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Effect of heterogeneous Fenton-like pre-treatment on anaerobic granular sludge performance and microbial community for the treatment of traditional Chinese medicine wastewater

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HIGHLIGHTS

- Rhein has metabolic or physiological toxicity on methanogens in anaerobic granular sludge.
- TCM wastewater containing rhein can be successfully treated by the combined treatment.
- The productions of the EPS of granular sludge increased after pre-treatment.
- *Methanoregula*, *Methanobacterium*, *Methanosphaerula* were predominant in the DC reactor after pre-treatment.

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ABSTRACT

The effect of a heterogeneous Fenton-like pre-treatment on the anaerobic processes, characteristics and microbial community of sludge was investigated for traditional Chinese medicine (TCM) wastewater containing rhein. When the concentrations of rhein were 50 mg/L and 100 mg/L, the toxic effect was physiological toxicity for anaerobic granular sludge. Using a single double circle (DC) reactor for the treatment of TCM wastewater containing rhein at concentrations of 15–20 mg/L, the chemical oxygen demand (COD) removal rate was 69%, and coenzyme F_{420} was nearly undetectable in the 3D-excitation-emission matrix (EEM) spectra of soluble microbial products (SMP). The abundances of *Methanoregula*, *Methanobacterium*, *Methanosphaerula* were only 5.57%, 2.39% and 1.08% in the DC reactor, respectively. TCM wastewater containing rhein could be successfully treated by the combination of the heterogeneous Fenton-like pre-treatment and the DC reactor processes, and the COD removal rate reached 95%. Meanwhile, the abundances of *Methanoregula*, *Methanobacterium*, *Methanosphaerula* increased to 22.5%, 18.5%, and 13.87%, respectively. For the bacterial community, the abundance of Acidobacteria_Gp6 decreased from 6.99% to 1.07%, while the abundances of Acidobacteria_Gp1 and Acidobacteria_Gp2 increased from 1.61% to 6.55% and from 1.28% to 5.87%, respectively.

1. Introduction

Over the past several years, advanced oxidation processes (AOPs) were found to be effective and have been applied to the degradation and mineralization of refractory organic pollutants, such as phenolic compounds, pharmaceuticals, agrochemicals, dyes, and so on [1,2]. Among the AOPs, the classical Fenton reaction has been widely reported to be effective for the degradation of recalcitrant pollutants because of its fast reaction rate and simple operation [3,4]. However, the homogeneous Fenton process has some disadvantages. The main drawback is the requirement of a high concentration of ferrous ion present in the treated wastewater in which the excessive ferrous ions must be removed, which may produce a large amount of sludge in the final step [2,3]. In addition, its reaction must be performed over a narrow pH range (2–3), which requires strong conditioning before and after treatment [5,6]. Therefore, these disadvantages limit the widespread application of the homogeneous Fenton process. To overcome these disadvantages, many efforts have been made to develop a heterogeneous Fenton process [7,8]. The use of heterocatalysts for the development of novel processes and technologies is a promising

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approach for a wide variety of future applications [9]. Heterogeneous Fenton catalysts are efficient and easily separated from the treated effluent [10]. Recently, many studies have been conducted, and various catalyst supports have been employed to prepare heterogeneous catalysts [10]. Zhou reported that a paper mill sludge-derived magnetically separable heterogeneous catalyst was prepared through a facile synthesis method under the optimum conditions, and 94.2% decolorization and 81% mineralization were achieved within 90 min [10]. Ersöz used iron(III) impregnated on rice husk ash as a heterogeneous catalyst for the oxidation of Reactive Black, and the best degradation efficiency of 59.71% and decolorization efficiency of 89.18% were obtained [11]. Activated carbon fiber has a larger surface area and pore volume with more uniform micropore size distribution, and it was applied as a heterogeneous Fenton-like catalyst support [8]. Clays are natural, abundant, economical, and environmentally friendly [5]. Hassan investigated the applicability of Fe-ball clay as a heterogeneous Fenton catalyst for the decolorization of Reactive Blue, with a 99% decolorization efficiency of RB achieved within 140 min of reaction time [5]. Our research group prepared the Fe-Mn-sepiolite catalyst by a homogeneous precipitation method for use as a heterogeneous Fenton-like catalyst that could efficiently remove reactive brilliant blue from aqueous solution [12].

