



Impact of electrochemically generated iron on the performance of an anaerobic wastewater treatment process



Zhetai Hu ^a, Shihu Hu ^a, Pei-Ying Hong ^b, Xueqin Zhang ^a, Veljko Prodanovic ^c, Kefeng Zhang ^c, Liu Ye ^d, Ana Deletic ^{c,e}, Zhiguo Yuan ^a, Min Zheng ^{a,*}

^a Australian Centre for Water and Environmental Biotechnology, The University of Queensland, St Lucia, QLD 4072, Australia

^b Biological and Environmental Science and Engineering Division, King Abdullah University of Science and Technology (KAUST), Thuwal, SA 23955, Saudi Arabia

^c School of Civil and Environmental Engineering, UNSW Sydney, NSW 2052, Australia

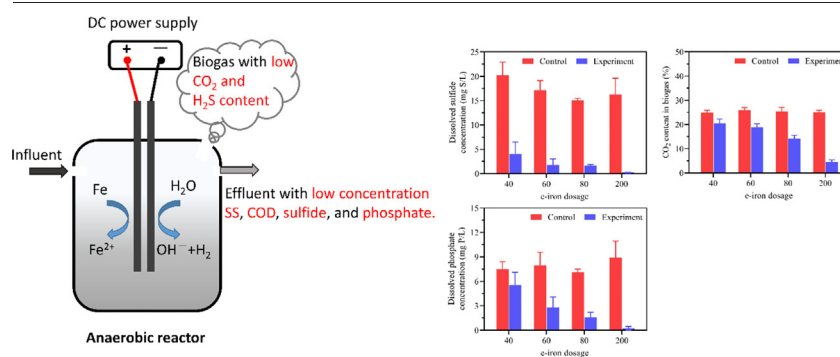
^d School of Chemical Engineering, The University of Queensland, St Lucia, Brisbane, QLD 4072, Australia

^e School of Civil and Environmental Engineering, Engineering Faculty, Queensland University of Technology, QLD 4001, Australia

HIGHLIGHTS

- E-iron dosage of 40–200 mg Fe/L was tested in an anaerobic sewage treatment process.
- An increase of 79.8–98.5 % in dissolved sulfide reduction was obtained.
- Phosphate removal efficiency increased by 26.0–96.0 %.
- CH₄ production rate increased by 12.0–21.3 % while CO₂ content in biogas decreased.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Huu Hao Ngo

Keywords:

Electrochemical iron production
Anaerobic wastewater treatment
Sulfide control
Phosphate removal
Biogas upgrading

ABSTRACT

Anaerobic treatment of domestic wastewater has the advantages of lower biomass yield, lower energy demand and higher energy recover over the conventional aerobic treatment process. However, the anaerobic process has the inherent issues of excessive phosphate and sulfide in effluent and superfluous H₂S and CO₂ in biogas. An electrochemical method allowing for in-situ generation of Fe²⁺ in the anode and hydroxide ion (OH⁻) and H₂ in the cathode was proposed to overcome the challenges simultaneously. The effect of electrochemically generated iron (e-iron) on the performance of anaerobic wastewater treatment process was explored with four different dosages in this work. The results showed that compared to control, the experimental system displayed an increase of 13.4–28.4 % in COD removal efficiency, 12.0–21.3 % in CH₄ production rate, 79.8–98.5 % in dissolved sulfide reduction, 26.0–96.0 % in phosphate removal efficiency, depending on the e-iron dosage between 40 and 200 mg Fe/L. Dosing of the e-iron significantly upgraded the quality of produced biogas, showing a much lower CO₂ and H₂S contents in biogas in experimental reactor than that in control reactor. The results thus demonstrated that e-iron can significantly improve the performance of anaerobic wastewater treatment process, bringing multiple benefits with the increase of its dosage regarding effluent and biogas quality.

1. Introduction

In contrast to conventional aerobic treatment process, the anaerobic process has the advantages of low energy demand, low sludge production,

* Corresponding author.

E-mail address: m.zheng@uq.edu.au (M. Zheng).

and superior energy balance through methane (CH_4) recovery (Li and Yu, 2016; Wan et al., 2016; Garfi et al., 2017; Liu et al., 2021a; Liu et al., 2021b; Lim et al., 2023; Wang et al., 2022). Despite these benefits, this process still has several inherent issues, i.e., i) sulfate in influent can be reduced by sulfate-reducing bacteria to generate notorious hydrogen sulfide (H_2S), leading to odour and safety concerns and risk of equipment corrosion (Vollertsen et al., 2008; Yongsiri et al., 2005); ii) as phosphorus cannot be removed, discharging the effluent rich in phosphorus can cause water eutrophication (Carpenter, 2005; Schindler et al., 2016); and iii) biogas normally contains high CO_2 (30–50 %), which significantly reduces the lower calorific value (LCV) of per unit volume biogas and makes the biogas difficult to be compressed (Angelidaki et al., 2018; Lai et al., 2021). Effluent of the anaerobic treatment process contains residual ammonia that can be primarily removed by an autotrophic nitrogen removal process (Wang et al., 2021; Hausherr et al., 2022; Zheng et al., 2023).

Iron salts are widely used in urban water management system and also favor anaerobic wastewater treatment process (Rebosura et al., 2018a). Dosing of iron salts can form insoluble ferrous sulfide (FeS) and vivianite ($\text{Fe}^{2+}\text{Fe}_2^{2+}(\text{PO}_4)_2\cdot 8\text{H}_2\text{O}$), results in dissolved sulfide and phosphate reduction, thereby mitigating corrosion, obnoxious odors emission and water eutrophication (Calderon et al., 2021; Hu et al., 2021; Rebosura et al., 2018b; Salehin et al., 2020; Wilfert et al., 2016; Yuan et al., 2020). Nevertheless, iron chemicals currently used in the wastewater industry are mostly manufactured as by-products in metallurgical processes, which are then trucked to wastewater treatment sites and facilities. This includes a long-distance transportation with high costs. Recently, a technology of using electrochemical cell to produce iron salts from iron plates was developed (Lin et al., 2017). The electrochemical cell was built by setting two iron plates in the reactor, where Fe^{2+} was produced from sacrificial anodes (Fig. S1). Transportation of solid iron plates is much more cost-saving and enables safe handling, in comparison with the transportation of corrosive concentrated iron salts solution.

