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Efficient organic pollutants removal from industrial paint wastewater plant employing Fenton with integration of oxic/hydrolysis acidification/oxic

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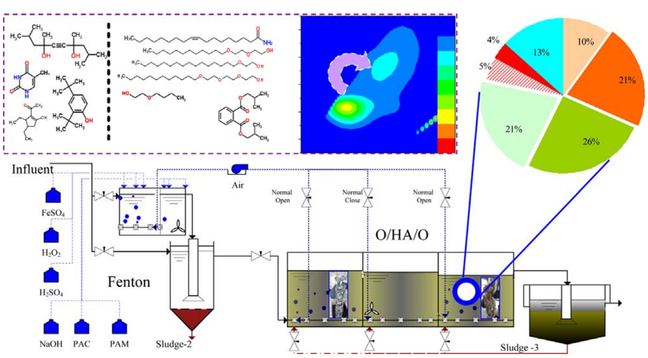
GRAPHICAL ABSTRACT



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ABSTRACT

Industrial paint wastewater (IPW) contains highly toxic and high concentration of organic refractory pollutants, which was normally treated through sole physicochemical technology. This paper introduces an effective approach for organic removal from a bench scale test by Fenton integrated with oxic/hydrolysis acidification/oxic (FT-O/HA/O) bioprocess. Then, the performance of the integrated FT-O/HA/O process was evaluated in a real IPW treatment plant: a significant COD removal of 97.3% was achieved, making the effluent COD stabilized at 430 mg/L in average (below discharge standard 500 mg/L). In the mechanism study, organic compounds degradation pathway was proposed using gas chromatography–mass spectrometer (GC–MS) which revealed that the various kinds of linear hydrocarbon appeared after the first stage aerobic stage (O_1). Meanwhile, considerable amounts of aromatic organic matters with benzene rings were degraded after Fenton and O_1 stage. Excitation-emission matrix (EEM) fluorescence spectra indicated that the Fenton and O_1 stage significantly reduced the fluorescence intensity of proteinaceous tryptophan-like matter. Furthermore, the molecular weight distribution elucidated that the biodegradable small weight organics were dominated in the following HA/O process. Microbial community structures revealed that *Proteobacteria* became the most dominant phylum in all

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stages, whereas *Acetobacter*, *Brachymonas*, *Sphingobium* and *Novosphingobium*, as the crucial contaminant degraders, proliferated in the microbial consortium of O/HA/O bioprocess, making the overall integration system more effective and reliable.

1. Introduction

The industrial paint wastewater (IPW) is mainly generated in the equipment-cleaning process of the paint manufacturing company, which contains binders, dyestuffs, emulsifying agents, pigments, solvent and additives [1]. The wastewater is characterized by highly toxic and high concentration of organic biorefractory contaminants, which has adverse effects on the aquatic life and human health [2,3]. Therefore, in China, most of the paint manufacturing companies are in the industrial park, where the centralized wastewater treatment plant (CWTP) accepts the effluent of treated IPW within the legal thresholds concentration.

In recent years, the state-of-the-art technologies were studied for the removal of organic contaminants, like coagulation-flocculation [4], modified membrane separation [5,6], enhanced biological degradation [7], electrochemical process [8], Fenton-like process [9,10]. Especially, the Fenton oxidation combined with the biological treatment is one of the most cost-effective technologies for treating the recalcitrant industrial wastewater [11–14]. It was reported that biodegradability of wastewater was improved through Fenton process that benefits the biological process [15,16]. However, only physicochemical process was reported for IPW treatment, like electro-coagulation [17], Fenton [18] and electrochemical oxidation [2,19]. The combination of physicochemical and biological process for IPW has not been well studied so far.

The biological treatment bioreactors with hydrolysis acidification/oxic (HA/O) process were extensively studied for treating high strength organic wastewater [6,14,20]. Highly polluted wastewater was treated through the use of anaerobic reactor due to the crucial step of the hydrolysis acidification stage and converted the refractory and inhibitory compounds into the readily biodegradable intermediates that were suitable for the following aerobic biological treatment. However, anaerobic bioreactor showed low growth rate of microbe and process instabilities which made it vulnerable when treating highly toxic wastewater, like IPW. In the literature, aerobic process was demonstrated as an option of detoxification for further hydrolysis acidification stage when treating high toxic coking wastewater [7]. It can be speculated that aerobic stage in front of HA/O system, i.e., O/HA/O bioprocess, might accelerate the efficiency of biological treatment of treating IPW, which needs substantiating.

