibility of UV detection of COD.

COD on-line monitoring system, which was developed by Zhao et al. [26], was based on UV-visible spectroscopy and consisted of pulsed xenon lamp, concave holographic grating and spectral scanning structure. The wavelength range was 200–720 nm, and the COD concentration range was 30–1,000 mg/L. The system could not only measure the real-time COD, but also measure other real-time water quality parameters such as chroma, turbidity and so on.

In addition to UV spectroscopy, Xie Zhigang et al. [27] found that near-infrared spectroscopy not only could monitor COD content, but also could obtain the ideal results in the rapid analysis of wastewater of total phosphorus and total nitrogen, and the monitoring and analysis of wastewater of BOD, COD and pH. The results had high correlation with the result achieved by national standard method. The feasibility of using near infrared spectroscopy to measure COD was studied by He Jincheng et al. [28]. In the range of 800–2,600 nm in the near-infrared spectral region, the partial least squares (PLS) regression prediction model between standard water samples and waste water samples was established. The correlation coefficient between the measured value of COD and the predicted value was 0.9999 and the cross-validation variance was 15.14 mg/L. The correlation coefficient between the real-measured COD and the predicted value of the water sample from sewage treatment plant wastewater was 0.9453 and the standard deviation was 35.4 mg/L. Meanwhile, they pointed out the temperature, pH value and turbidity might also affect the prediction of COD in the near infrared spectroscopy. The near-infrared spectroscopy and partial least squares (PLS) regression models was also used by John et al. [29], which successfully predicted the on-line COD of the industrial wastewater discharged from pulp and paper mills through a series of calibrations. The root error was 149 mg/L and was approximately 1/10 of the measured COD range. Zhong Yang et al. [30] studied the feasibility of using the information of ultraviolet spectrum and near infrared spectroscopy to predict the COD content in wastewater, and established the COD prediction model of waste water. The correlation between the predicted value and the measured value was 0.9671, and the standard error value was 24.8 mg/L, which indicted a good predictive effect.

Because of no need of chemical reagents, no secondary pollution and quick test, the physical method is suitable for on-line monitoring. However, problems still exist. For example, the actual composition of wastewater is complex and the ethanol, carbohydrates, organic acids and other organics are very common in the wastewater. They do not absorb UV, thus making UV spectrum unsuitable for monitoring the water rich in alcohols and carbohydrates, such as sewage from breweries, alcohol processing plants and sugar plants. Besides, the difference of pH, the variety of dissolved inorganic salts with different concentrations, the difference of size, shape and distribution of the suspended solids, the difference of the reflection and scatter of the light, all will hinder the spectrum from accurately representing the COD of water samples. In addition, the spectral analysis method requires a large number of manual comparison tests to correct the conversion coefficient, which makes the method only suitable to monitor the water that does change a lot over time. However, the pollutants in the sewage often change a lot under the condition of different production process, operating time and so on, which makes the spectral analysis method unable to effectively monitor the change of water quality. So, its application in on-line COD monitoring is obviously restricted.
Japanese HORIBA COD monitor based on UV method has the sensor with a rotary unit length adjustment system to virtually eliminate the effect of water pollution on the zero drift. The instrument can cover a wide range of measurement from low concentrations of 0~0.1 Abs to high concentrations of 0~5 Abs.

3.4. **Biological method**

Biological method measures COD by testing oxygen consumption during microbial decomposition after cultivating microorganism to decompose the organics in water. During the measurement process, firstly the biological matrix is acclimated and cultured by water samples to quickly degrade the organics in a special bioreactor. Secondly, the water sample in the bioreactor is subjected to aeration treatment until the dissolved oxygen reaches a saturated state, when the initial value of the dissolved oxygen concentration is measured. Then, the aeration is stopped, the water sample is injected into the bioreactor, and the organics in water sample are rapidly decomposed and dissolved oxygen is also consumed by the biological matrix. Last, the difference in dissolved oxygen in a bioreactor over a period is calculated and the oxygen absorption rate (OUR) of the biological matrix can also be calculated. Based on OUR, COD can be calculated. There are no chemical reagents and secondary pollution for the biological COD measurement method, and its operation and maintenance cost are low while the measurement cycle is short and precision is high. What is more, water samples need no filter in advance, so long as large particles impurities are not contained [4].

