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Countermeasures for rural domestic wastewater based on ecological environment security: a case study of an MBR-integrated process based on the PVDF@ZrO_2 flat membrane, China

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ABSTRACT

The harmonious coexistence of humans and nature has reached a broad consensus in the world. Maintaining the health of the ecological environment is the foundation of the existence and development of human civilization, and is also the inevitable choice for human beings to deal with the global ecological environment crisis. As an important factor affecting ecological stability, rural domestic wastewater has been neglected and not treated effectively for a long time because of its special geographical location and development limitations. In this paper, an integrated process of an MBR was applied to rural domestic wastewater treatment, inside which the modified PVDF@ZrO_2 membrane was used to replace the traditional PVDF membrane. A series of membrane analyses and project follow-ups have proven that the hydrophilicity, anti-fouling performance of the membrane, and the treated water quality were improved. Meanwhile, this research enlightens us to pay attention to the overall planning, the maintenance of the pipe network, and the stable investment of funds in the treatment of rural domestic wastewater.

Key words: harmonious coexistence of humans and nature, health of the ecological environment, improvement of water quality, underdeveloped areas, overall planning

INTRODUCTION

The harmonious coexistence of humans and nature refers to the development concept that takes the economy, society, and ecology as an indivisible whole, with low consumption, low emissions, and reasonable consumption as the main characteristics, and with the fundamental purpose of achieving harmony between people and nature (Popa 2022; Shein & Sukinarhimi 2022; Yu 2022). The harmonious coexistence between man and the natural environment is a worldwide consensus. The stability and health of the ecological environment are the foundation of human survival and development, and their changes directly affect the rise and fall of civilization (Donner 2011). Therefore, maintaining ecological security is a necessary choice to deal with the global ecological crisis facing mankind (Chen & Zhang 2013).

In recent years, due to the restriction of land resources, the need for rural employment, extensive production methods, and the widespread use of pesticides and fertilizers, etc., the problem of water pollution in rural areas has become increasingly serious, which runs counter to the concept of the harmonious coexistence of humans and nature. In addition, the lack of unified and standardized treatment of rural domestic wastewater has increasingly become one of the important factors that endanger the safety of the ecological environment (Peng *et al.* 2018).

Rural domestic wastewater mainly refers to toilet flushing and washing wastewater, and there may be a small amount of industrial and pesticide residues in some areas. The pollutants are mainly organic matter, nitrogen, phosphorus, and bacteria (Paruch *et al.* 2011). Different from the centralized collection and treatment of urban wastewater, rural wastewater treatment generally has problems such as a large demand for wastewater treatment plants (stations), large changes in wastewater quality, large fluctuations in water volume, and a lack of unified and standardized treatment procedures due to the relatively remote geographical location, loose residents, low economic development, and other specific problems (Lam *et al.* 2015; Rout *et al.* 2016).

Generally, it is appropriate to introduce a natural wastewater treatment system. For example, using wetland systems to treat rural wastewater has the advantages of high efficiency, low investment, low operation cost, and low maintenance technology (Doherty *et al.* 2015). However, the constructed wetland has obvious limitations, because it covers a large area, has a low wastewater treatment capacity, and is not suitable for some harsh areas, such as high altitudes and cold areas (Lu *et al.* 2020). The MBR-integrated wastewater treatment process is a new type of wastewater treatment technology combining membrane separation and biological treatment (Sun *et al.* 2010). Here, the use of membrane materials as the core components of MBR plays a decisive role (Al-Halbouni *et al.* 2009; Teng *et al.* 2020).

Polyvinylidene fluoride (PVDF) is a homopolymer of vinylidene fluoride or a copolymer of vinylidene fluoride and a small number of other vinyl monomers containing fluorine (Kong *et al.* 2022). It has good mechanical properties, chemical corrosion resistance, and stable thermodynamic properties, and is widely used to prepare the core polymer filter membrane materials in MBR (Fan *et al.* 2020a, 2020b; Zaliman *et al.* 2022). However, some research results generally indicate that the PVDF membrane is easy to attract bio-protein, bacteria, and other microorganisms adhere to multiply, resulting in membrane pollution due to the strong hydrophobicity of traditional PVDF materials (Du *et al.* 2022).