The electrochemical iron (e-iron) production and use were implemented and tested for sulfide control in sewers (Lin et al., 2017; Pikaar et al., 2019), and phosphorus control in effluents of wastewater treatment process (Hu et al., 2022). With a dosage of ~ 80 mg Fe/L, the e-iron significantly reduced dissolved sulfide and phosphate in the effluent of anaerobic bioreactor and H_2S in biogas (Hu et al., 2022). Moreover, e-iron production not only generates hydroxide ion (OH^-) but also H_2 that can be utilized by methanogens to consume CO_2 . Therefore, it is hypothesized that increasing an e-iron dosage can also enable in-situ biogas upgrading with a less CO_2 content. Together, it is possible to achieve simultaneous sulfide, phosphate, and CO_2 control by boosting the e-iron dosage, which requires more tests.

This study aims to perform a comprehensive assessment on the effect of different e-iron dosages on the performance of an anaerobic wastewater treatment process. Following our previous report at 80 mg Fe/L, three more different e-iron dosages (40, 60, and 200 mg Fe/L) were further studied in this work using experimental and control anaerobic bioreactors. During the 210 days of operation, effluent concentrations of total and volatile suspended solids (TSS and VSS), total chemical oxygen demand (TCOD), dissolved sulfur species, and phosphate, biogas production rates and its compositions in two reactors were monitored and compared.

2. Material and methods

2.1. Wastewater characteristics

Every two weeks, the fresh domestic wastewater was collected from a residential pumping station located at St Lucia, Queensland, Australia. After collection, the wastewater was immediately stored in a 1000-L storage tank located in a temperature-controlled (4°C) cold room to minimize biological transformation during storage (Duan et al., 2019). In the storage tank, the wastewater was mixed by a submerged pump (RSCD750, Ryobi) operated intermittently at an on/off ratio of 30/60 min. Prior to usage, the wastewater was warmed up to room temperature ($22 \pm 1^\circ\text{C}$) via a heater (IC-TH7100, RATEK). Table 1 summarizes characteristics of the used wastewater in this work.

Table 1

Characteristics of influent wastewater fed to anaerobic baffled reactors.

Parameters	Unit	Concentration (Mean \pm std)	Number of samples
TSS	mg SS/L	420.9 \pm 158.8	31
VSS	mg VSS/L	301.0 \pm 125.0	31
TCOD	mg COD/L	898.1 \pm 242.7	31
SCOD	mg COD/L	459.3 \pm 141.2	31
Ammonium	mg N/L	45.0 \pm 2.8	33
Phosphate	mg P/L	6.2 \pm 1.4	33
Sulfide	mg S/L	6.0 \pm 1.3	31
Sulfate	mg S/L	10.5 \pm 2.7	31
Sulfite	mg S/L	1.7 \pm 1.4	31
Thiosulfate	mg S/L	0.3 \pm 0.1	31
Total dissolved S (sulfide + sulfite + thiosulfate + sulfate)	mg S/L	18.4 \pm 6.2	32
pH		7.1 \pm 0.2	18

2.2. Reactors set-up, operation, and monitoring

Two identical anaerobic baffled reactors (ABRs) were constructed. The ABRs were made of polymethyl methacrylate with a height of 450 mm and an inner diameter of 200 mm, giving a total volume of 12 L (10 L working volume and 2 L headspace). They were sealed to ensure gas-tightness and covered with aluminum foil to prevent light exposure. Each ABR had six replicate compartments, separated by six baffles (Fig. 1). 2 L of anaerobically digested sludge collected from a local full-scale anaerobic digester (Brisbane, Australia) was equally distributed and inoculated into six compartments. The information of digested sludge was detailed in our previous study (Calderon et al., 2021). Afterwards, 10 L of real domestic wastewater was fed to ABRs by using peristaltic pumps (BT100-2J, Longer, China), which gave a hydraulic retention time (HRT) of 1 d. The effluent was controlled by using peristaltic pumps with the same flow rate. The produced biogas was recorded by using a tipping bucket gas meter and collected in a gas bag. To ensure the reliability of gas counter, gas meter was recalibrated monthly.

The experimental reactor was installed with an electrochemical unit for in-situ e-iron production, namely R-ferrous. Another one was operated in parallel without the electrochemical unit, serving as R-control. In R-ferrous, two iron plates were placed in the first compartment as anode and cathode of the electrochemical unit, respectively. Each iron plate had a dimension of 40 cm \times 3 cm \times 1 cm and a weight of about 960 g. Anode and cathode were symmetrically installed with interelectrode gap distance of 1.0 cm. Iron oxidation was achieved by maintaining a pre-designed constant current in each phase via a bench power supply (72-2685, TENMA, China) (detailed below).

The two ABRs were operated for 210 days, during which the operating conditions of R-control were unchanged and that of R-ferrous was divided into three phases with varied iron dosages. From day 370 to day 436, a low dosage of 40 mg Fe/L was used by setting the constant current at 16 mA in the electrochemical unit. The dosage was increased to 60 mg and 200 mg from day 437 to day 518 and from day 519 to day 585, by controlling the current at 24 mA and 80 mA, respectively.

Throughout the operation, concentrations of TSS, VSS, TCOD, SCOD, sulfur species (sulfide, sulfite, thiosulfate, and sulfate), NH_4^+ -N, and PO_4^{3-} -P in the influent and effluent were measured 2–3 times/week. The amount of produced biogas was monitored by a gas meter and manually recorded 2–3 times/week. The H_2S concentration in biogas and the effluent dissolved methane were measured weekly. The contents of CH_4 , CO_2 , and H_2 in the biogas were analysed 1–2 times/week. The pH of influent and effluent was monitored weekly.

2.3. Chemical analysis

TSS and VSS concentrations were measured according to the standard methods (APHA, 2005). TCOD and SCOD concentrations were

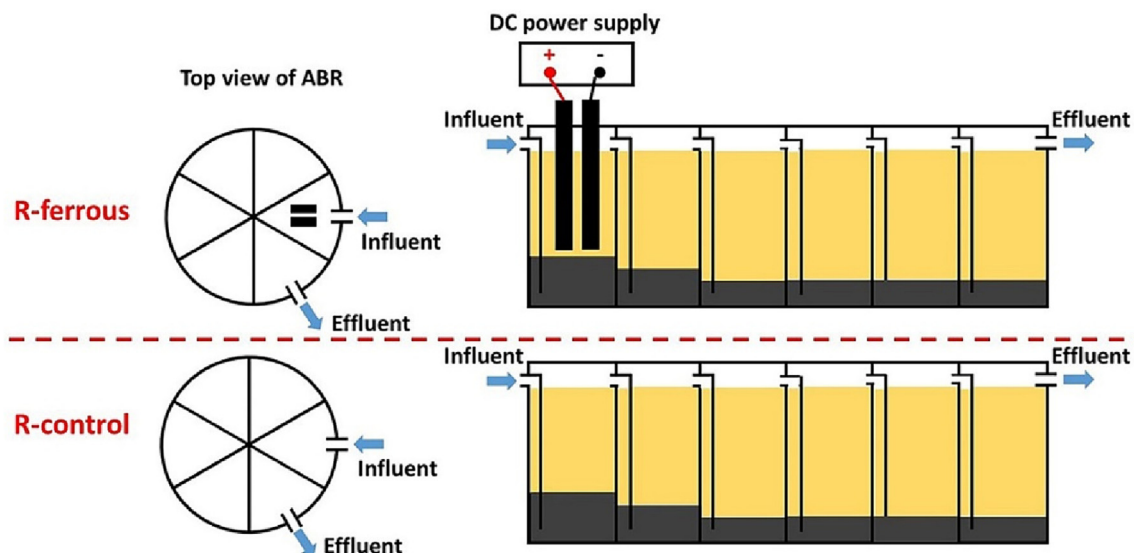


Fig. 1. Schematic of the control (R-control) and experimental (R-ferrous) laboratory anaerobic treatment systems.