3.5. **Correlation coefficient method (TOC method)**

Total organic carbon (TOC) is the amount of carbon found in an organic compound and it is a comprehensive indicator of the total amount of organic matter in water. There is a certain correlation between COD and TOC content in water, which enables to measure COD through measuring TOC. Based on different working principles, the correlation coefficient method can be divided into combustion oxidation-non-dispersive infrared absorption method, gas chromatography, conductivity method, photo-catalytic oxidation-non-dispersive infrared absorption method, wet oxidation-non-dispersive infrared absorption method as so on, and the main method used is the first mentioned above [4].

The conversion equation between the TOC and COD was established by Zhang Dan [31], who conducted accurate measurement of COD and TOC in two wastewater samples, the chlorine organic chemical wastewater and the chlorine-containing organic and inorganic mixed chemical wastewater and on the basis had the data obtained fitted by a linear regression equation to determine the correlation between COD and TOC of high chlorine wastewater. The data showed that the linear regression equation could be established between the TOC and COD, and there was a significant correlation between TOC and COD. A linear regression equation between TOC and COD was established by Sun Liyan et al. [32] based on the correlation analysis of COD and TOC of organic pollutants done by 18 surface water quality automatic monitoring stations. For each of the 18 monitoring stations, regression studies were performed base on at least 20 sets of valid data to obtain the TOC-COD conversion curve. The slope range was 1.03~4.3, the intercept range was -7.38~23.78, and the correlation coefficient was 0.727~0.998, which showed that the correlation between TOC and COD was good.

The correlation coefficient method simplifies the analysis, shortens the analyzing time, reduces the workload and improves the work efficiency. However, because of their narrow application scope and long test time, these empirical formulas cannot fully meet the requirements of the water treatment process [10].

Germany LAR's Quick COD on-line monitoring device is based on TOC combustion oxidation - non-dispersive infrared method. The device combusts water samples in the combustion furnace under the temperature of 1,200℃, uses the infrared analyzer to measure the amount of CO₂ generated by combustion, calculates the TOC and then convert TOC to COD. The response time of the instrument is 1 minute and its measuring scope can reach 100~200,000 mg/L.
3.6. Soft measurement method

Soft measurement method uses sensors to collect basic parameters such as pH, dissolved oxygen, temperature, conductivity, turbidity, mixed liquid suspended solids, ammonia nitrogen, total carbon and others of water samples, and on the basis, establishes COD on-line nonlinear model through the algorithm. At present, the most widely used algorithms is Neural Network (NN) and Support Vector Machine (SVM). The neural network algorithm has the characteristics of self-learning, self-adaptation, high robustness and nonlinear mapping, which makes it adapt to multi-variables, non-linear and large delay, which are characteristic of wastewater. The BP-based COD prediction model, which was built by Lv Yanghua et al. [33], had the maximum relative error from -17% to 8% between predicted value and actual values. The structure of neural network algorithm is difficult to determine, and it is prone to local minimum, which leads to the relatively big algorithm errors. However, the improved algorithms based on neural network algorithm greatly improve the accuracy. Unscented Kalman Filtering Neural Network (UKFNN) algorithm proposed by Li Qingling et al. [34] took six parameters of COD, pH, dissolved oxygen, suspension, ammonia nitrogen and total carbon in industrial wastewater as the model algorithm input, and took the COD as the algorithm model output. With this model, relative error between the predicted value and the actual value was reduced to 4.7%. Wavelet packet decomposition and neural network prediction model in [35] and the fuzzy reasoning neural network model in [36] were both the improved model based on a neural network algorithm, which could reduce the relative error of the COD prediction model. The least squares SVM algorithm developed by Li Qingling et al. [37-39] was used to solve the problems of small sample, nonlinear, high dimensional local minimum. The relative errors of prediction on-line COD model were less than 10%. Zhang Jie et al. [40], pre-estimated the COD with SVM and then estimated COD with BP and Elman neural network model values based on COD variation, respectively. The COD estimated by these two neural network was then merged to produce the output of the soft measurement. Experiments showed that the merged soft measurement result was better than that of single neural network.

COD on-line prediction model can reduce the measuring complexity and time consumption and decrease the cost of COD on-line monitoring equipment. However, the accuracy of the method depends on the accuracy of the model, which, will be influenced by the working condition where dramatic changes of the water composition and content may appear. In addition, the prediction model requires multiple sensors to measure the basic parameters, so the final prediction accuracy is also greatly affected by the accuracy of the sensors.

