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Study and design on chemical oxygen demand measurement based on ultraviolet absorption

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ABSTRACT

Chemical Oxygen Demand (COD) is an important parameter for the detection of organic pollutants in water. UV absorption detection method of COD is a simple physical method that can detect water samples online without secondary contamination from chemical reagent. In this paper, the detection of COD based on UV absorption method was studied. The UV absorption method was used to detect COD in water samples, and the COD online detection device was designed. Optical path and circuit design principle of the device were introduced to overcome the difficulties including weak signal and the output signal instability, and the size of the system was effectively reduced. Contrast experiments showed that the system performance and measurement results are reliable and can be used for accurate COD detection within its range (up to 1000 mg/L).

1. Introduction

With the rapid development of modern industry, the environmental problems have raised people's awareness significantly. With problems like depleting natural water resources and increasing population, demand on domestic and industrial water consumption increased, making it increasingly challenging for the water supply industry to maintain the safety of water. Untreated complex wastewater either gets mixed with surface water or used for agriculture purposes, posing serious risks to the ecosystem in general and to the human health in particular. Serious water shortage problem force us to use alternative water sources [1–3]. However, the phenomenon of waste water discharged secretly by the small-sized chemical plants, printing houses, paper mills and so on is getting more serious which lead to the pollution of river water and the death of a large number of aquatic organisms. The water ecological environment has been severely damaged. The regulation specification is formulated by the environmental protection department, in order to establish the parameters of river water online monitoring and focus on the secondary pollution of the water treatment. "Integrated Wastewater Discharge Standard" (GB 8978-1996) stated clearly that the maximum permissible discharge of pollutants must not be exceeded. But driven by interests, some small and medium sized enterprises are still secretly discharging industrial pollutants into rivers at night regardless of the decree. The mixed industrial pollutants discharged from different enterprises increase the types and level of pollutants in the water, which makes the composition of the water more complex. As a result, online monitoring in the wastewater outfall is needed in order to effectively control the pollutants secretly discharged from small enterprises in the same basin and to detect whether the wastewater meet the Integrated Wastewater Discharge Standard. Therefore, it is necessary to develop more rapid and reliable monitoring techniques to replace the traditional water quality parameter measurements [4]. The chemical fingerprint, which is an important evidence to identify the responsibility of the environmental pollution incident, is usually carried by the pollution source. The goal of governance of pollutants discharge can be achieved by combining the intelligent monitoring technology with traceability technology through a quantitative comparative analysis and identification of pollutant source by setting up the chemical fingerprint information database of discharge from related enterprises in the same basin.

COD [5] is one of the most important parameters in contaminated water quality evaluation. It refers to the amount of oxidant consumed when treating the water samples by strong oxidizing agent, then converted into the amount of oxygen under certain conditions, and its measurement unit is mg/L. It is usually used to measure the volume of organics in water, reflecting how seriously the water is polluted by reducing substances.

At present, the detection methods for COD include chemical methods and physical methods. COD chemical detection method mainly includes potassium dichromate method (GB 11914 – 89) and permanganate index method (GB 11892 – 89). The measure-

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ment results of COD chemical detection are relatively accurate, but its reaction time is too long and the operation process is more complicated [6]. On the same time, the potassium dichromate method is unsuitable to determine samples with COD concentrations lower than 50 mg/L [7]. Besides, mixing with other chemicals will cause the secondary pollution of water. Physical detection method mainly refers to the spectrophotometric method based on the Lambert-Beer's law. By measuring the sewage's absorbance of specific wavelength, COD concentration of water sample is calculated. UV absorbance method has been widely used in Europe, America and Japan in recent years. Its measurement time is short, and chemical treatment is unnecessary, which effectively avoids the secondary pollution.

The detection of COD based on UV absorption method was first brought up by Japanese scholars [8]. Manook Boghos A et al. [9] obtained patent for organism concentration detection method based on UV absorption in America. Baisheng Chen et al. [10] improved COD forecasting accuracy by using data fusion method in analyzing variable optical path. Jon Agustsson et al. [11] proposed a diffuse-reflection, non-contact, ultraviolet-visible absorption spectra method in pollutants detection. By using ultraviolet and visible light simultaneously in COD detection and PLS (partial-least-squares) in regression analysis, excellent result was obtained.