measured using standard test kits (range 25–1500 mg/L, Merck). Liquid samples were taken using a syringe and then filtered through disposable Millipore filter units (0.22 μm , Millipore, Millex GP) for the analyses of ammonium, phosphate and sulfur species (i.e. sulfide, sulfate, silfite and thiosulfate). Ammonium and phosphate were analysed using a FlowInjection Analyser (Lachat Instrument, Milwaukee, Wisconsin), and sulfur species were measured by Ion Chromatography with a UV and conductivity detector (Dionex ICS-2000) (Keller-Lehmann et al., 2006). Analysis of total and dissolved iron concentrations were conducted by using an inductive Column Plasma Optical Emission Spectroscopy (Perkin Elmer Optima 7300DV, Waltham, MA, USA). The pH was measured using a portable pH monitor and probe (pH 5+, Oakton). The content of CH_4 , CO_2 , and H_2 in biogas were measured by using the gas chromatography method (7890A, Agilent), as described in literature (Zhang et al., 2019). The dissolved CH_4 concentration (Guisasola et al., 2008) and biogas H_2S content (Rebosura et al., 2018b) were measured according to the methods detailed in literature.

2.4. COD mass balance assessment

To understand the fate of organic carbon in the raw wastewater, COD mass balance assessment was carried out in each phase. The COD in wastewater was consumed by three pathways, i.e., converted to gaseous CH_4 , used by sulfate reducing bacteria, and discharged with the effluent. Further, the dissolved CH_4 part in effluent was shown in the results separately. According to the Henry's Law and stoichiometric number, the consumption of 1 g COD should correspondingly produce 350 mL gaseous CH_4 or reduce 0.5 g dissolved sulfate as S.

2.5. Statistical analysis

To identify significant difference between experimental and control systems, a *t*-test was conducted. The *p* value was shown in the figures. The ns, *, **, ***, and **** represent the *p* value is >0.05 , <0.05 , <0.01 , <0.001 , and <0.0001 , respectively.

3. Results and discussion

3.1. Effect of e-iron dosage on solids removal

Fig. 2a presents the average influent and effluent TSS concentrations in R-control and R-ferrous. The influent TSS concentration averaged at

420.9 ± 158.8 mg TSS/L with a relatively large variation between 116.3 and 698.5 mg TSS/L during the long-term operation (Figs. 2a and S2a). The average effluent TSS concentrations in R-ferrous were 18.4 ± 6.1 , 64.4 ± 9.1 , 43.9 ± 2.7 , and 99.1 ± 7.7 mg TSS/L with the iron dosage of 40, 60, 80, and 200 mg Fe/L, respectively. Correspondently, the TSS concentration in the effluent of R-control in these four phases were 33.5 ± 11.1 , 113.6 ± 20.2 , 58.4 ± 12.4 , and 100.0 ± 23.5 mg TSS/L, respectively. The mean difference of effluent TSS concentration between two reactors were 15.0 ± 7.9 mg TSS/L at 40 mg Fe/L, 50.6 ± 22.5 mg TSS/L at 60 mg Fe/L, 15.1 ± 8.3 mg TSS/L at 80 mg Fe/L, and 1.0 ± 10.7 mg TSS/L at 200 mg Fe/L. The relative decrease was $17.7 \pm 8.5\%$, $62.1 \pm 27.1\%$, $25.9 \pm 9.0\%$, and $1.3 \pm 16.4\%$, respectively. The difference was statistically significant at 40, 60, and 80 mg Fe/L stages ($p < 0.05$) and insignificant at 200 mg Fe/L stage ($p > 0.05$). The contrast results revealed that e-iron dosing at a substantial high dosage of 200 mg Fe/L did

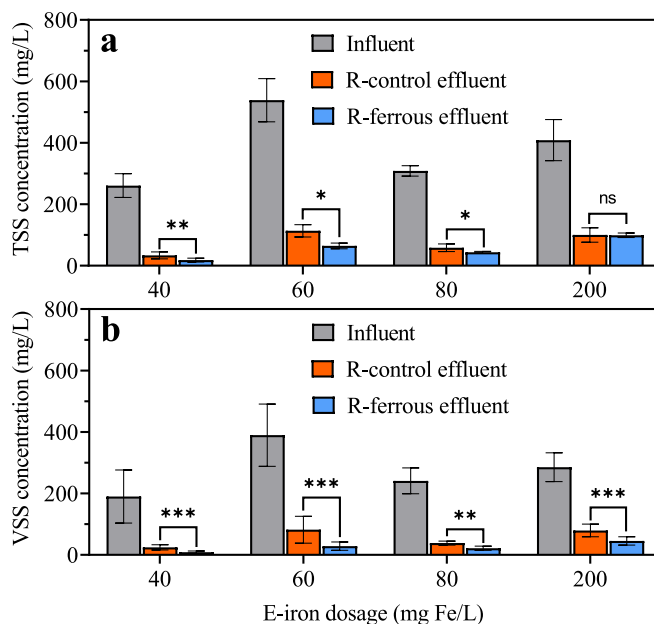


Fig. 2. TSS (a) and VSS (b) concentrations in influent and effluent of control (R-control) and e-iron reactors (R-ferrous). Average values of all sampling points are plotted. Error bars represent standard deviations of all measured data.

not favor TSS removal because of the increased effluent iron concentration (Table S1).

