Study of Water Quality of Artificial Water Body in Nankai University Based on COD Determination

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Abstract. Campus artificial water body is a significant component of micro-water ecosystem in cities, integrating landscape, ecological, educational and cultural functions. This study takes the artificial lakes in Balitai Campus of Nankai University as the research objects, carries out a systematic evaluation of current water quality through water quality sampling, COD determination and data analysis. This paper presents main pollution resource and ecological issues, proposes water improvement and long-term maintenance measures. The research used acidic potassium permanganate method to determine COD of lake water, and the results show that the mean value of COD of Xinkai Lake is 22.36mg/L, classified as Grade IV surface water which requires governance. The mean COD of Horseshoe Lake is 3.82mg/L, showing a decent water quality. Pollution of closed lakes is mainly due to sediment endogenous release and limited water exchange. This paper puts forward measures including building connecting channels and establishing regular monitoring mechanisms, providing a scientific basis for Nankai campus water management and an example for global campus water environment management.

Keywords: Campus artificial lake, Water quality assessment, Chemical oxygen demand, Ecological restoration.

1. Introduction

Ecological civilization construction is a major national development strategy of China. Universities, as hubs of talent cultivation, scientific researches and cultural inheritance, serve as important platforms for ecological civilization education and practice [1,2]. Campus artificial lakes, as typical closed or semi-closed small landscape water bodies, possessed features of low water environmental capacity and weak self-purification ability, making them prone to eutrophication, which leads to algal bloom and odorous water. Previous studies indicate that eutrophication exists in approximately 80% closed water bodies in China [3].

As a centennial school, Nankai University has long integrated its campus water systems into its campus culture. Balitai Campus constructs two artificial lakes named Xinkai Lake and Horseshoe Lake. Jinnan Campus has the other Horseshoe Lake next to the Datong Activity Center and Nankai Lake south of the library. Campus lakes serve multiple functions, including rainwater storage, landscape, and ecological education. However, during summertime, the abundance of carbon metabolism-related functional genes is significantly higher than in winter [4]. The decomposition of biological excreta and residue releases nitrogen, phosphorus, and substantial organic matter into the water. Consequently, the accumulation of dissolved organic matter leads to increased turbidity and unpleasant odours. To prevent the health risks, it is essential to conduct researches to determine whether water quality in summertime artificial lakes meets safety standards of surface water, and put forward systematic measures.

Carrying out research on the water quality determination and ecological restoration of small-scale water bodies helps improve the theoretical system of campus water environment, and further providing methodological references for similar micro-water ecosystem studies. Conducting pollution analysis enables to determine summer water quality conditions, and guarantee the physical health and safety of teachers and students' daily activities around the lakes. Furthermore, the combination of analytical chemistry methods and ecological civilization education can deepen

students' understandings of chemistry experiments and ecological knowledge, contributing to the cultivation of a green campus culture.

2. Methods

This study takes two lakes in Nankai University's Balitai Campus, named Xinkai Lake and Horseshoe Lake, as the research objects. The procedure involves four steps. A basic information survey of both lakes was first conducted, then sampling points were systematically established to collect surface water samples. Subsequently, chemical oxygen demand (COD) was determined using potassium permanganate as the oxidant, which is less hazardous than potassium dichromate. Finally, the water quality grade was assessed according to the Environmental Quality Standards for Surface Water (GB 3838-2002).

2.1. Objects

Balitai Campus is located in Nankai District, Tianjin, China. The lakes are closed artificial landscape water bodies without natural river inflow, relying mainly on rainfall and artificial replenishment to maintain the level. The lakes are surrounded by roads, benches, teaching buildings, serving as a recreational place. As the earliest campus lake in Nankai University, Horseshoe Lake was excavated in 1923, named from its horseshoe shape. It is located on the northern side of Eastern Dazhong Drive. Large areas of the lake are planted with lotus, making it a popular lotus viewing site in Tianjin. According to the first water census of Nankai District, the water area of Horseshoe Lake is 0.82 hectares. Xinkai Lake is on the west side of Horseshoe Lake and on the east side of the Teaching Building II. It was excavated based on the original reed pond in 1954, named from the school motto, with a water area of around 1.42 hectares. The lake features an open surface without any emergent plants.