Metal nanoparticles have strong polarity and bacteriostasis (Sonawane & Murthy 2022). It is an effective method to improve the hydrophilicity and anti-fouling performance of PVDF membranes by blending these nanoparticles with the traditional PVDF membrane in the casting solution stage (Fan *et al.* 2020a, 2020b). Based on this idea, researchers have tried many different metal nanoparticles, such as Al_2O_3 (Yan *et al.* 2005), TiO_2 (Takagi *et al.* 2000; Sun *et al.* 2020; Deng *et al.* 2021; Han *et al.* 2023), SiO_2 (Sun *et al.* 2017), etc., and achieved significant improvements. However, there is an obvious lack of relevant reports in specific practical cases.

In this study, with the concept of harmonious coexistence between humans and nature, a modified PVDF@ZrO_2 membrane was used as a core component of an MBR-integrated equipment. Based on this technology, remote rural domestic wastewater was treated on the spot. The MBR-integrated equipment replaced traditional sedimentation and the use of chemical agents. The micromorphology of the modified membrane was analyzed by scanning electron microscopy (SEM) and the hydrophilicity of the membrane was also tested by contact angle (CA) analysis. Meanwhile, the effluent water quality through this technology, including chemical oxygen demand (COD), ammonia-N, total nitrogen (TP), total phosphorus (TP), and suspended solids (S), etc., was also investigated and analyzed.

EXPERIMENTS AND METHODS

Materials

PVDF (Solef 6015, in powder form, industrial grade) was purchased from Solvay Chemicals Company, Belgium. N-methyl pyrrolidone (NMP, industrial grade) was purchased from East Sichuan Chemical, China. The Beijing Zhongkangda Ultramicro Technology Application Research Institute in China supplied industrial-grade ZrO_2. Flocculant polyferric sulfate (PFS, industrial grade) and polyacrylamide (PAM-1201, industrial grade) were purchased from Xinqi Polymer Co., Ltd, China.

Membrane

The membrane used in this project was the Xlkf-001 PVDF@ZrO_2 high hydrophilic membrane produced by Chongqing Zero-One environmental technology Co., Ltd, and the membrane for comparison was purchased from the traditional PVDF membrane on the market (Shanghai Sinap 1102-flat membrane).

Case background

The project was located in Yangping Village, Wuma Town, Fengjie County, Chongqing, China. Due to its remote geographical location, high altitude, multiple mountains and hills, the traditional constructed wetland cannot be used for rural wastewater treatment, as shown in Figure 1(a)–1(c). According to the field survey, the domestic wastewater treatment facilities in a rural area were seriously insufficient, and the direct discharge of most residents' domestic wastewater into the river was very obvious, which caused serious environmental pollution. Considering the special geographical location and loose residents, this project adopted an MBR-integrated