In coherence with TSS, the dose of ferrous iron resulted in a lower VSS concentrations in the effluent of R-ferrous than R-control (Figs. 2b and S2b). The average effluent VSS concentration difference between two reactors was 15.8 ± 5.8 at 40 mg Fe/L, 53.5 ± 32.3 at 60 mg Fe/L, 16.8 ± 8.7 at 80 mg Fe/L, and 33.9 ± 18.5 mg VSS/L at 200 mg Fe/L. This results in a relative decrease in VSS concentration of $62.9 \pm 9.2\%$ at 40 mg Fe/L, $62.1 \pm 14.6\%$ at 60 mg Fe/L, $37.4 \pm 10.1\%$ at 80 mg Fe/L, and $41.1 \pm 15.8\%$ at 200 mg Fe/L. All of them were statistically significant ($p < 0.05$) (Fig. 2b). As a result, the effluent ratios of VSS/TSS in R-control, i.e., $77.0 \pm 13.2\%$, $74.4 \pm 15.5\%$, $71.9 \pm 8.6\%$, and $80.5 \pm 12.3\%$ at 40, 60, 80, and 200 mg Fe/L stages, were higher than that of $46.4 \pm 6.8\%$, $48.6 \pm 8.8\%$, $47.5 \pm 6.4\%$ and $45.6 \pm 12.9\%$ in R-ferrous, respectively (Table S1).

3.2. Effect of e-iron dosage on COD removal and CH₄ production

Fig. 3a shows the average COD concentration in the influent and the effluent of R-control and R-ferrous. With the influent COD of 898.1 ± 242.7 mg COD/L, the average effluent COD concentrations in R-control at 40, 60, 80 and 200 mg Fe/L were 156.9 ± 34.5 , 273.4 ± 56.3 , 160.5 ± 24.1 , and 257.4 ± 61.1 mg COD/L, respectively. In comparison, R-ferrous had lower effluent COD concentrations, with the values averaged at 137.9 ± 27.0 , 202.6 ± 34.9 , 114.5 ± 15.9 , 196.8 ± 37.4 mg COD/L respectively in the four phases (Figs. 3a and S3a). Compared to R-control, the COD removal efficiency in R-ferrous was increased by $13.4 \pm 1.7\%$ at 40 mg Fe/L, $27.9 \pm 5.2\%$ at 60 mg Fe/L, $35.3 \pm 2.1\%$ at 80 mg Fe/L, and $28.4 \pm 2.9\%$ at 200 mg Fe/L. The difference at 40 mg Fe/L was not statistically significant ($p > 0.05$), and became significant ($p < 0.05$) at higher dosages. The result indicates that higher e-iron dosage over 40 mg Fe/L favored the enhanced COD removal.

The average CH₄ production rates in R-ferrous were 1323.1 ± 37.5 , 1976.9 ± 316.8 , 1514.0 ± 115.0 , and 2229.9 ± 275.6 mL CH₄/d, as compared to 1198.6 ± 138.1 , 1660.7 ± 289.1 , 1248.0 ± 88.6 , and 1855.8 ± 171.9 mL CH₄/d in R-control at 40, 60, 80, and 200 mg Fe/L, respectively. The average CH₄ production rate of R-ferrous was always higher than that of R-control ($p < 0.05$) (Figs. 3b and S3b). Overall, the result corresponds to elevated CH₄ production rate by $12.0 \pm 16.3\%$ at 40 mg Fe/L, $21.1 \pm$

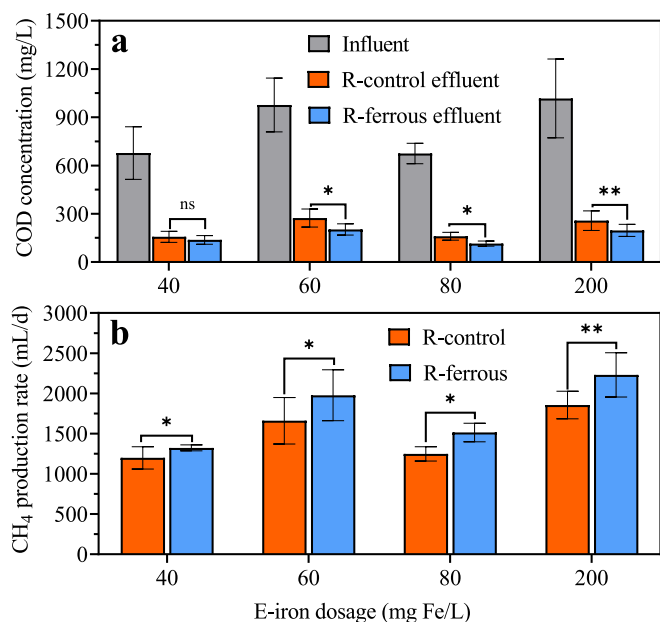


Fig. 3. TCOD concentration in the influent and effluent (a) and methane production rate (b) of R-control and R-ferrous. Average values of all sampling points are plotted. Error bars represent standard deviations of all measured data.

19.9% at 60 mg Fe/L, $21.3 \pm 9.5\%$ at 80 mg Fe/L, and $19.9 \pm 15.6\%$ at 200 mg Fe/L.

Mass balance evaluation was conducted to analyse the conversion of COD to CH₄ (Table S2). The increased CH₄ production was associated with not only the high COD removal efficiency but also additional H₂ formed by the electrochemical unit (i.e., hydrogenotrophic methanogens, $\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$). The calculation indicated that the increased COD removal of R-ferrous should contribute to more CH₄ production rates, as 67, 248, 193, and 227 mL CH₄/d at 40, 60, 80, and 200 mg Fe/L, respectively. The more CH₄ production by the hydrogenotrophic process was estimated to be 35 mL CH₄/d at 40 mg Fe/L, 50 mL CH₄/d at 60 mg Fe/L, 68 mL CH₄/d at 80 mg Fe/L, and 74 mL CH₄/d at 200 mg Fe/L. Combined, the theoretically increased CH₄ production rate should be 102, 298, 261, and 301 mL CH₄/d at 40, 60, 80, and 200 mg Fe/L. The calculated results were very close to the measured values of 124, 317, 266, and 373 mL CH₄/d, thus indicating that the increased CH₄ production was due to both enhanced COD removal and H₂ utilization.

The efficiency of in-situ H₂ utilization was 86%, 83%, and 84% at 40, 60, and 80 mg Fe/L, respectively (Table S2). This is generally higher than that (<80%) of the continuous stirred tank reactor (Díaz et al., 2015), attributed to the ABR design, i.e., the H₂ produced in the first chamber was forced to pass through all chambers before emitting in the last chamber. The efficiency decreased to 37% at 200 mg Fe/L stage, suggesting that additional gas recirculation is still needed to improve the efficiency.

The COD mass balance analysis also revealed similar flux in each phase of R-control (Fig. S4a), with ~60% of influent COD being converted to CH₄ (~52% in gas phase and ~8% in the effluent), and ~25% COD (without CH₄ and dissolved sulfide) residuals in the effluent. In contrast, the R-ferrous always had ~5% less of residual COD in each stage, resulted from the higher COD removal and more CH₄ production (Fig. S4b).

