

Article

New Technology for Degradation of Wastewater Containing High Concentrations of COD and Boron Based on Manganese-Iron Oxide Catalytic Support

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Abstract: The existing methods for simultaneous treatment of wastewater containing high concentrations of chemical oxygen demand (COD) and boron are too cumbersome and require a relatively long treatment time. The traditional oxidation method is easy to cause a large amount of sludge and other secondary pollution. Therefore, in this research, the wastewater was oxidized by the self-synthesized manganese-iron oxide catalytic support. This oxidation and adsorption combined method significantly increased the efficiency of wastewater treatment, reduced the treatment time and the replacement frequency of consumables. The efficiency in degradation of high-concentration COD (25,250 mg/L) was more than 90%, which could be reached within 40 min, while that of boron (500 mg/L) could reach above 95% within 20 min. After optimization of the parameters (daily treatment capacity: 5CMD) was combined to treat high-concentration wastewater containing high concentrations of COD (14,700 mg/L) and boron (486 mg/L), with treatment efficiency approaching 100% within 20 min. As proved by the research results, after being treated by the new manganese-iron oxide catalytic support and activated carbon, the wastewater has reached the emission standard and can be discharged directly. This combined method provides a new way for the treatment of wastewater containing high concentrations of COD and boron.



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Highlights:

- The method for synthesis of manganese-iron oxide catalytic support was researched.
- A combined treatment method was researched to efficiently degrade COD and boron.
- The high stability and reproducibility of this method provides the potential for its practical application.

1. Introduction

Boron is a trivalent semimetal, usually existing in natural water in the form of boric acid, borate, and perborate [1,2]. Most of the wastewater containing high concentrations of COD and boron discharged into the environment by human activities is relevant to agricultural and industrial development. With the enhancing awareness of environmental protection in recent years, the World Health Organization (WHO) and the European Union (EU) have incorporated boron into relevant control standards [3,4]. The national control on COD and boron (B) in various discharged water has also become stricter and stricter. Boron can be used to synthesize a variety of products, such as fertilizers, pesticides, buffers, dyes, bleaches, and borosilicate glass [5].

Boron compounds have been widely applied to various manufacturing fields, such as glass, semiconductor, bleaching, pharmaceutical, ceramics, and metallurgical industries. In Taiwan, the manufacturing of thin-film transistor liquid crystal display (TFT-LCD) is one of the most important industries. Moreover, an essential component of TFT-LCD is a polarizer whose manufacturing often generates wastewater containing high concentrations



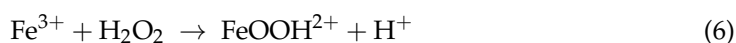
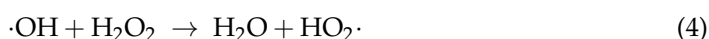
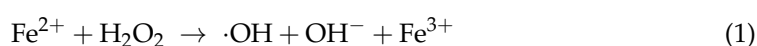
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of boron and COD [6]. High-tech factories and metal surface treatment plants are important entities in Taiwan. In the electronics and optoelectronics industry, raw materials or reagents containing high concentrations of boron are usually used as required in the manufacturing process; in the metal processing industry, a boron-containing antirust agent is commonly used for surface finishing [7]. As known, the wastewater produced in such processes often contains hundreds of milligrams/liters of boric acid [6].

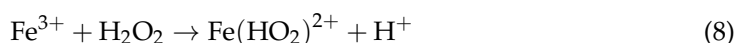
However, boron is an essential micronutrient of plants, animals, and humans [8]. Plants irrigated with water containing boron will be spoiled including damage on the edges and tips of leaves, losing photosynthetic capacity and fecundity [9]. For humans, excessive intake of boron may lead to human poisoning, causing nausea, headache, diarrhea, renal circulatory failure, and resulting in damage and death [10,11]. Therefore, the boron contained in wastewater—generated by the said processes—must be effectively removed to reach the standard for discharge water before being discharged.