2.2. Methods

To prevent the temporary effects from rainfall, the sampling time was 10:00-11:00AM in a sunny summer morning. The experiment follows the principles of homogeneity, representativeness, and scientific principles. Four sampling points were established at Xinkai Lake: near Teaching Building II (west side of Xinkai Lake), near Dazhong Drive (south side of Xinkai Lake), near Haibing Building (east side of Xinkai Lake), and near the old library (north side of Xinkai Lake). 125 mL of water was collected from each point, mixed thoroughly to obtain a 500 mL water sample. Four sampling points were established at Horseshoe Lake: near Haibing Building (northwest side of Horseshoe Lake), northeast side of the eastern shore of Horseshoe Lake, near Dazhong Drive (south side of Horseshoe Lake), and near the central island; 125 mL of water was collected from each point, mixed thoroughly to obtain a 500 mL water sample. Both water samples were stored in sealed containers at room temperature away from light. The COD determination was completed within 6 hours after water collection.

Balitai Campus is away from chemical plants, therefore the likelihood of water bodies being affected by heavy metal pollutants is relatively low. However, these lakes host abundant animals and plants, including fish and phytoplankton. Therefore, measuring nitrogen and phosphorus waste as well as organic matter generated by biological activity can effectively reflect the degree of water pollution at the Balitai Campus lakes. Most of these pollutants exhibit reducing properties and can be oxidized by strong oxidizing agents such as potassium permanganate or potassium dichromate. Studies have shown that dissolved organic matter (DOM) in artificial lakes is a major contributor to Chemical Oxygen Demand (COD), with its composition and humification degree closely correlating with the eutrophication status of the water body [5]. Consequently, this study employs COD determination as the analytical method, choosing potassium permanganate as oxidant [6-8]. Since the artificial lake within Nankai University is a freshwater lake with low chloride ion concentration, this experiment employs an acid digestion method for analysis. When processing the experimental data,

standard curves were plotted using the COD values of the water samples, and the concentrations were calculated accordingly.

3. COD determination Experiment

3.1. Principle

Chemical oxygen demand (COD) is an essential indicator to assess the degree of organic water pollution. It represents the amount of oxidant used to consume reducing substances, and is expressed by mg/L of oxygen. The component of reducing matters in water body is dominated by organic matters. In addition, nitrites, sulfides, and ferrous salts account for a relatively small proportion [8]. Therefore, higher value of COD indicates higher pollution level. The organic concentration of clean surface water in nature is relatively low, whose COD is usually below 4 mg/L, in offshore clean water, the COD concentration typically falls below 0.5 mg/L. When a water source is mildly polluted, the COD level may rise to the range of 4–10 mg/L; if the result is larger than 10 mg/L, it can be concluded that the degree of water pollution is relatively severe [8]. According to China's drinking water quality classification standards, the COD limits for Class I and II water bodies are set at ≤15 mg/L; for Class III water bodies, the limit does not exceed 20 mg/L; for Class IV water bodies, the upper limit is 30 mg/L; and for Class V water quality, the COD must not exceed 40 mg/L [7].

Currently, the mainstream methods for lab determination of COD include the potassium permanganate oxidation method and the potassium dichromate oxidation method. In this experiment, the potassium permanganate method is employed. In a strongly acidic medium, most organic compounds in aqueous solutions can be oxidized. Potassium permanganate within manganese in the +7 oxidation state, is reduced to manganese ions in the +2 oxidation state. However, the reaction process is quite complex, and part of this process can be represented by the following equation 1.

$$4MnO_4^- + 5C + 12H^+ = 4Mn^{2+} + 5CO_2 \uparrow + 6H_2O \quad (1)$$

The remaining potassium permanganate is reduced by a measured excess of sodium oxalate, followed by back-titration with a potassium permanganate solution until a faint red color appears in the solution, marking the endpoint. The following reaction follows equation 2.