3.3. Effect of e-iron dosage on sulfide and phosphate control

The average dissolved sulfate, sulfide, and phosphate concentrations in the influent and effluent and H₂S content in the biogas of R-control and R-ferrous are shown in Fig. 4. The influent sulfate and sulfide concentrations were 10.5 ± 2.7 mg S/L and 6.6 ± 1.3 mg S/L, respectively. In R-control, the sulfate was almost fully converted to sulfide, showing low sulfate of 0.2 ± 0.1 mg S/L and high sulfide of 20.2 ± 2.7 mg S/L in the effluent (Figs. 4a, b, S5a, and b). This caused the H₂S content as high as 1083.6 ± 133.1 ppmv in the biogas of R-control. The average effluent sulfide concentration in R-ferrous was 4.0 ± 2.5 mg S/L at 40 mg Fe/L, 1.8 ± 1.3 mg S/L at 60 mg Fe/L, 1.7 ± 0.2 mg S/L at 80 mg Fe/L, and 0.2 ± 0.1 mg S/L at 200 mg Fe/L, giving a relative reduction by $79.8 \pm 12.6\%$, $89.6 \pm 6.7\%$, $93.7 \pm 7.3\%$, and $98.5 \pm 0.7\%$, respectively. Similarly, the H₂S content in the R-ferrous biogas declined by $75.5 \pm 11.7\%$, $84.4 \pm 6.3\%$, $90.1 \pm 6.0\%$, and $95.8 \pm 1.7\%$, respectively (Figs. 4c and S5c). The reduction of both dissolved sulfide in effluent and H₂S in biogas was statistically significant ($p < 0.05$). Together, these results indicated that e-iron efficiently removed dissolved and gaseous sulfide, with removal efficiency positively correlated with dosage.

The effluent phosphate concentration in R-control was 7.5 ± 0.9 mg P/L, slightly higher than the observation of 6.2 ± 1.4 mg P/L in the influent (Fig. 5), due to the hydrolyzation of biomass under anaerobic conditions. The phosphate removal efficiencies were $26.0 \pm 20.6\%$, $63.3 \pm 17.8\%$, $77.5 \pm 5.2\%$, and $96.0 \pm 3.2\%$, at 40, 60, 80, and 200 mg Fe/L, indicating the effective control of phosphate by e-iron.

3.4. Effect of e-iron dosage on biogas composition

Fig. 6 shows the contents of CH₄, H₂, and CO₂ in the biogas of R-control and R-ferrous at different e-iron dosages. The gas compositions of the biogas produced in R-control were similar in the four phases ($p > 0.05$), showing ~75% CH₄, ~25% CO₂ and negligible H₂. In comparison, lower biogas CO₂ contents were obtained in R-ferrous (Fig. 5b). The biogas CO₂ contents significantly ($p < 0.05$) decreased with the increase of e-iron dosage, from

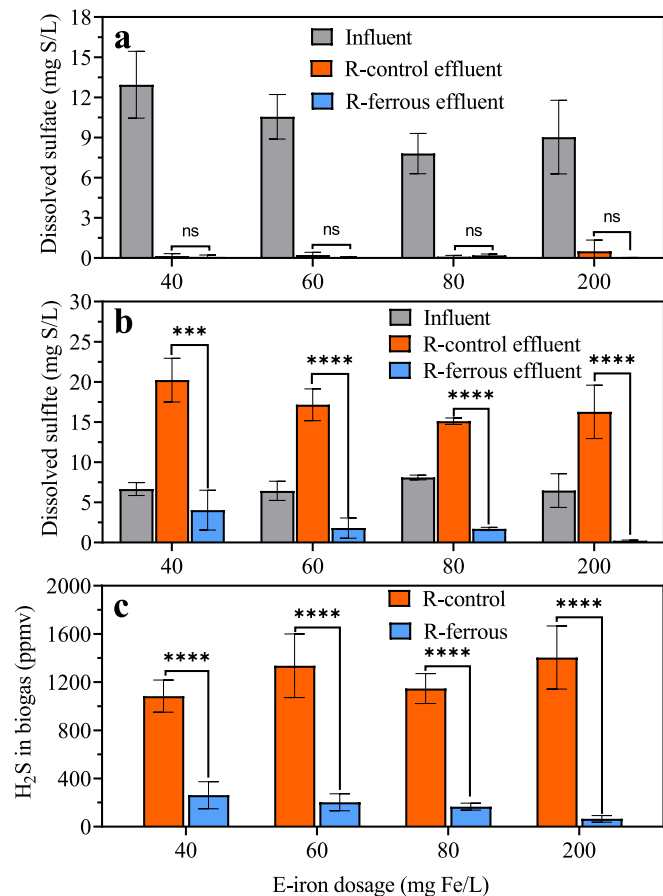


Fig. 4. Dissolved sulfate (a) and sulfide (b) concentrations in the influent and effluent of R-control and R-ferrous, and H₂S concentration in the biogas of R-control and R-ferrous (c). Average values of all sampling points are plotted. Error bars represent standard deviations of all measured data.

20.5% ± 0.7% at 40 mg Fe/L to 18.9% ± 0.5% at 60 mg Fe/L, 14.2% ± 0.6% at 80 mg Fe/L, and 4.5% ± 0.4% at 200 mg Fe/L. The CO₂ was removed by two pathways: i) utilizing H₂ produced in the cathode via the methanogenic reaction of CO₂ + 4H₂ → CH₄ + 2H₂O, and ii) utilizing OH⁻ generated in the cathode via the reaction of CO₂ + OH⁻ → HCO₃⁻. At 200 mg Fe/L, the CO₂ production rate of R-ferrous was about 480 mL CO₂/d lower than that of R-control, among which ~74 mL CO₂ was reduced to CH₄ by additional H₂ (approximately 15% of the reduction of the total CO₂ production rate) (Table S2). It suggested that the remaining ~85% of CO₂ could be removed by OH⁻ produced in the cathode. The H₂ content in the biogas increased to >20% at

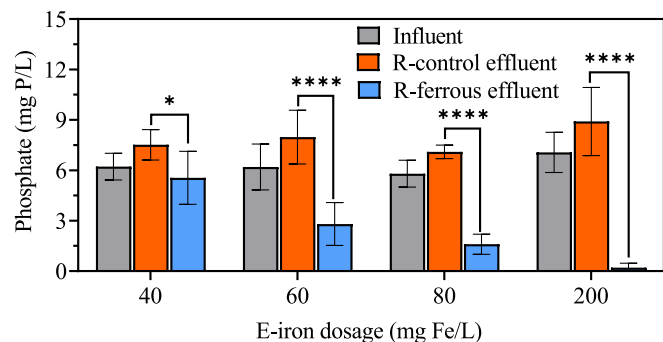


Fig. 5. Phosphorus concentrations in the influent and effluent of R-control and R-ferrous. Average values of all sampling points are plotted. Error bars represent standard deviations of all measured data.

