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Upgrading the Chinese biggest petrochemical wastewater treatment plant: Technologies research and full scale application

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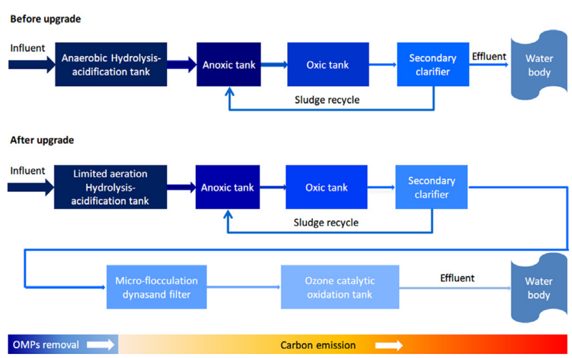
HIGHLIGHTS

- A combined process for the treatment of petrochemical wastewater is proposed.
- Good organic micropollutants removal can be achieved in the full-scale application.
- The effluent shows low acute toxicity and genotoxicity.
- Electricity need increases 44.1% for elimination of organic micropollutants.

GRAPHICAL ABSTRACT



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ABSTRACT

The components of petrochemical wastewater (PCWW) are very complex and it is one of the most important sources of organic micropollutants (OMPs) in water bodies. To improve the effluent qualities of PCWW, the Chinese government has promulgated a new Emission Standard of Pollutants for Petroleum Chemistry Industry. More than 60 types of OMPs, most of which are toxic organics, are added and strictly limited in the standard. Based on the bench- and pilot-scale experiments, a pretreatment (microaerobic hydrolysis and acidification, MOHA), biological (anoxic/oxic process, A/O) and advanced treatment (micro-flocculation dynasand filtration and catalytic ozonation, MFDF-CO) integrated process is proposed. The full-scale application in the Chinese biggest petrochemical wastewater treatment plant has demonstrated that the performance of the integrated process is stable and it can significantly improve the effluent qualities. The effluent COD decreased from 84.7 to 47.0 mg/L and most of the OMPs were removed. The EC_{50} of the effluent for luminescent bacteria assay, algal growth inhibition, *Daphnia magna* inhibition test and zebrafish eggs test are all higher than 100% and the

Abbreviations: A/O, anoxic/oxic process; AHA, anaerobic hydrolysis and acidification; AOPs, advanced oxidation process; BOD_5, 5 d biochemical oxygen demand; CMA, China Metrology Accreditation; CO, catalytic ozonation; COD, chemical oxygen demand; DO, dissolved oxygen; DOM, dissolved organic matter; EC_{50}, the concentration for 50% of maximal effect; EPS, extracellular polymeric substances; EU, European Union; FID, flame ionization detector; GC–MS, gas chromatography–mass spectrometer; HA, hydrolysis and acidification; HIS, hydrophilic substances; HOA, hydrophobic acids; HOB, hydrophobic bases; HON, hydrophobic neutrals; HRT, hydraulic retention time; I_R, induction rate; LB-EPS, loosely bound extracellular polymeric substances; LID, the lowest ineffective dilution; MFDF, micro-flocculation dynasand filtration; MLSS, mixed liquid suspended solids; MLSS, mixed liquor suspended solid; MOHA, microaerobic hydrolysis and acidification; OMPs, organic micropollutants; ORP, oxidation-reduction potential; PAFC, poly aluminum ferric chloride; PCWW, petrochemical wastewater; SOB, sulfate-oxidizing bacteria; SRB, sulfate-reducing bacteria; SS, suspended solids; SVOCs, semi-volatile organic compounds; TB-EPS, tightly bound extracellular polymeric substances; TN, total nitrogen; TOC, total organic carbon; VOCs, volatile organic compounds; WWTP, wastewater treatment plant.

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Full-scale application
Carbon emission

induction rate (I_R) for genotoxicity is only 0.76. The energy demand, however, with the electricity consumption increase by 44.1%, is very high for OMPs removal, leading to high indirect carbon emission.

1. Introduction

The potential accumulation of OMPs in the aquatic environment may cause negative impact on human health and other environmental problems (Deblonde et al., 2011). Study on OMPs, concerning the measurement, removal, toxicity and health impact, is one of the focuses in the field of environmental engineering (Jiang et al., 2013). It is reported that industries, such as petrochemical (Grandclément et al., 2017) and pharmaceutical (Kim et al., 2007), are the important sources of the OMPs to the aquatic environment. In the last decade, the petrochemical industry has developed very fast in China. The total business income was as high as 1.75 trillion dollars in 2015. There is a trend of gathering different producing plants, such as oil refining plants, petrochemical intermediates plants and synthesis material plants, into integrated petrochemical parks. In China, >390 petrochemical parks have been built and 2.66×10^9 t of PCWW is discharged per year (MEPPRC, 2014).