$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ = 2Mn^{2+} + 8H_2O + 10CO_2 \uparrow \quad (2)$$

In this experiment, the color change of potassium permanganate serves as the self-indicator, external indicators to the system are eliminated. Furthermore, the reaction rate is relatively rapidly without the need for a catalyst. Additionally, potassium permanganate causes less environmental pollution compared to potassium dichromate, making it suitable for the analysis of water samples with low pollutant concentrations, such as surface water, domestic water, and lightly polluted domestic wastewater.

The calculation formula is as follows:

$$COD(mg/L) = \frac{[5c_{KMnO_4}(V_1+V_2) - 2c_{Na_2C_2O_4}V_{Na_2C_2O_4}]\times 8\times 1000}{V_{Water\ sample}} \quad (3)$$

Here, V_1, V_2 represent the added volume and the volume consumed during back-titration, respectively (in mL).

Additionally, due to limitations in its oxidizing capacity, potassium permanganate cannot effectively oxidize organic components in industrial wastewater or municipal sewage, and the measured COD value will be significantly lower than the true value. In contrast, the potassium dichromate detection system, when combined with silver sulfate as a catalytic aid, can oxidize the vast majority of organic pollutants. Therefore, it is more suitable for determining samples of industrial and mining wastewater with high organic enrichment levels and severe pollution [8].

3.2. Instruments and Reagents

Instruments: PTFE burette (50 mL); beakers (100 mL, 400 mL); volumetric flask (100 mL); pipette (25 mL); graduated cylinder (10 mL, 100 mL); weighing bottle; analytical balance (0.1 mg); analytical balance (0.1 g).

Reagents: potassium permanganate; sodium oxalate (primary standard); sulfuric acid (3 mol/L); distilled water.

Weigh approximately 1.6 g of solid, dissolve in 500 mL of water, heat to boiling, and maintain the solution at a gentle boil for approximately 1 hour. Cool to room temperature, then filter through a microporous glass sand-core funnel. Pour the filtrate into a brown reagent bottle, and mix well.

Weigh accurately approximately 0.20 g of three portions of pre-dried $Na_2C_2O_4$ and place them in a 400 mL beaker. Add 80-90 mL of water and 20 mL of a H_2SO_4 solution to dissolve the sample. Heat slowly until vapor begins to emerge when the temperature is around 75–85 °C. While the solution is still hot, perform titration using the solution to be calibrated. Begin the titration with a slow rate. After adding the first drop of solution, keep shaking. Once the purple-red color has faded, add the second drop. Throughout the titration process, the temperature must not fall below 75 °C. Therefore, titration may be conducted while heating. Once vapor begins to form in the solution, the reaction rate increases, allowing the titration speed to be appropriately increased. However, the solution should not drip in a linear fashion. As the titration approaches the endpoint, the fading of the purple-red color occurs very slowly, thus slow down titration speed while stirring thoroughly to prevent overshooting the endpoint. The endpoint is reached when after adding one more drop of solution, no fading of the faint red color occurs within 30 seconds. Finally, calculate the concentration of the solution and its relative average deviation[8].

3.3. Experimental Procedure

3.3.1. Preparation and standardization of a 0.02 mol/L Potassium permanganate solution

Weigh approximately 1.6 g of potassium permanganatesolid, dissolve in 500 mL of water, heat to boiling, and maintain the solution at a gentle boil for approximately 1 hour. Cool to room temperature, then filter through a microporous glass sand-core funnel. Pour the filtrate into a brown reagent bottle, and mix well.