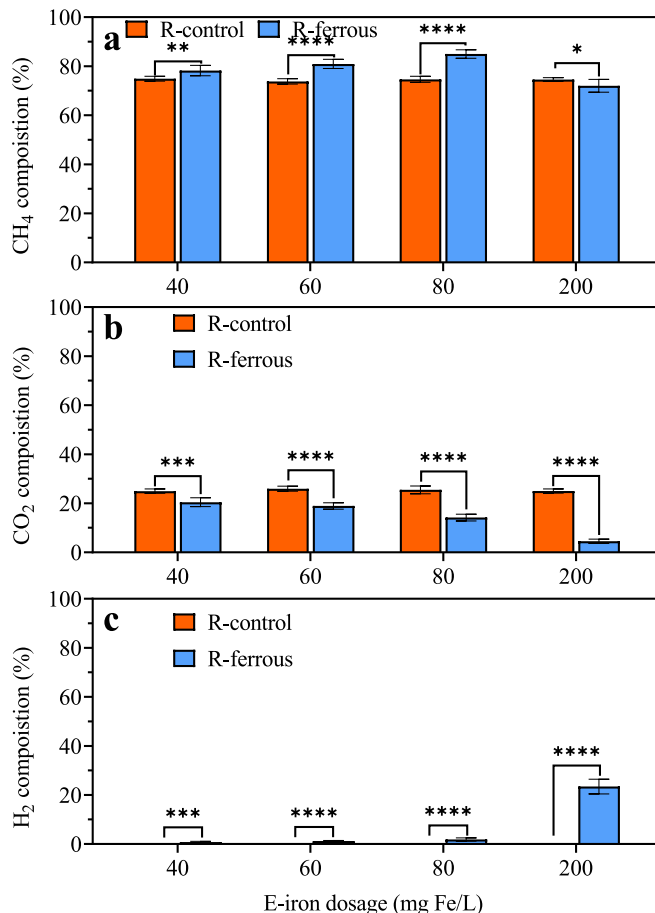


Fig. 6. CH₄ (a), CO₂ (b), and H₂ (c) compositions in produced biogas of R-control and R-ferrous. Average values of all sampling points are plotted. Error bars represent standard deviations of all measured data.

200 mg Fe/L (Fig. 6c). The biogas containing low CO₂ and high H₂/CH₄ means a high energy density (30.5 MJ/m³ of R-ferrous vs. 28.4 MJ/m³ of R-control) and has a wide application, e.g., as a fuel in the transportation sector.

3.5. Implication for anaerobic wastewater treatment

In this study, e-iron was developed to be an alternative to the conventional iron salts. The e-iron can avoid occupational health and safety (OH&S) concerns caused by transportation and storage of the corrosive and acidic iron salt solution. It can also avoid a decrease of wastewater pH caused by hydrolysis of conventional iron ions (Hu et al., 2021). The performance of anaerobic process treating domestic wastewater was comprehensively assessed with four different dosages, and the results showed that the e-iron significantly improved the efficiency of anaerobic wastewater treatment process, including dissolved sulfide and phosphate and gaseous H₂S and CO₂ reductions and CH₄ production enhancement. The reductions of effluent dissolved sulfide and phosphate over 75% were obtained at 40 and 80 mg Fe/L, respectively. The CO₂ content in biogas was reduced to below 5% with a higher dosage of 200 mg Fe/L. The e-iron dosing greatly enhanced the performance of the anaerobic wastewater treatment process, and the effectiveness relied on dosage. Nevertheless, the effluent iron concentrations at different dosages remained similar, as 4.4 ± 2.3 mg Fe/L, 5.8 ± 2.8 mg Fe/L, 6.4 ± 2.9 mg Fe/L, and 10.8 ± 5.2 mg Fe/L at 40, 60, 80, and 200 mg Fe/L, respectively (Table S1). The estimated operating cost of e-iron dosing was 34.6, 60.5, 92.2, and 576 AUD \$/ML at 40, 60, 80, and 200 mg Fe/L, respectively (see calculation in Table S3).

The dissolved sulfide and phosphorus were mainly removed in the form of FeS and $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$, respectively (Fig. S8). The phenomenon is consistent with previous reports using iron salts to remove dissolved sulfide and phosphate in wastewater management systems (Firer et al., 2008; Salehin et al., 2020; Wilfert et al., 2016). The removal efficiency of dissolved sulfide was higher than that of phosphate. More iron precipitated sulfide than phosphorus (Fig. S9) because of the different K_{sp} values of FeS ($\times 10^{-19}$) and $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ ($\times 10^{-29}$) (Chen and Faust, 1974; Davison, 1991).

It is noteworthy that the extremely high e-iron dosage (200 mg Fe/L) was for the first time investigated in this study. The experimental result showed that e-iron dosing enabled superior effectiveness for sulfide and phosphate removal, i.e., dissolved sulfide and phosphate were reduced to 0.1 ± 0.1 mg S/L and 0.2 ± 0.1 mg P/L, respectively (Fig. 4a and Fig. 5). The effluent phosphate concentration meets the highest discharge standard in many countries (Li et al., 2012; Piekema and Valsami-Jones, 2004; Schellenberg et al., 2020). This dosing also enabled biogas upgradation — the contents of H_2S and CO_2 in biogas were decreased to 25.2 ± 17.5 ppmv and 4.5 ± 0.4 %, respectively. The biogas is able to be compressed for value-adding applications (e.g. as a transport fuel), or further upgraded to biomethane for injection into the natural gas network (Angelidaki et al., 2018). This compares to the produced biogas used for thermal and electrical energy generation in current wastewater treatment plants (De Vrieze et al., 2018; Kougias et al., 2017; Szarka et al., 2013). Along with the continuous operation of anaerobic reactors, the sludge was not intentionally discharged. The majority of dosed iron was retained in the sludge, finally causing an iron-rich product (Table S4). The measurement showed that the amount of iron accounted for about 57 % of sludge mass, which is even in a range of iron ore (Holmes et al., 2022), indicating high recovery potential in future studies.