The PCWW is characterized by high organic pollutants and sulfate concentration (Wu et al., 2016a), high toxicity (Liu et al., 2014) and low biodegradation (Yang et al., 2015). Due to the toxicity of the wastewater, pretreatment is recommended during which HA is used as the most option (Wu et al., 2015a). HA can break macromolecular and particular organic compounds into micromolecular and simple soluble compounds such as VFAs. Thus, it can enhance the treatability of the PCWW (Bai et al., 2013). The sulfate content in the PCWW is relatively high (380–552 mg/L) (Yang et al., 2015). The high sulfate and its reduction product of HS^- or H_2S during HA can cause toxic and inhibition effect on biological process (Zhang et al., 2013a, 2013b), such as irreversible inhibition of the anaerobic digestion (Kanjanarong et al., 2017). To overcome the negative effect, some novelty technologies, such as acidification with Fe_2O_3 dosage, were proposed (Zhang et al., 2013a, 2013b). However, the Fe_2O_3 dosage obviously increases the operation cost and its effect on the performance of following biological unit is unknown. Previous study has shown that the MOHA is an effective PCWW pretreatment technology (Wu et al., 2015a, 2015b).

Many OMPs cannot effectively be removed by the conventional biological WWTP because some OMPs are not biological degradable (Luo et al., 2014; Altmann et al., 2015; Grandclément et al., 2017). Upgrading WWTP or adding additional process units are the essential options to control the OMPs emission. Previous studies also has shown that petrochemical secondary effluent treated by biological processes contains some OMPs (Rubio-Clemente et al., 2015), even shows a certain degree of aquatic toxicity (Wu et al., 2015b). The advanced treatment technology is needed to develop. AOPs, such as CO, is used as the most option for the advanced treatment (Giannakis et al., 2015). The SS of the petrochemical secondary effluent is approximately 35 mg/L, which is obviously higher than that in municipal secondary effluent of 3.8–5.1 mg/L as reported by Altmann et al. (2015). The wastewater particles adversely affect the ozonation efficiency (Zucker et al., 2015). To reduce the invalid ozone consumption, high removal of SS is needed before catalytic ozonation process. Previous study has proved that the MFDF is suitable as the pretreatment option for the CO for the advanced treatment of petrochemical secondary effluent (Wu et al., 2016b). However, the relationship between MFDF and CO, toxicity reduction and full-scale application are still needed to investigate.

To control the OMPs emission, many countries have released or revised discharge standards, such as the Micropoll Strategy for Switzerland (Giannakis et al., 2015) and Contaminants of emerging concern Decision 2015/495/EU in EU Environmental Quality Standards (Sousa et al., 2018). China has also revised many industrial wastewater emission standards to control the OMPs emission since 2008. For petrochemical industry, a new Emission Standard of Pollutants for Petroleum Chemistry Industry (GB 31571-2015) was implemented in July 1, 2017 to replace the implemented standard (GB 8978-1996) (MEPPRC, 2015). More than 60 types of OMPs, most of which are toxic organics (EPA, 2000a, 2000b), are added into the new standard with strict discharge concentrations (See Supporting Information, SI).

From 2012 to 2014, a series of bench-scale (2–10 L/h) and pilot-scale (1–2 m^3/h) experiments, targeting at the OMPs control treating PCWW, have been finished (Yang et al., 2015; Wu et al., 2015a, 2015b, 2016a, 2016b; 2017). Based on the research achievements, a full-scale petrochemical park WWTP, which is the biggest petrochemical WWTP in China, was upgraded in November 2014.

A few papers have been published so far to describe the full-scale application of OMPs removal in industrial wastewater treatment, especially in PCWW. Most of the previous studies focus on the OMPs removal efficiency and process-dependent performance in the advanced treatment of municipal WWTP (Hollender et al., 2009; Luo et al., 2014; Mousel et al., 2017). Since the type and concentration of pollutants in PCWW are obviously different from municipal wastewater and the OMPs removal is dependent on compound- and process-specific factors (Luo et al., 2014). More detailed descriptions of the standard, technology investigation process, OMPs removal, toxicity variation and energy distribution when upgrading petrochemical WWTP are lacking.

After upgrade, start-up and operation for more than one year, this paper reflects not only on the performance, such as COD and OMPs removal, but also on technology mechanism and investigation process, effluent toxicity and especially design considerations. Furthermore, the full-scale application energy demand and distribution concerning the carbon emission is also discussed in detail. The technologies developed by us have been recognized as a general upgrade technology for petrochemical WWTP, and it is now being recommended in China.

2. Materials and methods

2.1. Description of the petrochemical WWTP

The selected WWTP, located in the northeast of China, is the biggest petrochemical WWTP in China. It is the centralized WWTP of a petrochemical park. The petrochemical park has >50 sets of petrochemical production plants, including refinery plants, petrochemical intermediates (such as ethylene, aromatics and acrylonitrile) production plants, and petrochemical synthetic material (synthetic resins and rubbers) plants. The influent flowrate is about 5000 m^3/h. The main processing units of the WWTP are AHA tank, A/O tank and the secondary clarifier (Fig. S1). The volumes are 100,000, 120,000 and 19,500 m^3 with the HRT of 20, 24 and 3.9 h, respectively. The MLSS in the A/O tank is 4000–6000 mg/L with the SRT of 17–24 d. The sludge recycle rate is 100% as previously optimized (Wu et al., 2016a). The SVI of the sludge in A/O tank is 67–85 mL/g. The wastewater characteristics of influent and effluent are given in Table S2.

2.2. Research reactor setups and operation

The research plans of this study are shown in SI. The pretreatment and the advanced treatment of biological secondary effluent are the focusses of the research. To investigate the pretreatment of PCWW and the advanced treatment of biological secondary effluent, a serial