The Application of Biofortification in Natural Rubber Processing Wastewater Treatment

Wang Jing¹²; Li Jing-yu¹; Qin Juan-juan¹; Lu Yuan³; Zhang Rui¹¹²; Zhang Can⁴

¹Yunnan Agricultural University, Kunming, 650201, China
²Yunnan Key Laboratory of Water Security, Conservation and Sewage Reduction in Urban and Rural Area, Kunming, 650201, China
³Yunnan Tengxu Municipal Engineering Design Company, Kunming, 650228, China
⁴Ecological Environment Monitoring Center of Chongqing, Chongqing, 401147, China

Corresponding author: Zhang Rui¹², email: zhangrui_linkin@yahoo.com
Zhang Can⁴, 270614972@qq.com

Abstract. According to the water quality of natural rubber processing wastewater and related sewage discharge standards, a combination process of anaerobic and two-stage biological contact oxidation (A/O₁/O₂ biofilm) was used to treat natural rubber processing wastewater. Biofortification was considered as the core technology in this case that Bacterial agents were directly added and biological fillers were adopted to fix the microorganisms, and therefore strengthen the operation of the biological treatment system. After the commissioning of this process, it was officially put into operation, and related sewage discharge indicators (including pH, SS, NH₃-N, COD and BOD₅ ) had shown to meet all the first-level standard of "Integrated wastewater Discharge Standard"(GB8978-2002).

1. Introduction
Water shortage has become a serious problem in China. How to increase the water efficiency through wastewater treatment, achieve a healthy social water cycle, and make sustainable use of water have become a common concern in the field of water treatment technology research and application[1-3]. The natural rubber processing industry is a heavy polluting and energy intensive industry. It is also one of the important sources of industrial pollution emissions in Yunnan Province. At present, the wastewater treatment of state-owned enterprises and private enterprises in China is unbalanced. Some private enterprises have incompletely constructed sewage treatment facilities or have failed to meet the standard after they are completed. Even some state-owned enterprises have exceeded the standard due to the mismatch of pollution treatment equipment and production scale. Because of conventional sewage treatment process is generally ineffective, based on the results of previous laboratory research on biofortification technology, this process was applied to actual production. Hopefully, this new idea will
be proposed for the upgrading of natural rubber processing wastewater systems and the reuse of water resources.

By adding high-efficiency bacteria agents, the requirements for improving water quality could be realized, which was especially suitable for reconstruction projects. The wastewater treatment capacity can be improved without further expansion of construction land and the addition of water treatment facilities. Up to now, researches on biofortification technology were mostly at experimental stage[4-5], barely applied to production, and nearly all concentrated on the treatment of coking wastewater and domestic sewage. There were few studies on the application of biofortification technology in the engineering application of natural rubber processing wastewater treatment have been reported. In this study, the research results of the design and engineering operation of biofortification technology on the treatment of natural rubber processing wastewater have shown great social value.

2. Program Overview and Wastewater Quality

2.1 Program Overview
The natural rubber processing plant was located in Jinghong City, Yunnan Province. The plant mainly produced SCRS standard rubber and SCR10 and 20 standard rubber. The daily wastewater discharge was about 646m3, and the annual water consumption was about 126,000 m3. The production water used the top reservoir water and consumed a lot of water. In order to ensure that natural rubber processing wastewater met the discharge standards and realized the recycling of water resources, a new sewage treatment station needed to be established in this study, and the treated effluent must meet the water reuse standards, and all of them should be reused in solid rubber washing and vehicles washing.

2.2 Wastewater Quality
The design flow rate of sewage was 1000m3/d. Through the analysis and detection of the existing water quality of the sewage treatment station, the raw water quality indicators obtained from on-site monitoring shown in Table 1. The design standards of the effluent water quality refer to Class I Standard of "Integrated wastewater Discharge Standard"(GB8978-2002) shown in Table 2.

| Wastewater type                  | COD  | BOD₅ | NH₃-N | SS  |
|----------------------------------|------|------|-------|-----|
| Latex standard rubber wastewater | 6884 | 3561 | 128   | 450 |
| Gel standard glue wastewater     | 1760 | 1025 | 70    | 500 |
| Mixed wastewater                 | 3012 | 1315 | 83    | 453 |

Note: The unit of other indicators is mg/L except pH.

| PH     | COD  | BOD₅ | NH₃-N | SS  |
|--------|------|------|-------|-----|
| 6-9    | 100  | 20   | 15    | 70  |

3. Wastewater treatment process
According to the characteristics of natural rubber wastewater quality and water requirements, an anaerobic, two-stage bio-contact oxidation cell (A/O₁/O₂ bio-film) combination process with bio-enhanced technology as the core technology was adopted. The treatment process was shown in Figure 1. It aimed to build an efficient, stable, and diverse microbial system in the biological reaction system, and to create a long biological chain with a strong impact-resistant microbial ecological balance.
According to the actual situation of the natural rubber sewage treatment station, the method of direct dosing of microbial agents and the biological filler immobilization of microbial bacteria were adopted to strengthen the operation and maintenance of the biological and chemical treatment system. By supplementing microbial agents and aeration to regenerate biofilms at regular intervals, their biological activity was enhanced. By rationally arranging the internal compartment of the biological pool, the metabolic potential and degradation of aerobic and facultative microorganisms were better. By determining the appropriate processing period, the physiological requirements of the various microorganisms that have just been put into the system could be adapted [6-7].