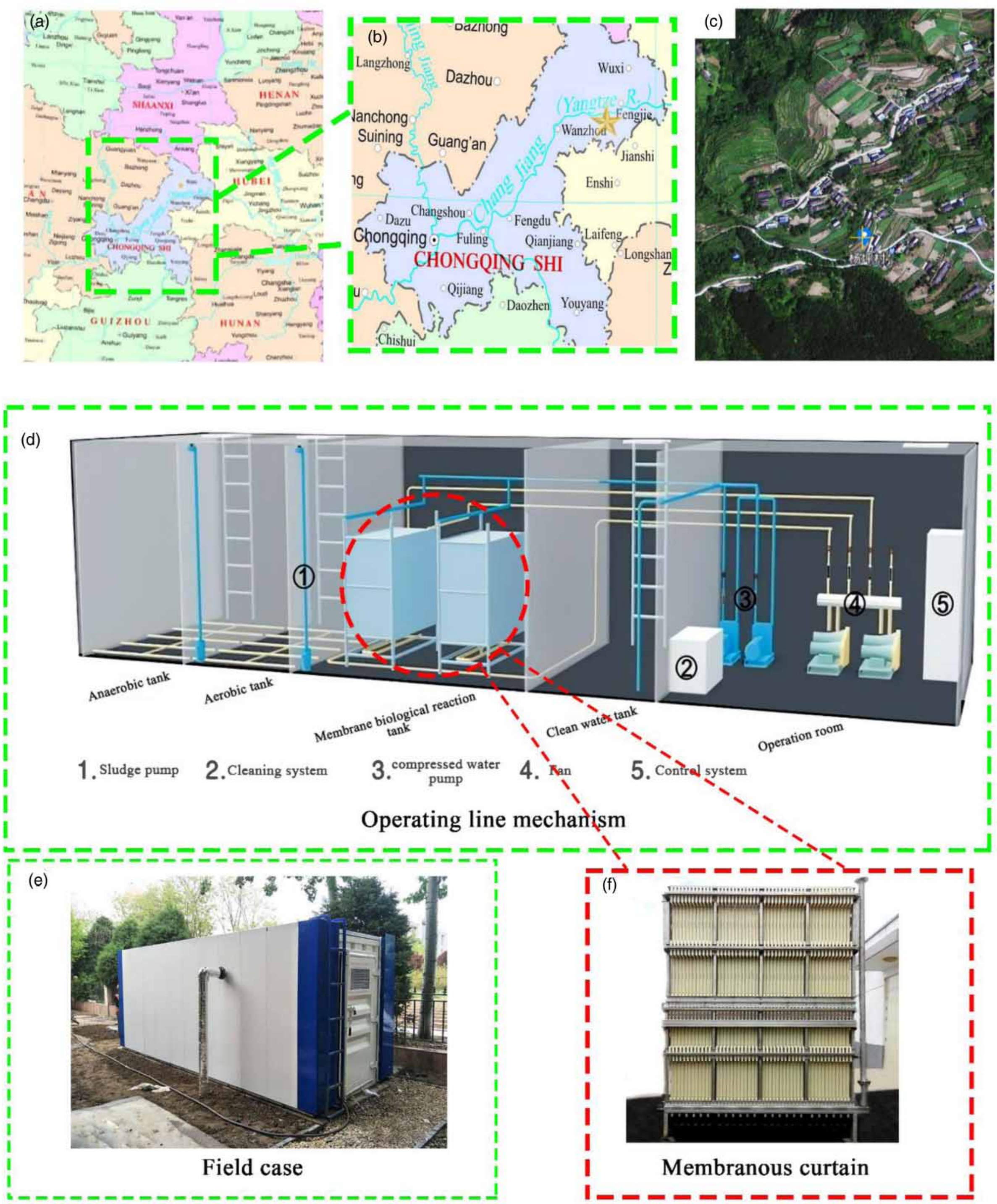

Figure 1 | Field case of an MBR-integrated process based on the PVDF@ZrO_2 flat membrane.

process technology to treat domestic wastewater, and the inlet and outlet water quality were designed as shown in Table 1, and the water quality testing methods are shown in Table 2.

Morphology study of the membrane

The membrane's surface and cross-sectional structure were studied by a LEO1530vp SEM (Germany). Because of the possible damage to the cross-sectional structure during the analysis process, the rapid freezing and brittle fracture treatment of the membrane samples with liquid nitrogen was needed before the test. Meanwhile, the sample needs to be sprayed with gold to further enhance the electrical conductivity of the sample.