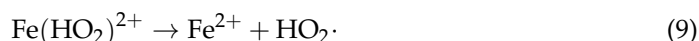
The existing boron removal technologies include adsorption, precipitation, reverse osmosis, ion exchange, adsorption membrane filtration (AMF), and chemical oxygen precipitation (COP) [8,12–19]. Due to the various chemical structures and variable amounts of boron existing in water, such boron can hardly be removed in a simple and economic method. Chemical precipitation is a simple and cost-effective method [20,21] commonly used in industry to remove high-concentration pollutants in water. Yet, Lin et al. researched the use of the COP method to remove boron in high-turbidity seawater, taking H_2O_2 as oxidant and FeCl_3 and BaCl_2 as coagulants. Consequently, the two coagulants were found to be incompatible with the coagulation of seawater in the COP process; and the COP showed no significant influence on the removal of boron [22]. Another way is the co-precipitation method, which, however, requires exact conditions, including using a large amount of coagulants, in order to realize efficient removal of boron [23].

It has already been proved that advanced oxidation processes (AOPs) have the potential of treating refractory compounds in water. Among the various AOPs, H_2O_2 /ferrous iron can effectively treat various organic pollutants [24]. The Fenton process is recognized as one of the most practical advanced oxidation technologies available due to the generation of hydroxyl radicals that can oxidize many types of chemicals. The Fenton reaction involves several reactions which can be described by Equations (1)–(6):

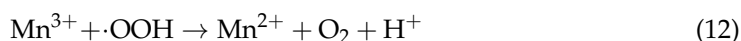
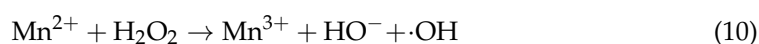


However, this method may cause precipitation which requires iron sludge, resulting in secondary pollution. To solve this problem, there have been extensive researches on the application of iron oxide as a catalyst in the oxidation of organic compounds. Various forms of iron oxide ore have been used as catalysts to treat organic pollutants [25]. As the crystalline types of self-synthesized iron oxide ore, three iron oxides including Hematite, Goethite, and Ferrihydrite can all be prepared by hydrolyzing ferric ion solution. Chou and Huang used the supported $\gamma\text{-FeOOH}$ catalyst, which was prepared by fluidized-bed crystallization, to oxidize benzoic acid. The formation of dissolved Fe was via the reductive dissolution of $\gamma\text{-FeOOH}$ as follows:





The properties of the synthesized product will be affected by the rate of hydrolysis, the pH of the solution, the temperature, the concentration of ferric ions, and the presence of anions in the environment. Under acidic conditions and at low temperatures (pH = 3.5–4.5), α -FeOOH is the main product of oxidative hydrolysis of ferrous salt; meanwhile, at low temperatures, a small amount of γ -FeOOH may be produced. Studies have shown that Mn/Fe oxide has excellent ferromagnetism and chemical stability, broad light absorption range, and high surface hydroxyl abundance [26,27]. In other words, Mn and Fe ions are believed to exert synergistic effects on the Mn/Fe catalytic system [28]. Because Mn/Fe oxide exhibits outstanding catalytic activity and visible light responses, it has been widely studied for pollutant degradation by catalytic ozonation, persulfate oxidation, and heterogeneous Fenton [27,29,30]. The contents of Mn (II) and Mn (III) changed after H_2O_2 activation, thus proving that Mn ions were under a cyclic reaction in the heterogeneous Fenton system. The conversion process is summarized as follows [28]:



In this research, manganese dioxide support and self-synthesized manganese dioxide/iron oxide composite were used to establish an experiment module for practical oxidative degradation tests. Further, H_2O_2 was added for oxidation. Then, activated carbon was used to further adsorb the remained COD and boron in the wastewater. The material developed in this research can be used for the long term, without secondary pollution, which greatly improves the efficiency and convenience in the treatment of wastewater.