In this study, the performances of R-control and R-ferrous were compared to reveal the impacts of e-iron on the anaerobic domestic wastewater treatment process. Still, the elevated CH_4 production rate in each phase was potentially associated with the increase of activity of hydrogenotrophic methanogens. A previous study has shown that dosing iron can inhibit the activity of sulfate-reducing bacteria and methanogens in sewer systems (Zhang et al., 2009). In this study, the performance of increased biogas production rate was observed during anaerobic treatment of domestic wastewater by dosing e-iron. This result was due to two main reasons: 1) more COD (solid COD in particular) was retained in the reactor due to the coagulative effect of dosed iron, which was subsequently converted to CH_4 by methanogens; and 2) the addition of H_2 gas facilitated the reduction of CO_2 to CH_4 by hydrogenotrophic methanogens. Nevertheless, the shift of microbial community induced by e-iron may also play a role and needs to be investigated in further studies.

4. Conclusion

This study performed a comprehensive laboratory assessment of the impact of different e-iron dosages on the anaerobic domestic wastewater treatment process. The results of long-term demonstrated that the reduction of sulfide and phosphorus concentrations in liquid and the decrease of H_2S and CO_2 contents in biogas were positively correlated with dosage. E-iron preferred to remove dissolved sulfide before removing phosphate. Also, the dissolved sulfide and phosphate were mainly removed as FeS and $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$. In addition, the biogas quality was obviously improved by dosing e-iron at an extremely high dosage of 200 mg Fe/L. These results collectively demonstrated that dosing of e-iron greatly improved performance of anaerobic wastewater treatment process, while the specific design for enhanced sulfide, phosphorus and CO_2 control depends on dosage.

CRediT authorship contribution statement

Zhetai Hu: Investigation, Formal analysis, Visualization, Writing-Original draft preparation.

Shihu Hu: Conceptualization, Project administration, Supervision.

Pei-Ying Hong: Funding acquisition.

Xueqing Zhang: Investigation, Writing- original draft preparation.

Veljko Prodanovic: Methodology, Writing- reviewing and editing.

Kefeng Zhang: Methodology.

Liu Ye: Supervision.

Ana Deletic: Methodology.

Zhiguo Yuan: Conceptualization, Project administration, Methodology.

Min Zheng: Conceptualization, Project administration, Methodology, Supervision, Writing- reviewing and editing.

Data availability

Data will be made available on request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This study was supported by the Centre of Excellence for NEOM Research at King Abdullah University of Science and Technology (KAUST). Dr. Min Zheng is the recipient of an Advance Queensland Industry Research Fellowship. Mr. Zhetai Hu is supported by the China Scholarship Council (CSC).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2023.162628>.

References

- Angelidaki, I., Treu, L., Tsapekos, P., Luo, G., Campanaro, S., Wenzel, H., Kougias, P.G., 2018. Biogas upgrading and utilization: current status and perspectives. *Biotechnol. Adv.* 36 (2), 452–466.
- APHA, 2005. *Standard Methods for the Examination of Water and Wastewater* Washington, DC.
- Calderon, A.G., Duan, H., Meng, J., Zhao, J., Song, Y., Yu, W., Hu, Z., Xu, K., Cheng, X., Hu, S., Yuan, Z., Zheng, M., 2021. An integrated strategy to enhance performance of anaerobic digestion of waste activated sludge. *Water Res.* 195, 116977.
- Carpenter, S.R., 2005. Eutrophication of aquatic ecosystems: bistability and soil phosphorus. *Proc. Natl. Acad. Sci. U. S. A.* 102 (29), 10002–10005.
- Chen, P.-J., Faust, S.D., 1974. The solubility product of ferrous phosphate. *Environ. Lett.* 6 (4), 287–296.
- Davison, W., 1991. The solubility of iron sulphides in synthetic and natural waters at ambient temperature. *Aquat. Sci.* 53 (4), 309–329.
- De Vrieze, J., Arends, J.B.A., Verbeeck, K., Gildemyn, S., Rabaey, K., 2018. Interfacing anaerobic digestion with (bio)electrochemical systems: potentials and challenges. *Water Res.* 146, 244–255.
- Díaz, I., Pérez, C., Alfaro, N., Fdz-Polanco, F., 2015. A feasibility study on the bioconversion of CO_2 and H_2 to biomethane by gas sparging through polymeric membranes. *Bioresour. Technol.* 185, 246–253.
- Duan, H., Ye, L., Wang, Q., Zheng, M., Lu, X., Wang, Z., Yuan, Z., 2019. Nitrite oxidizing bacteria (NOB) contained in influent deteriorate mainstream NOB suppression by sidestream inactivation. *Water Res.* 162, 331–338.
- Firer, D., Friedler, E., Lahav, O., 2008. Control of sulfide in sewer systems by dosage of iron salts: comparison between theoretical and experimental results, and practical implications. *Sci. Total Environ.* 392 (1), 145–156.
- Garfi, M., Flores, L., Ferrer, I., 2017. Life cycle assessment of wastewater treatment systems for small communities: activated sludge, constructed wetlands and high rate algal ponds. *J. Clean. Prod.* 161, 211–219.
- Guisasola, A., de Haas, D., Keller, J., Yuan, Z., 2008. Methane formation in sewer systems. *Water Res.* 42 (6), 1421–1430.
- Hauserr, D., Niederdorfer, R., Bürgmann, H., Lehmann, M.F., Magyar, P., Mohn, J., Morgenroth, E., Joss, A., 2022. Successful year-round mainstream partial nitrification anammox: assessment of effluent quality, performance and N_2O emissions. *Water Res.* X 16, 100145.
- Holmes, R.J., Lu, Y., Lu, L., 2022. Introduction: overview of the global iron ore industry. *Iron Ore* 1–56.
- Hu, Z., Duan, H., Wang, Z., Zhao, J., Ye, L., Yuan, Z., Zheng, M., Hu, S., 2021. Centralized iron-dosing into returned sludge brings multifaceted benefits to wastewater management. *Water Res.* 203, 117536.