Weigh accurately approximately 0.20 g of three portions of pre-dried sodium oxalate and place them in a 400 mL beaker. Add 80–90 mL of water and 20 mL of sulfuric acid solution to dissolve the sample. Heat slowly until vapor begins to emerge when the temperature is around 75–85 °C. While the solution is still hot, perform titration using the solution to be calibrated. Begin the titration with a slow rate. After adding the first drop of solution, keep shaking. Once the purple-red color has faded, add the second drop. Throughout the titration process, the temperature must not fall below 75 °C. Therefore, titration may be conducted while heating. Once vapor begins to form in the solution, the reaction rate increases, allowing the titration speed to be appropriately increased. However, the solution should not drip in a linear fashion. As the titration approaches the endpoint, the fading of the purple-red color occurs very slowly, thus slow down titration speed while stirring thoroughly to prevent overshooting the endpoint. The endpoint is reached when after adding one more drop of solution, no fading of the faint red color occurs within 30 seconds. Finally, calculate the concentration of the solution and its relative average deviation [8].

3.3.2. Preparation of a 0.075 mol/L sodium oxalate standard solution

Accurately weigh 1.0–1.1 g of sodium oxalate into a 100 mL beaker, and dissolve in an appropriate amount of water. Add 2 mL of a 3 mol/L sulfuric acid solution, then transfer quantitatively to a 100 mL volumetric flask. Dilute to the mark with water and mix well [8].

3.3.3. Determination of COD in acidic solutions

Take two equal portions (50.00 mL each) of water samples from Xinkai Lake and Horseshoe Lake, place them in four 400 mL beakers, label them accordingly, and dilute with water to a final volume

of 100 mL. Add 25.00 mL of standard potassium permanganate solution, 30 mL of 3mol/L H_2SO_4 solution, and heat until boiling for 10 minutes (if the red color disappears during this process, add an appropriate amount of the standard solution); immediately add 25.00 mL of sodium oxalate standard solution. While the mixture is still hot, titrate with the solution until a faint red color appears and the color does not fade within 30 seconds; this point marks the endpoint. Calculate the COD and the relative average deviation [8].

3.4. Calculation and result

The concentration of the potassium permanganate solution was determined to be 0.02187 mol/L; the concentration of the prepared sodium oxalate standard solution was 0.07551 mol/L; for the back-titration of two new Xinkai water samples, the volumes of the potassium permanganate standard solution used were 10.69 mL and 10.92 mL, respectively; for the back-titration of the Horseshoe Lake water sample, the volumes of the potassium permanganate standard solution used were 9.78 mL and 9.71 mL, respectively.

Substituting into the equation yields:

$$COD_{Xinkai1}(mg/L) = 20.35mg/L \tag{4}$$

$$COD_{Xinkai2}(mg/L) = 24.38mg/L \tag{5}$$

$$COD_{Xinkai}(mg/L) = 22.36mg/L \tag{6}$$

$$COD_{Horseshoe1}(mg/L) = 4.43mg/L \tag{7}$$

$$COD_{Horseshoe2}(mg/L) = 3.21mg/L \tag{8}$$

$$COD_{Horseshoe}(mg/L) = 3.82mg/L \tag{9}$$

The measured chemical oxygen demand (COD) for Xinkai Lake was 22.36 mg/L, and for Horseshoe Lake it was 3.82 mg/L.

4. Discussion on pollution causes and improvement measures

The average COD concentration in Horseshoe Lake is 3.82 mg/L. According to the "National Standard for Surface Water Environment Quality" (GB 3838-2002), this value is significantly lower than the limit of 15 mg/L for Class I/II water quality, indicating that the water quality is clean and meets the requirements for source water and centralized drinking water sources. In contrast, the average COD concentration in Xinkai Lake is 22.36 mg/L, exceeding the limit of 20 mg/L for Class III water quality and complying with the Class IV water quality standard—meaning it can only meet the requirements for general industrial use or non-direct-contact recreational purposes [7]. Thus, it no longer meets the water quality required for campus landscape water bodies and shows a risk of eutrophication and algal blooms at summertime.

Both lakes are in Balitai Campus, which gives them similar climate and water replenishment conditions. Thus, the different water qualities mainly due to pollution loads.