On the other hand, the effectiveness of bioprocess in treating wastewater is determined by the microbial community structure, which could be examined through 16S rRNA-based high-throughput pyrosequencing technology [21,22]. However, a wide array of factors might affect the determination of the microbial community structure from 16S rRNA gene amplicons. For example, conserved 16S primer selection can significantly affect species evenness [23]: primer pairs targeting V1-V3 [24], V3-V4 [21] and V4-V5 [25] region had been applied in both aerobic and anaerobic bioreactors. To make a clear vision of the microbial community structure h stage of O/HA/O bioprocess treating IPW, it is essential to select different sets of bacteria-specific primer pairs for each biosample.

Therefore, in this study, the bench scale experiment was carried out to determine a suitable IPW treatment proposal. Then, the performance of the integrated process (FT-O/HA/O) was further evaluated in a real IPW treatment plant. Furthermore, the proposed degradative pathway was identified via GC–MS. The variation of organic contaminants during each stage of the integration process was characterized using ultraviolet–vis (UV–VIS) spectrophotometry, excitation-emission matrix (EEM) fluorescence spectroscopy and molecular weight distribution. Finally, the microbial community structure was investigated to evaluate the reliability of O/HA/O bioprocess in treating IPW.

2. Materials and methods

2.1. Proposal optimization in bench scale experiment

For bench scale test, raw wastewater presenting kermesinus with aldehydes-like pungent odor was fetched from the storage tank of the paint manufacturing company (Fig. S1). It was characterized as shown in Table 1. Four proposals of different physic-chemical-biological processes were compared as shown in Fig. 1. Poly-aluminum chloride (3% PAC) dosage at 0.15 (v/v) was selected as the flocculant for coagulation/flocculation process (CF) in Proposal 1 and 2 (P1, P2). In P2 to P4, Fenton reactions were conducted respectively in 1 L beaker with a magnetic stirring apparatus (Fig. S1). The wastewater was acidified to a certain pH using 1 M H_2SO_4 or 1 M NaOH. Then, certain amount of $FeSO_4{\cdot}7H_2O$ and H_2O_2 was added. After a certain duration time of Fenton reaction, 3 mM sodium hydroxide was added to quench the residual H_2O_2 by approximately 99.3% (Fig. S2). Immediately, Fe(III) hydroxides was formed and removed by precipitation. According to the preliminary study of Fenton reaction (Table S1) and the previous studies [26–28], 3 mM $FeSO_4{\cdot}7H_2O$ and the reaction time of 2 h were adopted. Then, response surface methodology (RSM, version 8.05, Stat-Ease, Inc., USA) was utilized to optimize residual conditions of Fenton reaction, i.e., pH and H_2O_2, in which the coded levels of the variables were designed in Table S2. As shown in Table S3, the statistical significance of the models ($p < 0.001$) and their terms were evaluated by ANOVA. The mathematical regressions could be obtained as R_{COD} (%) $= 24.98 + 11.85 \times pH + 5.19{\cdot}H_2O_2 - 0.13 \times pH{\cdot}H_2O_2 - 1.68 \times pH^2 - 0.18{\cdot}H_2O_2$, where R_{COD} means the predicted COD removal efficiency. According to 3D surface graphs (Fig. S3), Fenton reaction could be thus optimized at pH 3.0 and H_2O_2 dosage of 12.9 mM.

During the biological treatment process of HA/O in P1 to P3, hydrolysis acidification stage (HA) was operated for 8 d, while aerobic stage (O) was adopted subsequently for 5 d. While in P4, the first aerobic stage (O_1) was arranged initially for 4 d, followed by 4 d of HA and 5 d of second aerobic stage (O_2), named O/HA/O process. During each stage, COD of the wastewater was assayed. The characteristic and pretreatment method for the activated sludge used for biological treatment process was detailed in Supplementary Information.

Table 1
IPW influent characteristic and effluent discharge standard.

Contaminants (mg/L)	Bench scale[a]	Full scale[b]	Discharge standard[c]
COD_{-total} (TCOD)	17,080 ± 1100	15,890 ± 4790	< 500
BOD	1450 ± 270	1060 ± 590	< 300
NH_3-N	Not test	45 ± 12	< 40
SS	915 ± 330	860 ± 280	< 400
Color (Times)	2400	2000	< 60
pH	6.5	6–9	69

[a] Raw wastewater for bench scale test was obtained from the storage tank of IPW, which is collected from the equipment cleaning procedural of the paint manufacturing company.
[b] Values are collected during the full regime period, which was presented as means ± deviations.
[c] Discharge standard was referred to Shanghai local regulation of "Discharge Standard For Municipal Sewerage System" detailed in DB31/445-2009.