By reviewing the COD on-line automatic monitoring methods, as shown in table 1, the comparisons among the above methods, in addition to soft measurement method, are made and listed. It can be concluded that different methods have different advantages and disadvantages. For example, chemical method is accurate, but its operation is cumbersome and it is easy to cause secondary pollution; The electrochemical method has little secondary pollution while its instrument cost is high and it is difficult to promote; Physical method does not consume chemical reagents and have short test time, but it is not universal and its accuracy will be influenced by water turbidity and pH value [1]. The biological method needs no chemical reagents, enjoys low cost and short measurement cycle, but it is particular with the water as no large particles of water impurities are tolerated; Correlation coefficient method simplifies the analysis and shortening the analyzing time, but its application scope is narrow and the test time is still relatively long; The soft measurement method still needs more tests before it is put into application. Therefore, the selection for COD on-line automatic monitoring equipment will depend on the actual water samples. The TOC combustion oxidation-non-dispersive infrared absorption method uses high-temperature combustion oxidation. Its oxidation rate of organics is almost 100%, the detection limit is relatively low, and the resolution and reproducibility of the measured values at low concentrations are relatively good. Therefore, the correlation coefficient method can be top choice for automatic monitoring equipment when the wastewaster concentration is relatively low. As the chloride ion at 254 nm cannot absorb the UV, it is advisable to use ultraviolet spectroscopy when the chloride ion concentration of sewage and seawater is greater than 5,000 mg/L. Meanwhile, CO₂ will not be produced during chloride ion combustion, so combustion oxidation-
disperse infrared absorption method is also adaptive to the above situation. For the automatic monitoring to low concentration sewage, the combustion oxidation-non-dispersive infrared absorption method can be preferentially selected. As the components of general industrial wastewater often change, and the water whose chloride ion concentration is less than 5,000 mg/L, it is preferred to use potassium dichromate digestion method because this method is closest to the national standard method and thus has a wide range of applicability.

Table 1. Comparisons among different measurement methods.

| Type of instruments | COD$_{Cr}$ | COD$_{Mn}$ | Electrochemical method | UV Metric | TOC |
|---------------------|------------|------------|------------------------|-----------|-----|
| Measurement accuracy| ±5%        | ±5%        | ±5%                    | ±3%       | ±3%|
| Reliability         | relatively low | relatively low | relatively high | very high | very high |
| Daily cost          | very high  | relatively high | very high | relatively high | very high |
| Purchase cost       | relatively low | relatively low | very high | appropriate | relatively high |
| Application scope   | very wide  | very wide  | relatively small | very wide |

4. Development trend of COD on-line automatic monitor

(1) Presently, under the constraint of the national standard method, potassium dichromate digestion method and permanganate index method are most commonly used in domestic COD automatic monitoring instruments. However, there exist the disadvantages of low monitoring frequency, secondary pollution and other shortcomings in both methods. With the further development in measurement accuracy, stability, application scope and time consumed of the physical method, electrochemical method, correlation coefficient method, biological method and other fast, environmentally friendly measurement technology, COD on-line automatic monitoring system based on above measuring technologies will be the trends in the future.

(2) The applications of integrated, intelligent, multi-sensor integration and intelligent algorithm further enhance the model accuracy and convergence speed of the COD monitoring equipment, which is used to build the COD prediction model. The use of intelligent algorithms equipped the instrument with self-learning, self-management and self-adaption functions, so that the instruments can do the active adjustment or give early warning according to the water environment and their own states.

(3) Mobile Internet, big data technology and APPs for data processing and analyzing allow non-professional analysts to quickly deal with the collected data and provide the data with lower cost, wider coverage and more information, which greatly improves the real-time capacity and efficiency of COD on-line monitoring system.

5. Conclusions

Measuring instruments of COD on-line automatic monitoring system need to be fast and simple process large amount of real-time accurate data. Due to the shortcomings of long test cycle and secondary pollution, widely used potassium dichromate digestion monitoring instruments in China will gradually be replaced by environmentally-friendly monitoring instruments based on UV spectroscopy, TOC, electrochemistry and so on.

At the same time, with the improvement of embedded system and intelligent algorithms, on-line monitors will become more compact, integrated and intelligent. And the remote HMI and data sharing will make the real-time data display and remote operation control of the monitoring instrument much simpler. Besides, Water quality warning and sewage optimization options will become possible with the support of big data and cloud technology. “Monitoring problems-finding problems-early warning issues-optimizing solutions” can be achieved for the COD on-line monitoring equipment.
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