2. Materials and Methodology

In this research, activated carbon, manganese dioxide, and self-synthesized manganese dioxide/iron oxide composite were used as the treatment supports to compare their performances in the treatment of wastewater containing COD and boron. The self-synthesized manganese dioxide/iron oxide composite was synthesized by continuous dosing. The particle size of manganese dioxide was set as 500 μm to calculate the required concentrations of ferrous iron and hydrogen peroxide. Then, H_2O_2 and FeSO_4 were successively added to the bottom of the reactor. A schematic diagram of the synthesis device is presented in Figure 1. All experiments were carried out at room temperature (24 ± 4 °C). Before using the peristaltic pump for continuous dosing, the pumping flow was determined. An air pump was used for providing the required airflow to maintain the reaction in a fluidized bed reactor in good condition to avoid precipitation. The reaction height of the fluidized bed should be 50%. Further, a pH control unit was used to control the pH at the required level to ensure continuous synthesis for 7–12 days. FeOOH was the main type of iron oxide.

The method for reproducing manganese-iron oxide support was as follows: first, 1% hypochlorous acid and the manganese-iron oxide to be reproduced were mixed and stirred for at least eight hours in a fluidized and circulated manner; then, the mixture was filtered, washed quickly, and finally dried up.

In the experiment, the first step was to determine various experimental parameters; then different methods and processes were used to treat different organic substances in wastewater. Next, the treatment efficiencies were discussed to optimize the configuration.

The cleaner used for existing metal processing lines was the main source of the aqueous samples to be tested in this study. The cleaner consisted of 1% corrosion inhibitor (KORRO 60–9, Germany) and 1% defoamer (Entschaumer 155, Germany). To be more specific, the aqueous samples to be tested refer to the wastewater produced from the cleaning process of the existing metal processing lines and the wastewater disposal systems. The pH value of

the wastewater before disposal was 9–10 with COD concentration at 14,000–23,000 mg/L and boron concentration at 40–55 mg/L. The study aims at practically testing the wastewater collected from the processing lines before and after wastewater disposal.

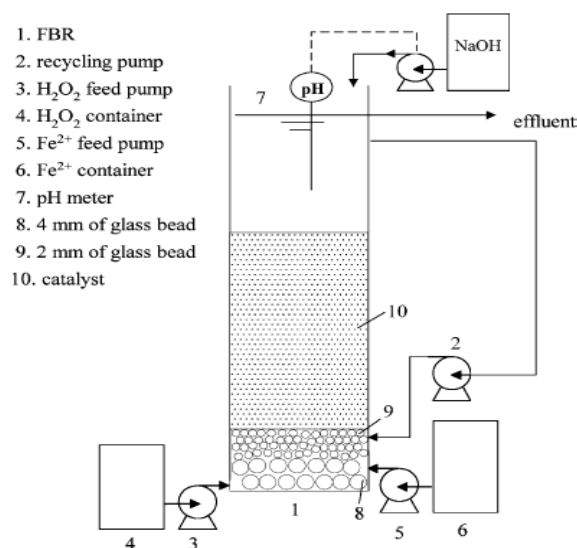


Figure 1. Schematic diagram of catalytic support synthesis device.

Before practical application, various catalytic supports were individually conducted pipe string tests on a laboratory scale (Figure 2). First, the configuration was optimized; then, the self-designed low-energy siphon treatment system was used to continuously test the small-scale treatment system for practically discharged industrial wastewater. The changes in the treatment efficiency were recorded, as shown in Figure 3. After sampling, the samples were divided into the COD test group and boron test group and tested by using the Merck prove 600 spectrophotometers. Next, the obtained data were used to analyze the samples. Merck's COD Cell Test (Product Number 1.18753) was adopted for making COD and Boron analyses. The potassium dichromate close reflux method and spectrophotometer were used to test and analyze COD. Boron cell Test (Product Number 1.00826), The Boron method applied in weakly acidic solutions borate reacts with azomethine H to form a yellow compound that is determined photometrically.