Table 1 | Designs of inlet and outlet water quality

	pH	COD ($mg{\cdot}L^{-1}$)	Ammonia-N ($mg{\cdot}L^{-1}$)	TN ($mg{\cdot}L^{-1}$)	TP ($mg{\cdot}L^{-1}$)	SS ($mg{\cdot}L^{-1}$)
Inlet water	6–9	130–430	25–50	30–60	3–7	70–200
Outlet water	6–9	≤50	≤5	≤15	≤0.5	≤15

Table 2 | Water quality testing methods

Test items	Test method
pH	Glass electrode method
COD	Potassium dichromate ($K_2Cr_2O_7$) method
Ammonia-N	Nessler's reagent spectrophotometry
TN	Potassium persulfate ($K_2S_2O_8$) digestion ultraviolet spectrophotometry
TP	$K_2S_2O_8$ digestion molybdenum antimony resistance spectrophotometry
S.S.	Gravimetric method

CA change of different membranes

An Attension Theta System (KSV Instruments Ltd, Finland) is required for measuring the CA of the membrane. A drop of about 5 μL of pure water was placed on the surface of the testing membrane, and the CA was analyzed and calculated using the camera and software.

RESULTS AND DISCUSSION

Case study

In this project, the geographical remoteness, the dispersed nature of residences, and the complexity of the terrain do not allow for uniform processing through the municipal wastewater pipe network. Meanwhile, there is no large-scale industry around, and the pollutants are mainly from domestic wastewater. Combined with these factors, this project adopts MBR wastewater treatment technology. The process has the advantages of a small area, a low energy consumption, low initial investment, convenient construction and installation, and lower requirements for operation and management personnel, as shown in Figure 1(e).

The flocculation and sedimentation process are not required as the content of SS in domestic wastewater is relatively low. Polyethylene (PE) pipes can be directly used for centralized collection and treatment by an MBR-integrated process technology, as shown in Figure 1(c).

PVDF has been widely used in ultrafiltration (UF) and microfiltration (MF) membranes because of its high mechanical strength, thermal stability, and chemical resistance. However, due to the strong hydrophobicity of the PVDF membrane, the non-polar solute can be easily adsorbed to plug the membrane hole during the process of wastewater treatment and purification, which results in a decrease in separation performance and flux attenuation, shortening the service life of the membrane, and increasing the running cost (Lü *et al.* 2016). Based on this obvious problem, a flat PVDF@ZrO_2 membrane with higher cleaning efficiency, hydrophilicity, and anti-fouling was used in this case and replaced the hollow fiber membrane for wastewater treatment. After the equipment had been running for 1 year, the effluent condition was stable, and the membrane fouling problem was effectively alleviated, as shown in Figure 1(f).

The cross-section and surface morphology of the PVDF@ZrO_2 flat membrane

The stable load of metal nanoparticles on the surface and inside of the membrane can be determined by analyzing the micromorphology of the membrane. Figure 2 shows the cross-section and surface morphology of the PVDF@ZrO_2 flat membrane analyzed by SEM. The cross-section of the membrane presents a classic asymmetric finger-like pore structure. Meanwhile, there are many ZrO_2 nanoparticles stably adhered to the pores of the membrane after locally magnifying, as shown in Figure 2(a)–2(c). In addition, the protrusions of some nanoparticles loaded on the membrane surface and many uniform pores were observed and distributed on the surface by magnifying, as shown in Figure 2(d)–2(f).