- Hu, Z., Zheng, M., Hu, S., Hong, P.-Y., Zhang, X., Prodanovic, V., Zhang, K., Pikaar, I., Ye, L., Deletic, A., Yuan, Z., 2022. Electrochemical iron production to enhance anaerobic membrane treatment of wastewater. *Water Res.* 225, 119202.
- Keller-Lehmann, B., Corrie, S., Ravn, R., Yuan, Z., Keller, J., 2006. Preservation and Simultaneous Analysis of Relevant Soluble Sulfur Species in Sewage Samples. *Citeseer*, p. 28.
- Kougias, P.G., Treu, L., Benavente, D.P., Boe, K., Campanaro, S., Angelidaki, I., 2017. Ex-situ biogas upgrading and enhancement in different reactor systems. *Bioresour. Technol.* 225, 429–437.
- Lai, C., Zhou, L., Yuan, Z., Guo, J., 2021. Hydrogen-driven microbial biogas upgrading: advances, challenges and solutions. *Water Res.* 197, 117120.
- Liu, T., Lu, Y., Zheng, M., Hu, S., Yuan, Z., Guo, J., 2021a. Efficient nitrogen removal from mainstream wastewater through coupling partial nitrification, anammox and methane-dependent nitrite/nitrate reduction (PNAM). *Water Res.* 206, 117723.
- Liu, H., Li, X., Zhang, Z., Nghiem, L.D., Gao, L., Wang, Q., 2021b. Semi-continuous anaerobic digestion of secondary sludge with free ammonia pretreatment: focusing on volatile solids destruction, dewaterability, pathogen removal and its implications. *Water Res.* 202, 117481.
- Li, W.-W., Sheng, G.-P., Zeng, R.J., Liu, X.-W., Yu, H.-Q., 2012. China's wastewater discharge standards in urbanization. *Environ. Sci. Pollut. Res.* 19 (5), 1422–1431.
- Li, W., Yu, H., 2016. Advances in energy-producing anaerobic biotechnologies for municipal wastewater treatment. *Engineering* 2 (4), 438–446.
- Lim, Z.K., Liu, T., Zheng, M., Rattier, M., Keller, J., Yuan, Z., Guo, J., Hu, S., 2023. Membrane reciprocation as energy-efficient fouling control with high biogas recovery in a pilot-scale anaerobic membrane bioreactor. *Resour. Conserv. Recycl.* 190, 106849.
- Lin, H.-W., Kustermans, C., Vaiopoulou, E., PrévotEAU, A., Rabaey, K., Yuan, Z., Pikaar, I., 2017. Electrochemical oxidation of iron and alkalinity generation for efficient sulfide control in sewers. *Water Res.* 118, 114–120.
- Piekema, P., Valsami-Jones, E., 2004. *The Case Study of a Phosphorus Recovery Sewage Treatment Plant at Geestmerambacht, Holland-design and Operation*. IWA Publishing, London, pp. 19–27.
- Pikaar, I., Flugen, M., Lin, H.-W., Salehin, S., Li, J., Donose, B.C., Dennis, P.G., Bethke, L., Johnson, I., Rabaey, K., Yuan, Z., 2019. Full-scale investigation of in-situ iron and alkalinity generation for efficient sulfide control. *Water Res.* 167, 115032.
- Rebosura Jr., M., Salehin, S., Pikaar, I., Sun, X., Keller, J., Sharma, K., Yuan, Z., 2018. A comprehensive laboratory assessment of the effects of sewer-dosed iron salts on wastewater treatment processes. *Water Res.* 146, 109–117.
- Rebosura, M., Salehin, S., Pikaar, I., Sun, X., Keller, J., Sharma, K., Yuan, Z., 2018. A comprehensive laboratory assessment of the effects of sewer-dosed iron salts on wastewater treatment processes. *Water Res.* 146, 109–117.
- Salehin, S., Rebosura, M., Keller, J., Gernjak, W., Donose, B.C., Yuan, Z., Pikaar, I., 2020. Recovery of in-sewer dosed iron from digested sludge at downstream treatment plants and its reuse potential. *Water Res.* 174, 115627.
- Schellenberg, T., Subramanian, V., Ganeshan, G., Tompkins, D., Pradeep, R., 2020. Wastewater discharge standards in the evolving context of urban sustainability—The case of India. *Front. Environ. Sci.* 30.
- Schindler, D.W., Carpenter, S.R., Chapra, S.C., Hecky, R.E., Orihel, D.M., 2016. Reducing phosphorus to curb Lake eutrophication is a success. *Environ. Sci. Technol.* 50 (17), 8923–8929.
- Szarka, N., Scholwin, F., Trommler, M., Fabian Jacobi, H., Eichhorn, M., Ortwein, A., Thrän, D., 2013. A novel role for bioenergy: a flexible, demand-oriented power supply. *Energy* 61, 18–26.
- Vollertsen, J., Nielsen, A.H., Jensen, H.S., Wium-Andersen, T., Hvitved-Jacobsen, T., 2008. Corrosion of concrete sewers—The kinetics of hydrogen sulfide oxidation. *Sci. Total Environ.* 394 (1), 162–170.
- Wan, J., Gu, J., Zhao, Q., Liu, Y., 2016. COD capture: a feasible option towards energy self-sufficient domestic wastewater treatment. *Sci. Rep.* 6, 25054–25054.
- Wang, Z., Zheng, M., Hu, Z., Duan, H., De Clippeleir, H., Al-Omari, A., Hu, S., Yuan, Z., 2021. Unravelling adaptation of nitrite-oxidizing bacteria in mainstream PN/A process: mechanisms and counter-strategies. *Water Res.* 200, 117239.
- Wang, Y., Zheng, K., Guo, H., Tian, L., He, Y., Wang, X., Zhu, T., Sun, P., Liu, Y., 2022. Potassium permanganate-based advanced oxidation processes for wastewater decontamination and sludge treatment: a review. *Chem. Eng. J.* 452, 139529.
- Wilfert, P., Mandalidis, A., Dugulan, A.I., Goubitz, K., Korving, L., Temmink, H., Witkamp, G.J., Van Loosdrecht, M.C.M., 2016. Vivianite as an important iron phosphate precipitate in sewage treatment plants. *Water Res.* 104, 449–460.
- Yongsiri, C., Vollertsen, J., Hvitved-Jacobsen, T., 2005. Influence of wastewater constituents on hydrogen sulfide emission in sewer networks. *J. Environ. Eng.* 131 (12), 1676–1683.
- Yuan, T., Wang, Y., Nuramkhaan, M., Wang, X., Zhang, Z., Lei, Z., Shimizu, K., Utsumi, M., Adachi, Y., Lee, D.-J., 2020. Coupling biogas recirculation with FeCl₃ addition in anaerobic digestion system for simultaneous biogas upgrading, phosphorus conservation and sludge conditioning. *Bioresour. Technol.* 315, 123811.
- Zhang, L., Keller, J., Yuan, Z., 2009. Inhibition of sulfate-reducing and methanogenic activities of anaerobic sewer biofilms by ferric iron dosing. *Water Res.* 43 (17), 4123–4132.
- Zhang, X., Xia, J., Pu, J., Cai, C., Tyson, G.W., Yuan, Z., Hu, S., 2019. Biochar-mediated anaerobic oxidation of methane. *Environ. Sci. Technol.* 53 (12), 6660–6668.
- Zheng, M., Li, H., Duan, H., Liu, T., Wang, Z., Zhao, J., Hu, Z., Watts, S., Meng, J., Liu, P., Rattier, M., et al., 2023. One-year stable pilot-scale operation demonstrates high flexibility of mainstream anammox application. *Water Res.* X 19, 100166.