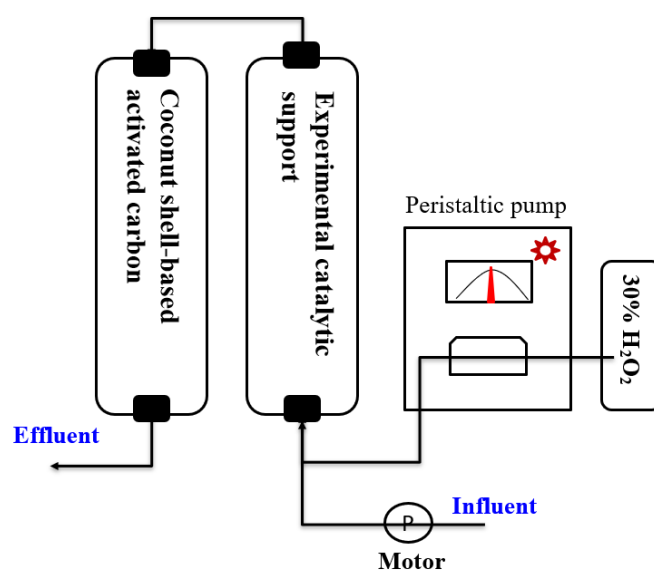


Figure 2. Schematic diagram of the laboratory pipe string test module.

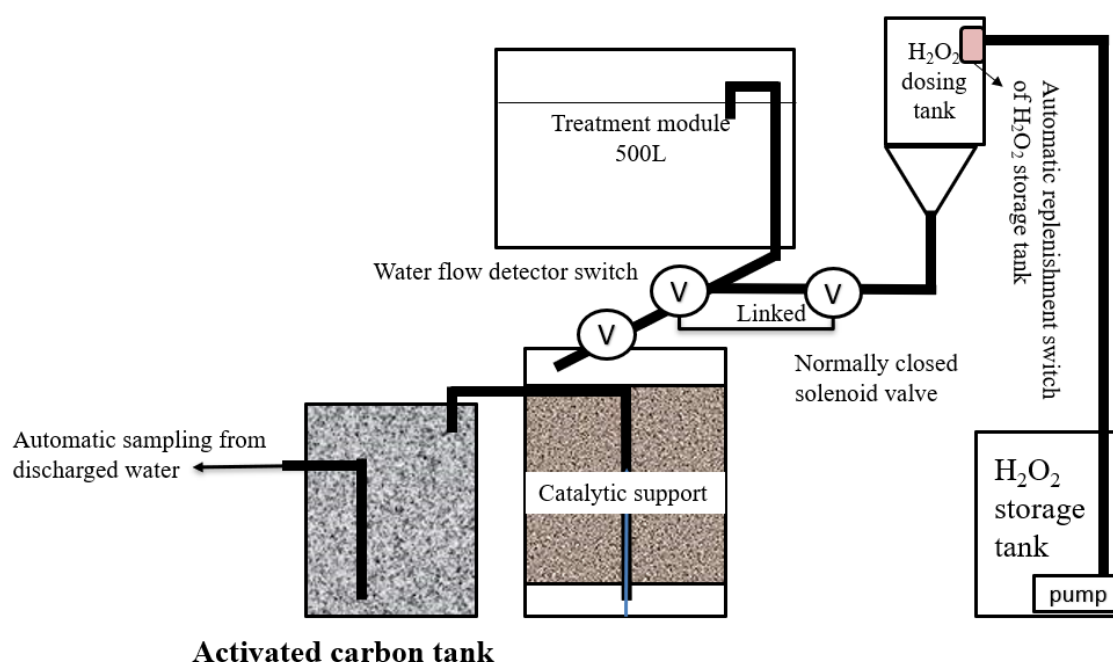


Figure 3. Schematic diagram of the test module of low-energy siphon treatment system.