![Diagram of wastewater treatment project in Jinghong](image)

Fig.1 The process of wastewater treatment project in Jinghong

4. Program operations
The active substances on the biofilm were mainly composed of microbial groups such as bacteria, fungi, bacteria micelles, protozoa and metazoan. The treatment efficiency of the natural rubber wastewater biological treatment system mainly depended on the composition, quantity, and external environment of the microbial cells. Whether this system could be started mostly depended on the biomass of bacteria and sludge acclimation.

4.1 Preparation of MDEM culture
In this program, the culture medium with MDEM was used as the bacteria source. Before added to the system, it has to be expanded and prepared. Firstly, the original culture solution was inoculated into a triangular flask containing liquid medium, shaken in a laboratory shake flask for 24 h, then transferred into a culture tank, and aerated for 24 h to 48 h. Secondly, the original culture solution was transferred into a fermentor containing the fermentation medium. Finally, the expanded bacterial solution was ready to use. The bacterial source of the original culture in this case was obtained from activated sludge and artificial bacterial liquid (concentration around 107-109/mL).

4.2 Culture of Activated Sludge
The purpose of activated sludge culture was to allow microorganisms to proliferate to a certain concentration of sludge. By eliminating and inducing the mixed microbial population, the domestication process was realized, and the microorganisms having the activity of degrading the rubber wastewater became the dominant bacteria group. This project adopts the inoculation culture method. The inoculated sludge was obtained from the anaerobic tank and secondary sedimentation tank of a natural rubber processing plant. It was used for the addition and domestication both in the anaerobic tank and aerobic tank in this project. Biofortification could effectively increase the formation of bacterial biomass and enhance the ability to degrade pollutants. This system adopted intermittent-continuous culture method, in which engineering bacteria and inoculation sludge were added at the same time. When starting sludge culture, it was necessary to increase the amount of bacteria for the first time in order to ensure the quantity advantage of foreign bacteria and gradually increase the Influent flow rate and organic load of influent water.
4.3 Installation of modular packing
After field monitoring, the organic matter content of natural rubber wastewater was very high, and it was difficult to achieve the water reuse standard through traditional biological treatment alone. In order to meet water reuse requirements, suspended fillers were placed in anaerobic tanks and aerobic tanks. On the one hand, it could increase the area of microbial attachment and increase the concentration of microorganisms. On the other hand, it could enhance the mass transfer effect of the system and enhanced the removal of carbon by microorganisms. An important characteristic of natural rubber processing wastewater was that the ammonia nitrogen concentration was very high, and the removal of ammonia nitrogen by the system mainly relied on the nitrification of nitrosating bacteria and nitrifying bacteria. Because of the interception and adsorption of the fillers on these two kinds of autotrophic bacteria, they could form biofilms on the surface of the fillers, and the residence time of nitrifying bacteria in the reactor was much longer than their generation time. So that they grew in large numbers in the system, and the total amount of microorganisms increased substantially. In addition, due to the installation of the filler, the flow state of the wastewater in each reaction tank was changed, the turbulence of the wastewater in the system was enhanced, the mass transfer effect of the system was enhanced, and the mass transfer efficiency of the pollutants and the utilization of oxygen were improved. Therefore, the A/O\textsubscript{1}/O\textsubscript{2} process increased the pollutant removal efficiency of pollutants.

At present, among the fillers used in the field of sewage treatment, we had selected suspended soft-semi-soft fiber composite fillers in which the fillers sheets were vertically spaced 80 mm apart and each fillers center was separated by 150 mm.

4.4 Engineering Commissioning
The system start-up scheme adopted the biological enhanced bacteria-activated sludge synchronous compound culture method, that was the natural rubber wastewater entered the A/O\textsubscript{1}/O\textsubscript{2} reaction tank through the grid and the grit chamber. At the same time, the initial sludge cultivation was carried out by adding biological sludge consisting of the engineering bacteria and inoculum sludge to the pond, and then the rapid culture and domestication of the sludge were completed simultaneously with continuous water intake and trace aeration. The quality and quantity of natural rubber waste water depended entirely on the quantity and production time of fresh latex and gel collected by natural rubber processing plants. The quality and quantity of natural rubber processing waste water were very unstable, which had a great negative impact on the traditional activated sludge process. Adding combined fillers and engineering bacteria could improve the impact resistance of the waste water treatment system. After the system was started up, the strengthening effect of the engineering bacteria was quickly brought into play, and the sludge in the biochemical pool completed logarithmic proliferation and adaptive domestication in a short period of time (8 days), which ensured the biomass of the biochemical pool.

At a water temperature of 25°C, the A/O\textsubscript{1}/O\textsubscript{2} biofilm system was started in half a month.