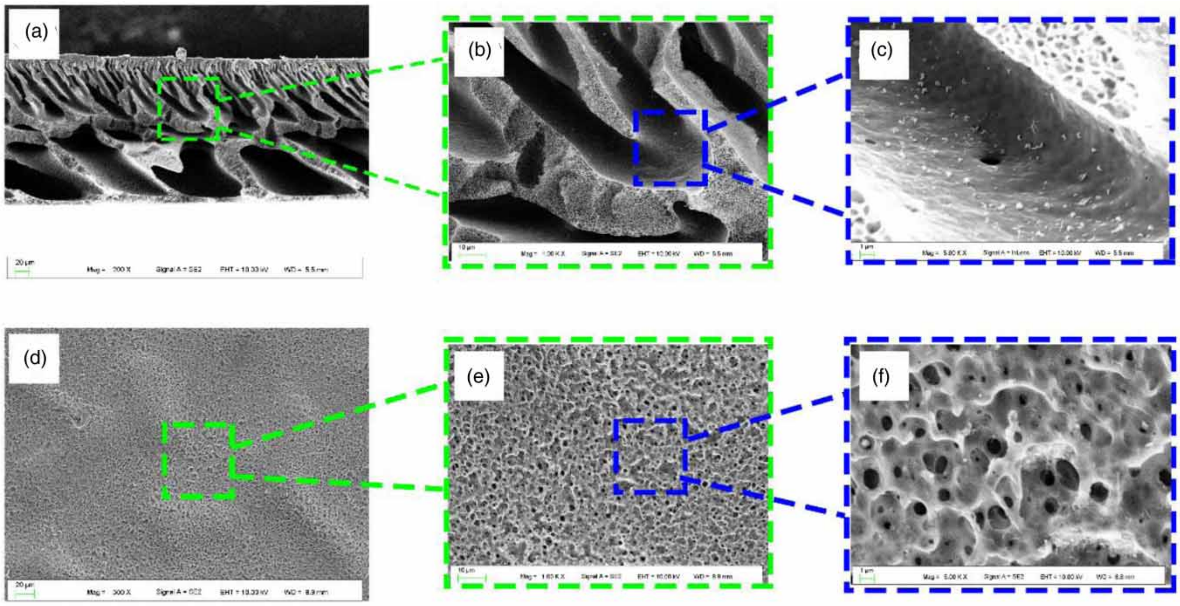

Figure 2 | Cross-section and surface micromorphology of the PVDF@ZrO_2 flat membrane.

The CA of different membranes and their change with time

In recent years, major studies have confirmed that traditional PVDF membranes have strong hydrophobicity, easily adsorbing proteins, colloids, and some hydrophobic macromolecules on the surface and pores of the membrane, which is the key factor leading to membrane fouling (Huang *et al.* 2022; Liu *et al.* 2022). The hydrophilicity of the membrane can be effectively evaluated by measuring the CA of the membrane surface and its change with time. In this case, we chose the traditional PVDF membrane on the market to compare with the PVDF@ZrO_2-modified membrane to measure the CA of different membranes, and the result is shown in Figure 3. The traditional PVDF membrane showed strong hydrophobicity, and its CA began to decrease from 77.1° to 66.9° after 50 s. In contrast, the initial CA of the PVDF@ZrO_2 membrane used in this case was 60.1°, and significantly reduced to 41.8° after 50 s, as shown in Figure 3(a) and 3(b). This result showed that the hydrophilicity of the PVDF@ZrO_2 membrane used in this case was significantly improved compared with the traditional PVDF membrane, possibly alleviating the problem of membrane fouling to a certain extent.