3. Results and Discussion

In this research, the required concentration (COD: 22,500 mg/L; boron: 50 mg/L) of wastewater was prepared independently in the laboratory and treated in oxidation and adsorption methods. Then, an exploration was conducted on the treatment performance of activated carbon and manganese-iron support for individual adsorption and that of oxidant for oxidation. Finally, the adsorption and oxidation combined method was adopted to explore its efficiency in the treatment of practical industrial wastewater. Specifically, pure activated carbon was used to adsorb COD and Boron in the wastewater. As shown in Figure 4A, the COD treatment efficiency of this method was only about 26% and the adsorption saturation was reached after 20 min, while the boron adsorption efficiency was lower than 20% and the treatment speed was quite low. After reaching the adsorption saturation, the activated carbon was reproduced for the retreatment test repeatedly. As illustrated in Figure 4B, the treatment capacity of this method began to reduce from the 60th day, reached 50% on the 70th day, and became zero on the 100th day.

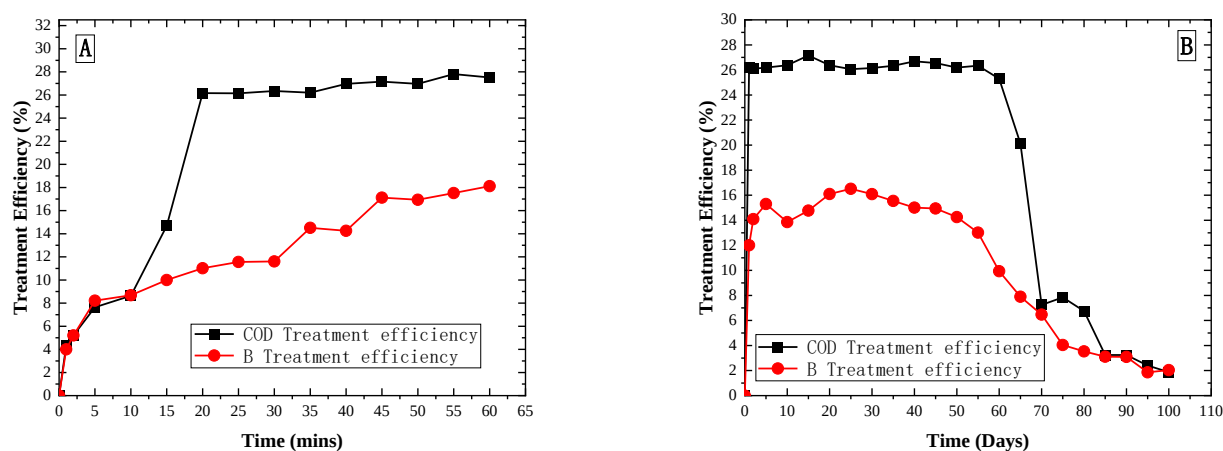


Figure 4. The adsorption efficiency and saturation test curves of activated carbon. (A) COD and Boron adsorption efficiency (B) COD and Boron treatment efficiency at 100 days.

Over practical research on the adsorption of the self-synthesized manganese-iron support, it is discovered that such support has not any adsorption capacity, as shown in Figure 5. In the treatment system, such support was used as a catalyst. Hence, an oxidant was required to drive the manganese dioxide and iron oxide to produce superoxide substances and hydroxide radicals for oxidation treatment. Theoretically, the manganese-iron support as a catalyst can be used for a long time without consumption and maintains the oxidizing ability during the supply of oxidant.

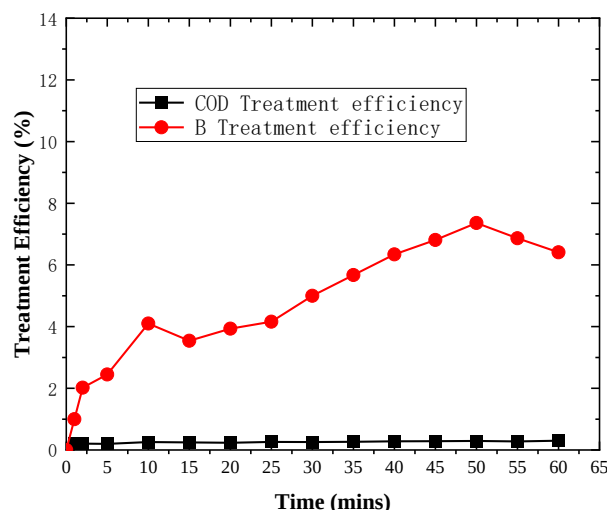


Figure 5. The adsorption treatment efficiency curve of manganese dioxide/iron oxide support (without oxidant).

