

Article

Waste Ochre for Control of Phosphates and Sulfides in Digesters at Wastewater Treatment Plants with Enhanced Biological Phosphorus Removal

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Received: 5 January 2020; Accepted: 7 February 2020; Published: 6 March 2020



Abstract: Ochre, waste iron sludge from the treatment of iron rich groundwater for potable use, makes up a significant waste problem. Furthermore, wastewater treatment plants with enhanced biological phosphorus removal and the digestion of sludge are in lack of iron for the prevention of hydrogen sulfide production and the release of phosphorous during anaerobic digestion. Thus, the addition of ochre to anaerobic digestion is a potential beneficial reuse of ochre. Sludge from wastewater treatment plants with enhanced biological phosphorus removal was used for the experiments. Batch and continuous pilot-scale tests were performed for the mesophilic digestion of primary and waste-activated sludge with different doses of ochre. Two different doses of ochre corresponding to molar ratios of 1 and 2 moles Fe^{3+} /mole P released in the batch test resulted in 29% and 57% reductions of phosphates respectively in the sludge liquor compared to the control sludge without inhibiting the digestion process. In the pilot experiment, the dosing of ochre at both a high and low dose (molar ratios of 1.6 and 0.8 $\text{Fe}^{3+}/\text{S}^{2-}$, respectively) resulted in an immediate drop in the H_2S concentration (from >2000 ppm down to 570 ppm), while the control reactor still produced biogas with a high hydrogen sulfide concentration. The inhibition of the digestion process was observed (accumulation of acetate) at the higher dose. In a second pilot scale experiment, lower doses of ochre were tested continuously (1.5 and 0.75 mole Fe^{3+} /mole $\text{P}_{\text{released}}$) to avoid any inhibition, while evaluating the phosphate precipitation. A reduction of phosphates in sludge liquor (33% and 66% for the low and high doses respectively) was obtained.

Keywords: waste ochre; biogas; enhanced phosphorus removal; hydrogen sulfide; phosphates precipitation

1. Introduction

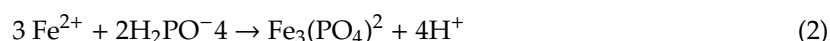
In wastewater treatment plants (WWTPs) with enhanced biological phosphorus removal, the internal recycling of phosphates and potential production of hydrogen sulfide are limiting factors for the digestion of the surplus sludge. The internal recycling of sludge liquor with a high concentration of phosphate is usually the cause of the overloading of such plants with phosphates [1–4]. Phosphate concentrations of up to about 500 mg $\text{PO}_4\text{-P/L}$ have been found in the sludge liquor due to the release of phosphates by phosphate accumulating organisms (PAOs) during anaerobic digestion [5], while normal concentrations are often below 10 mg $\text{PO}_4\text{-P/L}$ in conventional WWTPs with the chemical

precipitation of phosphorus. The anaerobic digestion of sludge from plants with biological phosphorus removal is also risky if sulfates are present in the feed sludge [6,7], since no chemicals are available to capture the sulfur in the digester. A high content of hydrogen sulfide in produced biogas can corrode the equipment and is a health risk for the personnel at the treatment plant [8,9].

The addition of commercial products based on iron chloride (FeCl₃) is the common preventive method for solving both problems [2,8–11]. In some reported cases, the addition of iron salts impaired the digestion process [12,13] and reduced the methanogens activity [14]. Other research [15,16] demonstrated small decreases in VS (volatile solids) degradation as well as a reduction in organic sulfur generation during the digestion process of sludge dosed with iron (Fe:P 3:1 molar ratio).

Ochre (Fe₂O₃) is a waste product from the production of potable water based on groundwater with a high content of reduced iron [17–19]. High concentrations of dissolved iron can cause an unpleasant taste, brown color of the water, and the corrosion of steel pipes and water-distribution networks [20]. Water with iron levels of more than 1 mg/L can cause health problems [21]. Typically, ochre is reduced to very low levels, and the iron rich sludge is normally disposed into landfills as waste [19,22]. A possible method for utilizing ochre is to use it as an alternative source of iron for the reduction of the hydrogen sulfide content, and for solving problems related to the internal recirculation of phosphates at WWTPs with biological phosphorus removal processes [19,23]. Since commercial precipitation chemicals based on iron or aluminum are expensive [19,24], ochre might be a good alternative in countries where biological phosphorus removal is required [25].