At Horseshoe Lake, large areas of lotus flowers and other emergent plants have been planted. On one hand, the root systems of these plants can directly absorb small molecule organic compounds, nitrogen and phosphorus based nutrients from the water body, thus reducing pollutant concentrations. On the other hand, the indigenous degrading microorganisms enriched on the root surfaces can accelerate the decomposition of organic pollutants [9,10]. Additionally, the root systems can fix surface sediments and inhibit the endogenous release of organic matter from the sediments, resulting in relatively clean water quality. In contrast, Xinkai Lake features open water surfaces with a vegetation coverage rate below 5%. The absence of a biofilm system further weakens the water body's capacity for nitrogen metabolism and organic matter degradation and the lack of effective purification means the water body's self-purification capability is weaker than that of Horseshoe Lake [4]. Furthermore, the water body is enclosed which due to its poor fluidity and weak re-oxygenation

capacity. Suspended sediments and endogenous releases significantly affect the composition and humification degree of the dissolved organic matter (DOM) in the water [5]. As a result, it suffers from low transparency, abnormal water color and occasional unpleasant odors.

To address the water quality improvement issues at Xinkai Lake, a small connecting canal can be constructed between the two lakes, paired with low power circulation pumps to achieve water circulation between the two lakes, thereby breaking the closed state of Xinkai Lake. Simultaneously, environmental protection dredging shall be carried out at Xinkai Lake to remove highly polluted sediments from the surface layer to reduce the endogenous pollution load. Subsequently, replant emergent plants such as water bamboo and cattail along the lake shore, while submerged plants such as duckweed and black algae are introduced in the central lake area to form a composite purification system [9,10]. Additionally, indigenous degrading bacteria agents, can be introduced to establish a complete micro-food web and maintain the aquatic ecological balance. Furthermore, Cheng et al., in their study of enclosed water bodies within Suzhou gardens, found that the wax medium surface can effectively colonize indigenous microorganisms, among which enriched microbial communities belonging to the Proteobacteria, Chloroflexi, and Bacteroidetes phyla play a critical role in organic matter degradation and nitrogen metabolism [4]. Introducing biofilm carriers such as wax medium into enclosed water bodies can effectively enrich indigenous functional microorganisms, enhance nitrogen metabolism and organic matter degradation functions, and significantly reduce nutrient concentrations and improve transparency during summer [4]. For severely eutrophic enclosed water bodies, photocatalytic technology also represents a viable supplementary approach, demonstrating effective removal capabilities for inorganic nitrogen, organic pollutants, and algae [3].

5. Conclusion

The study takes artificial lakes in Nankai University, Balitai Campus as objects. Through field study, sampling and COD determination, the current water quality was investigated and the governmental measure is purposed.

The main conclusion is that water quality shows significant difference in two lakes in Balitai Campus. the water quality of Horseshoe Lake is Class I/II clean levels in terms of COD due to its stable ecosystem. The water quality of the Xinkai Lake is classified as Class IV which indicates a risk of eutrophication and requires remediation efforts. The primary causes of the differences in water quality are vegetation and sediment pollution. Among all, the bioremediation capacity of emergent plants plays a key role in maintaining the water quality in artificial lakes.

This study conducted a water quality assessment using only Chemical Oxygen Demand (COD) to indicate water pollution degree. Future tests could further include total nitrogen, total phosphorus, and ammonia nitrogen to comprehensively evaluate the eutrophication risk. In the future, online water quality monitoring device to enable real-time data collection and early warnings can be introduced. By noticing the warnings of water quality changes, this approach can shift from passive remediation to proactive prevention, thereby providing data support for the management of campus water quality. Moreover, small scale trials could be conducted using the proposed methods to verify their actual effectiveness.

The improving plan should first include a sediment removal at Xinkai Lake. Then construct canals linking the two lakes and campus rivers, while installing water pumps to enhance water circulation and suppress algal growth. Furthermore, emergent plants could be planted along the shores of Xinkai Lake, and submerged plants could be planted in the lake's center. And new species could be cautiously introduced to build a complete and stable food web. In the future, this research model could be extended to Jinnan Campus to establish a water protection system that covers both campuses, even serving as a reference for water quality improvement projects in global universities.

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