In order to clearly observe the treatment efficiency of the manganese-iron support and activated carbon combined method, experiments were done on the manganese-iron support with or without activated carbon respectively. As a result (Figure 6A), the COD treatment efficiency of manganese-iron support combined with oxidant (35% H_2O_2 at a dosing rate of 10 mL/min) reached 90% within 40 min, while that of manganese-iron support combined with activated carbon exceeded 90% and even approached 100% within 60 min.

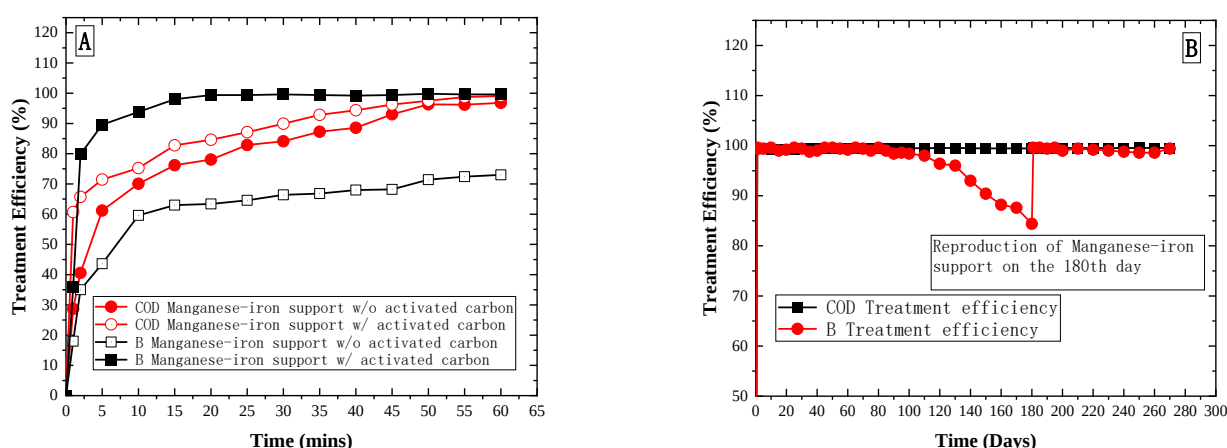


Figure 6. Catalytic treatment efficiency curve and saturation curve of manganese dioxide/iron oxide support (oxidant: H_2O_2). (A) Mn/Iron support treatment compares with and without activated carbon (B) Mn/Iron support treatment at 280 days.

Regarding the removal of boron from wastewater, the treatment efficiency of the former combination was about 70% at most, while that of the latter combination was up to 95% in the early 10 min and reached 100% within 20 min. This result revealed that after subjecting to oxidation, the boron in wastewater was partially converted into borate, which could be further adsorbed by activated carbon simply. As can be observed from the test result of the long-term combined use of manganese-iron support and activated carbon (Figure 6B), during the supply of oxidant, manganese-iron support as a catalyst has a continuous oxidizing ability and thus continuously has high efficiency in removing the COD in boiling water. As for boron, it was mainly adsorbed by activated carbon. When being used in combination with manganese-iron support, activated carbon underwent a reduction in the treatment load so that its effective treatment efficiency was maintained for up to 180 days and its high treatment efficiency was restored after reproduction.