Many different chemical reactions might be involved when ochre is added to an anaerobic digester for the reduction of hydrogen sulfide and soluble phosphorous. A comprehensive presentation is given in [19], where ochre is assumed to dissolve in the presence of organic material under the reducing conditions in the digester. Furthermore, sulfide and phosphate are precipitated with the dissolved iron according to Equations (1) and (2):



In Lithuania, potable water is largely based on iron rich groundwater [26]. The iron content in groundwater around Vilnius is about 1.1 mg/L, and the total phosphorus (total-P) in the influent to the WWTP is typically 5–10 mg/L, demonstrating that the supply of iron is insignificant on a molar basis, so that all ochre from the water supply can easily be utilized for wastewater treatment.

Demands on the effluent quality from wastewater treatment plants have been more stringent during recent years [2,4,27]. Furthermore, resource-saving and cost-reducing measures should be taken into account. One such measure could be to use ochre for the optimization of the anaerobic sludge digestion.

This study evaluates if waste ochre can be used to control hydrogen sulfide production, and to prevent the high internal recirculation of phosphorus at the growing numbers of treatment plants with biological phosphorus removal. Since the addition of ochre contributes to sludge production in the digesters and consequently reduces the retention time, there is a practical limit for the dose. Besides that limitation, the addition of ochre may lead to the inhibition of the methane production, just as other iron-based chemicals do [14–16,18,19]. The experiments were planned based on all these considerations. Initially, batch experiments were performed for the evaluation of any inhibitory effect and potential for the reduction of dissolved phosphorus through digestion. A subsequent experiment with a continuous operation in pilot scale was performed for the evaluation of the potential for rapid reduction in hydrogen sulfide formation, and we also conducted a longer experiment for the evaluation of the potential for reduction of the internal phosphorus recirculation. Together, the experiments shall demonstrate the potential use of ochre for solving significant problems for plants with biological phosphorus removal that digest the surplus sludge.

2. Experiment Section

Ochre from the Antaviliai water treatment plant (WTP) (Vilnius, Lithuania), which supplies drinking water for 250,000 people (~41% of Vilnius city inhabitants), was used in the experiments. The incoming groundwater contains about 1.1 mg/L of iron, which is reduced to 0.04 mg/L after treatment. The ochre used in this experiment had a total solids content (TS) of about 40%, and one g TS of ochre contained approximately 350–400 mg Fe³⁺. Table 1 presents the major constituents of ochre from the analysis.

The sludge for the experiments was obtained from Öresundsverket WWTP in Helsingborg (Sweden). The plant treats wastewater from 120,000 people and from many different industries. The plant is operated with enhanced biological phosphorus removal and pre-denitrification, with hydrolyzed primary sludge as the additional carbon source [28]. No chemicals for phosphorus removal are used at the plant. A minor dose of FeCl₃ is added in the thickener to the primary sludge before digestion to prevent hydrogen sulfide (H₂S) formation in the digester. Primary sludge was therefore sampled before the addition of FeCl₃ and manually thickened, which resulted in a total solids (TS) content of 3.6% (average value), while waste-activated sludge had about 3% of TS. Sludge was mixed in the proportions 0.35:0.65 (volume basis) in accordance with the sludge production at the treatment plant. Fresh sludge was collected from the WWTP every week and stored in a cold room <+4 °C.

Table 1. The major constituents of ochre. In total, 48 elements were detected.

