Water Research 101 (2016) 457–466

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres

# Coupling of iron shavings into the anaerobic system for enhanced 2,4-dinitroanisole reduction in wastewater

Changjin Ou [a], Jinyou Shen [a, *], Shuai Zhang [a, c], Yang Mu [b], Weiqing Han [a], Xiuyun Sun [a], Jiansheng Li [a], Lianjun Wang [a, **]

[a] Jiangsu Key Laboratory of Chemical Pollution Control and Resources Reuse, School of Environmental and Biological Engineering, Nanjing University of Science and Technology, Nanjing 210094, China
[b] CAS Key Laboratory of Urban Pollutant Conversion, Collaborative Innovation Centre of Suzhou Nano Science and Technology, Department of Chemistry, University of Science and Technology of China, Hefei 230026, China
[c] Jiangsu Changhuan Environmental Science Co. LTD, Changzhou 213022, China

ARTICLE INFO

*Article history:*
Received 7 April 2016
Received in revised form
1 June 2016
Accepted 2 June 2016
Available online 4 June 2016

*Keywords:*
Reduction
Upflow anaerobic sludge blanket
Iron shavings
2,4-Dinitroanisole
Microbial community

ABSTRACT

Packing of iron powder into anaerobic system is attractive for enhancing removal of recalcitrant pollutants from wastewater, but is limited by various inherent drawbacks of iron powder, such as easy precipitation and poor mass transfer. To address the above issues, iron shavings were packed into an upflow anaerobic sludge blanket (UASB) for enhancing 2,4-dinitroanisole (DNAN) reduction in this study, with system stability and microbial biodiversity emphasized. The results showed that both DNAN reduction and 2,4-diaminoanisole (DAAN) formation could be notably improved in the iron shavings coupled UASB system. Moreover, the ability to resist environmental stress was also strengthened through the addition of iron shavings in the UASB reactor. Compared with a loose and rough surface of the sludge in the control UASB reactor, the sludge in the coupled system presented a compact, rigid and granular appearance under iron shavings simulation. Furthermore, high throughput sequencing analysis indicated that the diversity of microbial community in the iron shavings coupled UASB system was significantly higher than that of the control UASB reactor. Additionally, species related to DNAN reduction and methane production were enriched in the coupled system. The observed long-term stable performance highlights the full-scale application potential of iron shavings coupled anaerobic sludge process for the treatment of nitroaromatic compounds containing wastewater.



## 1. Introduction

Anaerobic biotechnology has been widely used for the removal of various organic contaminants from industrial effluent, owing to its high removal efficiency and low operation cost (Chan et al., 2009). Under anaerobic condition, various oxidative contaminants such as nitroaromatic compounds (NACs) succumb to electrophilic attack more readily, resulting in the reduction of nitro group and the formation of corresponding aromatic amines. Compared with the parent NACs, the corresponding aromatic amines are less toxic and easier to be mineralized in the aerobic biosystem (Shen et al., 2014). However, due to the highly recalcitrant and toxicological nature of NACs, conventional anaerobic bioprocess is usually limited by low removal rate and poor stability. Furthermore, NACs transformation could be severely inhibited due to the competition of electron donor by other side reactions, e.g., methanogenesis, denitrification or sulfate reduction. As a consequence, the consumption of electron donor far exceeded the theoretical dosage, resulting in the remarkably increase of operation cost. Therefore, how to improve the efficiency of anaerobic bioprocess for the remediation of NACs wastewater presents an imperative but also challenging task.

ZVI, as an effective reducing reagent ($E^0 = -0.44$ V vs SHE), has been widely applied in the treatment of wastewater and groundwater, for the removal of less biodegradable pollutants, such as azo dyes, halogenated organic compounds and NACs (Chatterjee et al.,

* Corresponding author.
** Corresponding author.
*E-mail addresses:* shenjinyou@mail.njust.edu.cn (J. Shen), wanglj@mail.njust.edu.cn (L. Wang).

http://dx.doi.org/10.1016/j.watres.2016.06.002
0043-1354/

2010; Su et al., 2012; Agrawal and Tratnyek, 1995). In light of the previous studies, ZVI is usually used in the pretreatment process prior to the biological treatment for the increase of biodegradability (Oh et al., 2005). However, due to the direct involvement of $H^+$ in the corrosion reactions and the mass transport limitations imposed by the precipitation of a passive film on the metal surface, the reactivity of ZVI drops sharply with the increase of pH and thus ZVI technology is generally only efficient under acidic conditions (Guan et al., 2015). Recently, attentions have been increasingly paid to the combined utilization of ZVI into the anaerobic wastewater treatment system (Yu et al., 2006; Liu et al., 2011). The inspiration of this coupled system was based on the fact that the passivation on the ZVI surface could be alleviated under anaerobic condition, which permitted it to function stably. Meanwhile, considering its reductive property, ZVI corrosion process may create a more favorable anaerobic environment for microorganisms by lowering oxidation-reduction potential (ORP) and buffering acid (Liu et al., 2011). More importantly, the hydrogen released from iron corrosion can act as a potential electron donor for hydrogen-consuming microorganisms, such as methanogenic and denitrifying bacteria, as well as some reduction related species (Son et al., 2006). Several recent studies have indicated that azo dye decolorization could be remarkably improved through the combined use of anaerobic sludge and ZVI (Liu et al., 2012; Li et al., 2013). In addition, anaerobic sludge digestion process could also be significantly accelerated through the addition of ZVI particles (Feng et al., 2014).