5. Operation effect
The project was officially put into operation after more than a month of commissioning, and its effluent indexes all met the urban reclaimed water industry reuse standards. Table 3 shows the results of water quality monitoring, which was tested during project acceptance. The test results for three consecutive days show that the five indicators of pH, SS, NH\textsubscript{3}-N, COD and BOD\textsubscript{5} all meet the “Integrated Wastewater Discharge Standard” (GB8978-2002). The bio-enhanced A/O\textsubscript{1}/O\textsubscript{2} biofilm process is a technically feasible and stable process with a particularly prominent effect of nitrogen removal. According to the analysis, this may be related to the action of highly effective bacteria and the formation of biofilms in the two-stage biological contact oxidation tank. Biofilm systems provide a suitable place for growth and reproduction of bacteria that have slow growth but special metabolic capabilities, such as nitrifying bacteria.
| Time      | Result | 1     | 2     | 3     | Average value |
|-----------|--------|-------|-------|-------|---------------|
| Monitoring| pH     | 7.52  | 7.40  | 7.39  | 7.43          |
| Standard value | 6-9  | 6-9   | 6-9   | 6-9   | 6-9           |
| Evaluation | Reach the standard | Reach the standard | Reach the standard | Reach the standard |
| Monitoring | SS     | 23    | 43    | 40    | 35            |
| Standard value | 70   | 70    | 70    | 70    | 70            |
| Evaluation | Reach the standard | Reach the standard | Reach the standard | Reach the standard |
| Monitoring | NH₃-N  | 0.21  | 0.14  | 0.45  | 0.27          |
| Standard value | 15   | 15    | 15    | 15    | 15            |
| Evaluation | Reach the standard | Reach the standard | Reach the standard | Reach the standard |
| Monitoring | COD    | 40    | 38    | 43    | 40            |
| Standard value | 100  | 100   | 100   | 100   | 100           |
| Evaluation | Reach the standard | Reach the standard | Reach the standard | Reach the standard |
| Monitoring | BOD₅   | 21    | 15    | 17    | 18            |
| Standard value | 30   | 30    | 30    | 30    | 30            |
| Evaluation | Reach the standard | Reach the standard | Reach the standard | Reach the standard |

Note: The unit of other indicators is mg/L except pH.

6. Economic and Environmental Benefit Analysis of Bioaugmented A/O₁/O₂ Biofilm Technology

Taking the A/O₁/O₂ biofilm process of a natural rubber processing plant in Jinghong City as an example, the economic efficiency of bio-enhanced technology in the treatment of natural rubber processing wastewater was analyzed. The project had a total investment of more than 4 million RMB. Compared with traditional projects, it increased the cost of the fixed packing which was 4375m³ and the steel racks required for combined fixed fillers, as well as the costs for the production of bio-enhanced bacteria and the commissioning of the project. The cost of adding fillers, microbial production and commissioning technologies was less than 10% of the total investment. The successful operation of the biofortification process could shorten the start-up time of the system and enhanced its impact resistance, ensuring an efficient and stable effluent effect. In addition, the A/O₁/O₂ bio-enhanced biofilm system realized zero discharge of waste water and the system produced almost no excess sludge, which saved the cost of the return sludge lifting equipment and the power cost required for sludge return flow. About 20% to 40% of operating costs could be saved.

7. Conclusion

The application of bio-enhanced technology had greatly reduced the concentration of organic pollutants and ammonia nitrogen in the effluent of the system. It had improved the quality of effluent from biochemical treatment systems, reduced the total amount of hard-to-degrade substances, and reduced the adverse impact of wastewater on the surrounding ecological security. The A/O₁/O₂ bio-enhanced biofilm system had good economic benefits, environmental benefits and broad prospects for promotion.
Acknowledgment

Fund:
[1] Yunnan Agricultural University Youth Fund Project
[2] Yunnan Applied Basic Research Project (2017FD081)
[3] Yunnan Provincial Key Laboratory Construction Project Support Project (20163709)

References

[1] Wang B.Zh. (1990) Water Pollution Control Project [M]. Beijing: Higher Education Press: 189-254.
[2] Wang Q.W. (2013) Discussion on Wastewater Treatment of Rubber Industry [J]. Rubber Plastic Technology & Equipment, 39(7): 45-48.
[3] Zhang H.J. (2006) Characteristics of domestic sewage treated by lateral flow aeration biological filter and its dephosphorization and denitrification efficiency [D]. Chongqing: Chongqing University.
[4] Zhu X.B. Research on characteristics, (2012) mechanism and drainage bio-toxicity of coking wastewater treatment [D]. Beijing: Tsinghua University.
[5] Zhang Y.F. (2009) Research on bio-enhanced microbial agents for degradation of coking wastewater [D]. Chongqing: Chongqing University.
[6] Ellis D E, Lutz E J, Odom J M. (2000) Bioaugmentation for accelerated in situ anaerobic bioremediation [J]. Environmental science & technology. 34(11): 2254-2260.
[7] Gentry T, Rensing C, Pepper I. (2004) New approaches for bioaugmentation as a remediation technology [J]. Critical Reviews in Environmental Science and Technology. 34(5): 447-494.