However, the use of the Fenton oxidation only one time for complete mineralization of organic pollutants may be expensive, and the stability of the processing efficiency cannot be guaranteed. In recent years, the combination of the Fenton oxidation and biological processes has received increasing attention [13]. According to the characteristics of recalcitrant wastewater, showing a low biodegradability and high organic carbon content, a good coupling strategy consists of a pre-oxidation step using AOPs [14,15]. In the pre-treatment, the recalcitrant organic compounds are transformed into easily biodegradable intermediates, enabling the use of a biological process as a post-treatment to comply with the discharge limits [14,15]. Therefore, the combined Fenton oxidation and biological processes were widely used to treat different types of recalcitrant wastewater, such as hydrolyzed polyacrylamide wastewater, textile wastewater, wastewater from detergent production, and so on [16]. For the combination of the Fenton oxidation and biological oxidation for the treatment of industrial wastewater, the stability of the system can be improved, and the processing cost of the wastewater can be reduced. Because H_2O_2 consumption is the critical issue in the economy of the Fenton oxidation, the ecotoxicity and biodegradability of the effluents from this process at different H_2O_2 doses have been analyzed [17]. Sanchis indicated that working at 40–60% of the stoichiometric H_2O_2 dose in the Fenton step was the best option for the combined treatment [17]. Therefore, when using the Fenton oxidation as the pre-treatment, the dosage of hydrogen peroxide in the Fenton system could be reduced, thus decreasing the cost of the process.

Unfortunately, the current studies are a one-sided pursuit focused on a homogeneous Fenton process for high chemical oxygen demand (COD) removal rate as the pre-treatment step. The effect of treating the wastewater by a homogeneous Fenton pre-treatment on the sludge characteristics and microbial community in the biological post-treatment unit was ignored. The sludge characteristics and microbial community play a key role in the efficient operation of a biological treatment unit. Currently, the combined heterogeneous Fenton-like oxidation and biological treatment process for the treatment of industrial wastewater containing toxic pollutants has rarely been reported. After a heterogeneous Fenton-like pre-treatment, research on the effluent effects on the microbial community structure and the physical and chemical properties of the anaerobic granular sludge in the post-treatment biological treatment unit has not been reported.

In the present work, the combined process of a heterogeneous Fenton-like oxidation and a double circle (DC) anaerobic reactor process was applied to treat traditional Chinese medicine (TCM) wastewater containing a high concentration of rhein (1,8-dihydroxy-3-carboxy anthraquinone). The inhibitory effect of rhein on the methanogenic activity of anaerobic granular sludge was investigated. Similarly, the treatment performances of TCM wastewater by the combined process were evaluated in this study. In addition, the effect of a heterogeneous Fenton-like oxidation pre-treatment on the anaerobic granular sludge characteristics and the microbial community was evaluated using 3D-excitation-emission matrix (EEM), Fourier transform infrared (FTIR) spectroscopy, and Miseq Illumina.

2. Materials and methods

2.1. TCM wastewater characteristics

The TCM wastewater in this study was obtained from a TCM plant in Guangxi, China. The composition of the wastewater was as follows: COD 3500–4000 mg/L, BOD 1300–1800 mg/L, rhein 1–5 mg/L, and pH 5.0–5.5.

2.2. Methanogenic inhibition of rhein and recover experiments

To investigate the effect of rhein on methanogens, anaerobic toxicity and recovery experiments were performed. In the anaerobic toxicity tests, 1.5 ± 0.1 g VSS/L of stabilized anaerobic granular sludge was added to 150 mL serum bottles. Anaerobic granular sludge was obtained from a DC reactor treating TCM wastewater in our laboratory. The anaerobic conditions were established by flushing the headspace with N_2 and adding 2000 mg COD/L cosubstrate (glucose) and rhein (concentration of 20 mg/L, 50 mg/L and 100 mg/L) to the bottles. The pH value of the solution in each bottle was adjusted to 7.0–7.5 using sodium bicarbonate. Then, the bottles were sealed with butyl rubber stoppers and incubated in a shaker (120 r/min) at 30 ± 1 °C. Methane productions were measured at certain time intervals during a 5-day reaction [18,19]. After the end of the toxicity experiment, all of the bottles were kept stationary for 2 h for the precipitation anaerobic granular sludge. Then, the anaerobic granular sludge in the bottle was cleaned with deionized water. A glucose solution with a COD of approximately 2000 mg/L was added to the bottle. The accumulative methane production of each bottle was analyzed as the anaerobic toxicity experiment. The methane-producing relative activities (RA) was then calculated as the percentage of the ratio of accumulated methane production in the rhein bottles and the control bottle (without rhein) [19].

2.3. Heterogeneous Fenton-like oxidation pre-treatment process

Heterogeneous Fenton-like oxidation was performed in batch mode using a 1000 mL beaker with a TCM wastewater volume of 1000 mL and an increasing rhein concentration to 15–20 mg/L. Fe-Mn-sepiolite was used as a heterogeneous Fenton-like catalyst and was prepared by a homogeneous precipitation method according to a previous procedure [12]. Heterogeneous Fenton-like catalyst (0.6 g) was added to the beaker, and then, 1.27 mL of hydrogen peroxide was added to the mixture. In the following step, the solution was mixed with a magnetic stirrer at 150 r/min for 1 h [20]. After the oxidation, the catalyst descended to the bottom of the beaker. The supernatant was withdrawn for the anaerobic biological step treatment. The pH value of the supernatant was adjusted to 7.0–7.5 using sodium bicarbonate.