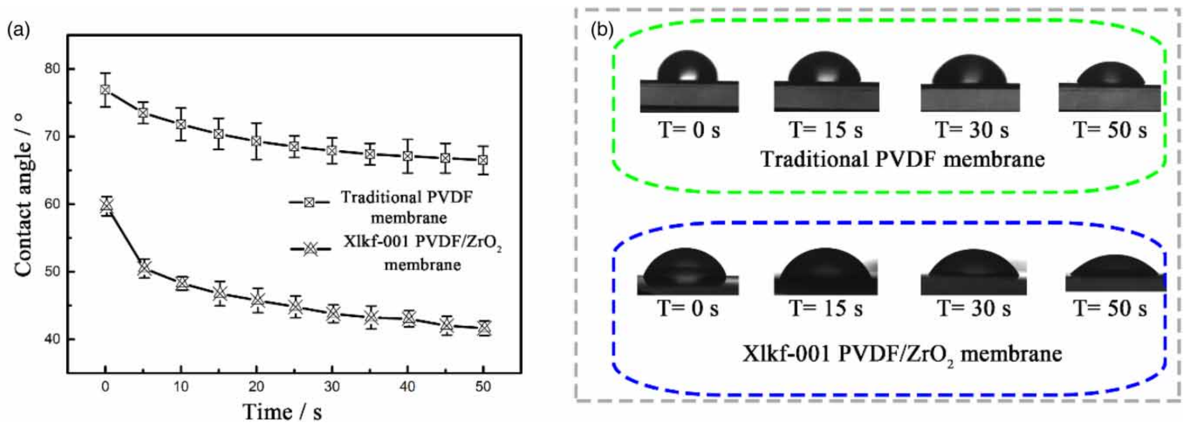

Figure 3 | The CA of different membranes and their change with respect to time.

Actual operation effect

The civil construction and equipment installation phases of this project were completed in June 2021, and then the commissioning and operation stages were also smoothly entered. In July 2021, the equipment began to operate normally. After nearly a year of continuous operation, the collected water quality test results are shown in Figure 4.

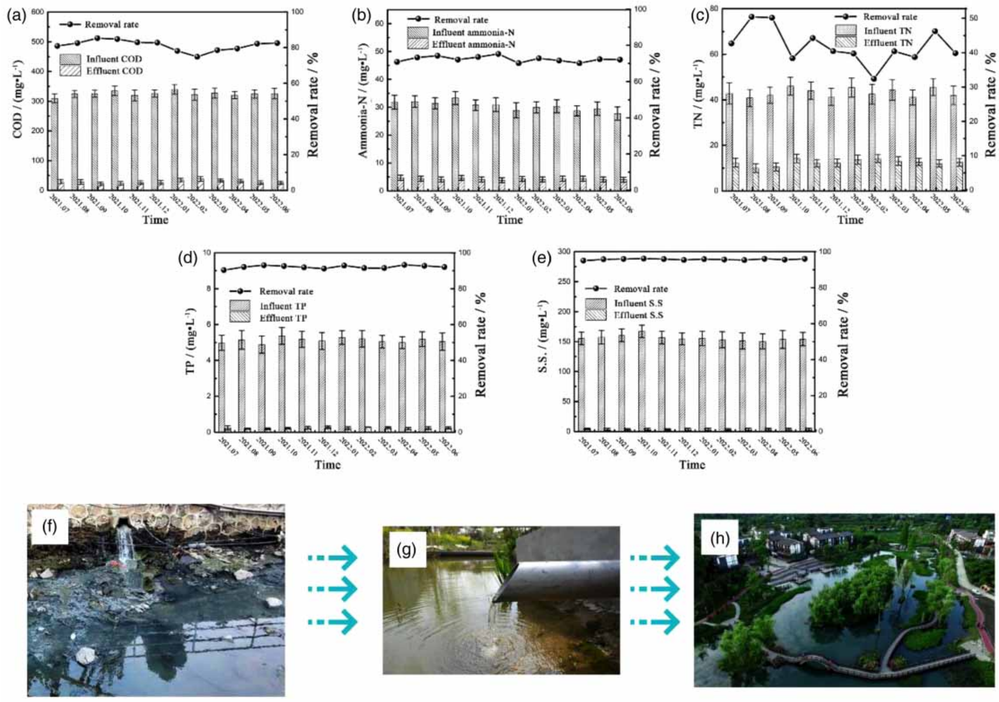

Figure 4 | The inlet and outlet water quality analyses and actual operation effect in this case.

The equipment has been in continuous operation from July 2021 to June 2022 with good operating conditions. When the equipment was operated in October 2021, January 2022, and May 2022, respectively, the quality concentrations of COD, ammonia-N, TN, TP, and SS in the influent were relatively high, which may be due to the National Day, Labor Day, and the Spring Festival, leading to the increase of rural residents and the deterioration of the quality of rural domestic wastewater, but the effluent could maintain a relatively stable state, indicating that the equipment has strong resistance to impact loads.