In recent years, many Chinese scholars also made corresponding research. Xiaobo Dai [12] verified the liability of physical method for detecting the water quality parameters by doing comparison experiment. At the same time, some scholars established COD prediction model using artificial intelligence method and statistical method. And Yunping Mi [13] established mathematical model to predict actual COD concentration using LM-BP neural network. Guoqiang Zhang [14] used multiple linear regression method to establish model to predict COD concentration and later revised the model. But this method of establishing predicting model can only improve the accuracy of prediction while the actual detection accuracy depends on the sensors. In this paper, based on UV absorption method and online detection technology, we made adjustment and innovation in designing the sensors like redesigning the optical path and the electric circuit, which fundamentally improved the accuracy of initial data before being collected by the embedded system.

Based on the online optical detection technology, this paper proposed an online UV absorption detecting method for COD, which reconstructed the optical detection system, using Czerny Turner orthogonal dual grating structure. A narrowband filter was added to filter stray light in order to obtain more accurate wavelength for Czerny Turner orthogonal dual grating structure and reduce the incident stray light that may pass through the flow-through cell at the front part of the structure. Organics, the dominant role of water pollution, have strong absorption at UV 254 nm as indicated by a lot of literature [15]. The COD value of the sample is measured by detecting the absorbance value at 254 nm which is in linear relationship with COD concentration. This paper designed a more stable and reliable COD detection device and provided a strong guarantee for the monitoring of pollutants and traceability technology. This monitoring method has the advantages of low cost, pollution free and high precision, thus accomplished online monitoring and remote transmission of information on COD pollution in river.

2. Detection principle

2.1. Lambert-Beer's law

Measuring the concentration of COD by UV absorption method in water sample is consistent with Lambert-Beer's law [15]. When a beam of UV light pass through the solution, a part of the light is absorbed by the light-absorbing substances in the solution. The energy of the light radiation is reduced. With higher the concentration of the solution, thicker the liquid-permeable layer and higher the concentration of light absorbing substances, comes with more absorbed light and less UV light through the solution.

Each light-absorbing substance has a certain cross-sectional area A_m within which photons are absorbed, the total effective cross-sectional area of the light-absorbing substance in the dilute solution is nA_m. If the number of light-absorbing substance is n, and the number of light-absorbing substance increases by dn, the effective area will increase by $A_m$dn. If the total area of the beam through the solution is A_t, then the rate of change of light intensity I is proportional to the rate of change of the light absorption area.

$$-\frac{dI}{I} = K'\frac{A_m dn}{A_t} \tag{1}$$

where K' is a proportional constant. Considering the volume of the beam passed through by the measured solution is V, L is solution thickness (optical path), we can obtain as:

$$V = AtL \tag{2}$$

By substituting Eq. (1) with Eq. (2) and integrating can get as:

$$-\ln\frac{I_T}{I_0} = K'A_m n\frac{L}{V} \tag{3}$$

Where I_T represents the transmitted light intensity, I_0 is the incident light intensity. Let $\frac{n}{V} = K''C$which represents the number of absorbing particles per unit volume. It is proportional to the concentration of the light-absorbing substance solution C. And K" represents another proportional coefficient.

$$-\ln\frac{I_T}{I_0} = \alpha LC \tag{4}$$

Eq. (4) can be shown as

$$-\lg\frac{I_T}{I_0} = KLC \tag{5}$$

Where α = K'K" = 2.303 K, K is absorption coefficient. Eq. (5) is the law of absorption of monochromatic light. Studies have indicated that different light-absorption substances have different absorption coefficients. K varies when the incident light wavelength changes. Each material has a maximum absorption wavelength. The absorption coefficient is related to the optical path and concentration of solution. Literature [16] had shown as:

$$I_T(\lambda) = I_0(\lambda)\exp\left\{-L\left|\sum_{i}^{M} k_i(\lambda)\, c_i(\lambda) + \varepsilon(\lambda)\right|\right\} + N(\lambda) \tag{6}$$

Where λ is the wavelength of the incident UV light, $I_T(\lambda)$ represents the transmitted light intensity, $I_0(\lambda)$ is the incident light intensity when the concentration is zero, L is the optical path, $K_i(\lambda)$ is the absorption coefficient, $c_i(\lambda)$ is the concentration of the tested sample, $\varepsilon(\lambda)$ is the scattering coefficient of the total suspended solids in the tested sample, and $N(\lambda)$ is the overall noise. The absorbance is defined as:

$$A(\lambda) = -\lg T = -\lg\frac{I_T}{I_0} = LK(\lambda)\,C(\lambda) \tag{7}$$

In Eq. (7), T is transmission degree. For a specific flow-through cell, its absorption optical path L stay unchanged. For the particular measured wavelength as well as the specific water sample, the absorption constants K(λ) are also constant. Therefore, the absorbance is proportional to the sample concentration. The concentration of COD in water sample can be measured by detecting the UV absorbance of organic compounds.