In the practical research, a self-built automation module and self-synthesized manganese-iron support were used for the practical treatment of industrial wastewater, with a daily treatment capacity of about 5CMD. The wastewater contained COD (14,700 mg/L) and boron (48.6 mg/L). After being tested in the laboratory, the parameters were optimized and H_2O_2 was added at an inflow rate of 20 mL/min. In the modified method, the removal rates of COD and boron reached 100% within 15 min (Figure 7A) and the optimum treatment efficiency lasted for 180 days (Figure 7B).

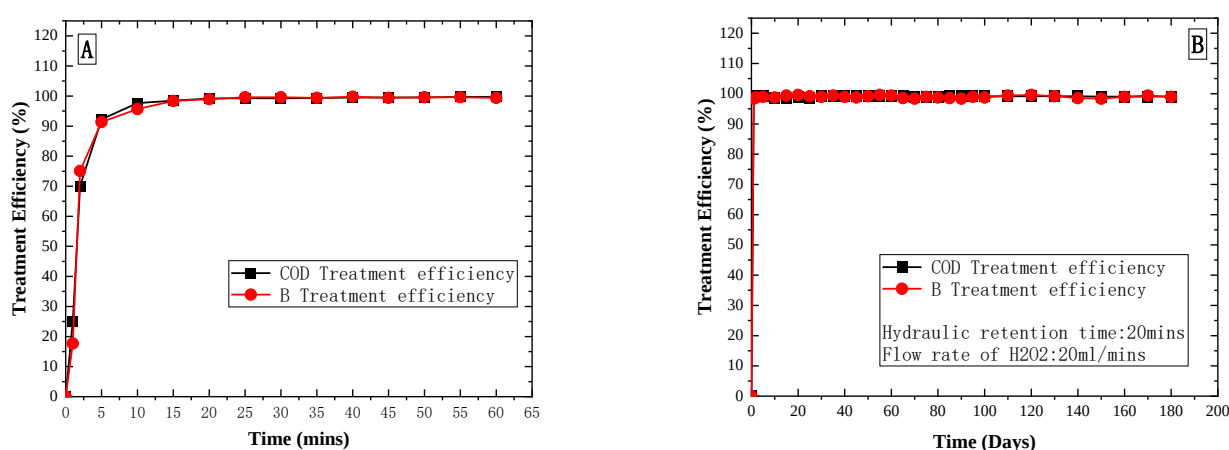


Figure 7. The treatment efficiency curve of real factory modular device. (A) COD and Boron treatment efficiency with H_2O_2 (B) COD and Boron treatment efficiency at 180 days.

In previous AOPs, a large amount of iron sludge was known to be the cause [31] and sometimes excessive dosing would waste reagent and cause the need for sludge disposal. In this research, a Fenton-like advanced oxidation treatment method was taken on the basis of manganese-iron support. Having the features of manganese and iron, and with FeOOH as the main type of iron oxide, this method has significantly improved efficiency in the treatment of boron-containing wastewater. Moreover, to treat wastewater containing a high concentration of COD and boron, this method is more convenient and easier to use compared with chemical precipitation, adsorption, and coagulation methods which require many cumbersome steps and longtime [32–34].

4. Conclusions

The anthropogenic emission of boron has become a serious problem for the environment and even endangering the ecosystem. Over a review of the latest boron removal technologies based on catalytic oxidation and adsorption, it is confirmed that the technology proposed in this paper is applicable to the treatment of complex wastewater containing a high concentration of COD and boron.

In this research, manganese-iron oxides were successfully applied to treat wastewater with high efficiency, which significantly affected the oxidation time of wastewater containing a high concentration of COD, and greatly reduced the production of sludge, avoiding secondary pollution. Furthermore, in combination with the adsorption method, the removal efficiency of COD reached over 90% within 40 min and that of boron reached over 95% within 20 min. As revealed in the results, the treatment efficiency is directly proportional to the amounts of H₂O₂ and adsorbing material. After optimizing the parameters, the self-built low-energy siphon treatment module was used to degrade the COD and boron in wastewater, with treatment efficiency approaching 100% within 10 min. Moreover, the duration of the consumables also increased, which reduced the operation cost.

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