After nearly a year of continuous operation, the average mass concentrations of COD, ammonia-N, TN, TP, and SS in influent water were about 331.3, 28.6, 40.2, 5.03, and 151.4 mg/L, and the average mass concentrations of COD, ammonia-N, TN, TP, and SS in effluent water were reduced to 36.8, 4.2, 2.5, 21, and 3.3 mg/L, with the removal rates reaching 87.5, 84.7, 70.3, 96.2, and 98.1%, respectively, as shown in Figure 4(a)–4(e). The effluent water is superior to the relevant emission standards and has significantly improved the local ecological environment, as shown in Figure 4(f)–(4h). These results show that the process has a very significant effect on rural domestic wastewater treatment, and has a strong practical value for such a remote geographical location and scattered villages.

Construction and operation costs

The construction cost of the 30 t/d wastewater treatment system is mainly composed of a sedimentation tank, pipe network, and treatment system. The construction cost of each sedimentation tank was CNY 8,000. The construction cost of the pipe network was CNY 340/m, and the length of the pipe network was 742 m. The treatment system cost CNY 0.25 million per set, of which the membrane cost was CNY 220/m^2. The total construction cost was about 0.46 million. The operation cost of the wastewater treatment system was CNY 1.17/m^3, mainly including electricity costs, labor costs, chemical agent costs, etc. Compared with common stabilization ponds, constructed wetlands, and land infiltration technologies, this process has a better wastewater treatment effect, but higher operating costs. Therefore, it is necessary to select the appropriate wastewater treatment process according to the actual situation, taking into account the main factors such as effluent standard and investment cost.

Countermeasure analysis of rural domestic wastewater treatment

At present, the ecological environment of some underdeveloped rural areas in the world tends to deteriorate because of problems such as a lack of overall planning, inadequate operation and management, and a lack of funds for operation and maintenance. The author believes that the following aspects can be targeted for improvement.

The special plan for the treatment of rural domestic wastewater should be prepared at the overall level. Collecting rural wastewater into the pipe network system is one of the key factors for rural domestic wastewater treatment. The current situation of rural domestic wastewater treatment should be comprehensively sorted out and focused on analyzing the existing problems in pollution sources, facility construction, operation, management, etc., and finally forming guiding opinions and suggestions.

The construction and maintenance of the township wastewater pipe network should be improved. The prominent problems, such as internal and external leakage in the wastewater pipe network, need to be rectified and reformed. In the process of rectification, attention should be paid to optimizing the rainwater and wastewater diversion and gradually improving the construction of the township wastewater treatment pipe network.

A diversified financing model may be an effective way to solve the problem of insufficient funds. The specific measures are to encourage, guide, and support enterprises, social groups, individuals, and other social forces to participate in the establishment of a long-term security mechanism for operation and maintenance funds.

CONCLUSION

In this case study, an MBR-integrated equipment was applied to treat rural wastewater based on the concept of harmonious coexistence between humans and nature, which effectively solved the site limitation and reduced labor costs. The traditional PVDF membrane was replaced with a modified PVDF@ZrO_2 membrane. The micromorphology of the membrane was analyzed by SEM, and there was a stable load of nanoparticles on the surface and internal pores of the membrane. The CA of the PVDF@ZrO_2-modified membrane was reduced compared with the traditional PVDF membrane, indicating that the hydrophilicity and anti-fouling performance of the membrane had been improved. The output water of rural domestic wastewater treated by the integrated MBR equipment with PVDF@ZrO_2 membranes as the core component was stable, and the effluent quality improved. In the treatment countermeasures for rural domestic wastewater, attention should be paid to the overall planning, the maintenance of the wastewater pipe network, and the stable investment of funds. The report of this case provides some references for the application of the MBR-integrated process in rural wastewater treatment.

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CONFLICT OF INTEREST

All authors disclosed no relevant relationships.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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