The previous studies on the ZVI coupled anaerobic system were mainly focused on the use of ZVI powder, which has high surface area and reactivity (Liu et al., 2012; Li et al., 2013; Feng et al., 2014). However, coupling of ZVI powder into an anaerobic system was restricted, probably due to the inherent characterization of ZVI powder, such as large density and easy precipitation, resulting in encapsulation of bacteria and inhibition of bacterial activity (Shrout et al., 2005). In addition, the mobility of sludge could be seriously restricted at the presence of ZVI powder (Zhang et al., 2014). As a result, the mass transfer efficiency between sludge, ZVI and liquid is likely to be limited in this coupled system. Iron shavings might be a better choice to address the above issues in anaerobic biosystems. The primary reason for the selection of iron shavings was the excellent mechanical and hydraulic characteristics (e.g., high porosity) as a filter medium, which could allow better mass transfer compared to ZVI powder. In addition, the abundant local supply and the relatively low cost (~$0.25/Kg) make it promising for large-scale application as a substitute for conventional iron powder (Ma and Zhang, 2008). However, the available information is still limited on the coupling of the iron shavings in the anaerobic process for the bioremediation of various recalcitrant contaminants, such as, NACs. Additionally, as an important participator, the microorganisms are vital to the performance of the coupled system. However, the clear microbial community succession under the iron shavings simulation has not yet been fully understood.

Therefore, this study aimed at investigating the feasibility of coupling iron shavings into the UASB system for efficient NACs reduction from wastewater. DNAN was selected as a model pollutant because of its potential ecological risks and poor biodegradability. The effectiveness and stability of the coupled system were tested under variable operational conditions, including hydraulic retention time (HRT), DNAN concentration and salinity. Moreover, the long-term performance of the coupled system was also evaluated. Additionally, the succession of microbial community structure in this coupled system was characterized to reveal synergistic effect of iron shavings and anaerobic microorganism for pollutant removal.

## 2. Materials and methods

### 2.1. Reactor, inocula and substrate

The schematic diagram of the coupled system is depicted in Fig. S1 in Supplementary Information (SI). A ZVI bed ($\phi$80 mm × 250 mm) was installed near the bottom of a UASB reactor ($\phi$100 mm × 500 mm). The UASB reactor was made of plexiglass column with working volume of 3.9 L. The ZVI bed was consisted of titanium mesh basket packed with 500 g iron shavings (30CrMoSi steel) collected from a mechanical factory. In addition, a same UASB reactor was operated without the addition of iron shavings inside as the control.

The composition of the synthetic wastewater was as follows: $KH_2PO_4$ 0.1 g $L^{-1}$, $NH_4Cl$ 0.24 g $L^{-1}$, $MgCl_2$ 0.2 g $L^{-1}$, $CaCl_2$ 0.02 g $L^{-1}$, NaCl 10 g $L^{-1}$, SL-4 10 mL $L^{-1}$, methanol 1.67 g $L^{-1}$ and DNAN at a desired concentration. The trace element solution SL-4 was prepared according to our previous study (Shen et al., 2009). In order to prevent pre-degradation prior to anaerobic treatment, the synthetic wastewater had been sterilized in an autoclave sterilizer before methanol was added. In addition, the synthetic wastewater was replaced every 4 days to keep it fresh. Both coupled and control systems were inoculated with sludge from an anaerobic baffled reactor treating real wastewater containing NACs. Both coupled and control systems were inoculated by 6.0 g $L^{-1}$ mixed liquor volatile suspended solids (MLVSS). In order to enrich functional microbes, the DNAN concentration was gradually increased from 50 to 120 mg $L^{-1}$ during the startup period. The operational temperature was maintained at 35 ± 2 °C through water jackets.

### 2.2. Reactor operation

After 35 days' acclimatization, both the coupled system and the control UASB reactor reached to a steady status, judging from the slight variation of DNAN reduction efficiency as well as the COD removal efficiency. Thereafter, the experimental period was divided into four phases and the experimental conditions of each phase are summarized in Table 1. In phase I, the influent containing 120 mg $L^{-1}$ DNAN was continuously fed into the iron shavings coupled UASB system at a rate of 1.2 L $d^{-1}$, resulting in a HRT of 78 h. Once DNAN was completely degraded in the coupled system, the HRT started to be shortened and gradually reduced to 38 h to evaluate the system performance at low HRT. In phase II, the effect of DNAN concentration on the performance of the coupled system was investigated. The influent DNAN concentration was gradually increased from 120 to 160 mg $L^{-1}$ at a fixed HRT of 58 h. In phase III, the effect of salinity on system performance was evaluated in the range of 1%–5% (w/v) with NaCl as a salinity source. DNAN concentration and HRT were maintained at 120 mg $L^{-1}$ and 58 h, respectively. In phase IV, the long-term performance of the coupled system was evaluated, where DNAN concentration, HRT and salinity were maintained at 120 mg $L^{-1}$, 58 h and 1%, respectively. The same procedures were also conducted in the control UASB reactor. At least five independent samples were taken and analyzed in order to confirm the reactor reached a steady state. The five independent analysis data were averaged and the standard deviation was calculated in this study.

### 2.3. Analytical methods

DNAN and its reductive products such as DAAN were identified and quantified by HPLC. The HPLC analysis was conducted using an RP18 column (5 μm, 4.6 × 250 mm) with temperature of 35 °C and a UV–vis detector at 254 nm. DAAN formation efficiency was evaluated as the ratio of DAAN in the effluent (mol) and DNAN in the