Symbol	Element	Concentration (%)	Standard Deviation (%)
Fe	Iron ¹	35.27	1.29
Ca	Calcium	4.63	0.12
Si	Silicon	2.53	0.16
P	Phosphorus	2.26	0.04
Mn	Manganese	0.38	0.01
Al	Aluminum	0.28	0.10
S	Sulphur	0.25	0.04
Mg	Magnesium	0.23	0.01
Ti	Titanium	0.14	0.01
Ba	Barium	0.12	0.00
K	Potassium	0.04	0.01
Sr	Strontium	0.03	0.00
Cr	Chromium	0.008	0.00
Pb	Lead	0.003	0.00
Zn	Zinc	0.003	0.00
Cu	Copper	0.002	0.00
Ni	Nickel	0.001	0.00
As	Arsenic	0.001	0.00
Cd	Cadmium	B.D.	0.00

¹ One g TS of ochre contains approximately 350–400 mg Fe³⁺.

Inoculum used for the start-up of the pilot digesters came from the mesophilic reactors at Öresundsverket WWTP, operated at 35 °C. Inoculum used in the batch test was taken from the pilot-scale digesters after operation for more than three solid retention times (SRTs) in order to remove the effect of the iron used for sulfide control in the full-scale installation.

Total Solids (TS) and total volatile solids (VS) of the inoculum and sludge used for the batch and pilot experiments are presented in Table 2.

Table 2. The characteristics of the inoculum and the feed sludge used in the batch and pilot experiments.

	Batch Experiment			Pilot Experiment		
	Inoculum	Primary Sludge	Bio-Sludge	Inoculum	Primary Sludge	Bio-Sludge
TS _{average} (%)	1.65	4.84	3.84	2.75	3.58	3.27
VS _{average} (%)	1.12	2.79	2.12	1.95	2.85	2.44

2.1. Digestion Tests

2.1.1. Dose of Ochre

The dosing of ochre, as solids, in the batch experiments was set at two levels, Low ($0.5 \text{ g Fe}^{3+}/\text{L}$) and High ($1.0 \text{ g Fe}^{3+}/\text{L}$), where the lower dose corresponded to a molar ratio of 1:1 mole $\text{Fe}/\text{P}_{\text{released}}$. $\text{P}_{\text{released}}$ is the release of phosphate into the liquid phase during digestion, which was determined by the batch digestion of the sludge from Öresundsverket (around $260 \text{ mg PO}_4\text{-P/L}$). The high dose was chosen in order to evaluate any inhibitory effect and the effect of the increased dose on the phosphate binding capacity.

The dosing of ochre, as solids, during the pilot experiment was divided into two separate experiments. In the first period, high doses were added for only three days at two different levels in two different reactors, and a third was used as the control without any addition. The idea was to evaluate the potential to use ochre for the rapid reduction of hydrogen sulfide production and to check if very high doses of ochre have any impact on the anaerobic digestion process. In the second period, lower doses of ochre were added (two levels in two different reactors and one control without addition) during 15 days to evaluate the influence on the phosphate release.

2.1.2. Laboratory Batch Test for Methane Potential

Batch tests were used for the examination of the methane potential according to the methodology described in [29,30]. Batch tests were performed in glass reactors of ~2 L. The tests were made under mesophilic conditions ($35 \text{ }^\circ\text{C}$). The total volume of inoculum, sludge, and ochre was about 500 mL, with the substrate representing about 45% of the total volatile solids (VS) content. The dose of ochre corresponded to $0.5 \text{ g Fe}^{3+}/\text{L}$ and $1 \text{ g Fe}^{3+}/\text{L}$ (1 and 2 mole Fe^{3+} per mole of P released) of ochre, with the composition shown in Table 1. Each bottle was flushed with nitrogen gas after filling to ensure anaerobic conditions in the reactors. The duration of the experiment was 24 days. The production was followed by six measurements during the experiment, and each reactor was set in triplicates. Cellulose powder was used as the reference substrate to test the function of the inoculum. The amount of VS of cellulose added was similar to the VS of the tested substrate, according to the methodology described in [29,30].

2.1.3. Pilot-Scale Digestion Experiment

Three pilot-scale reactors (20 L of working volume) were continuously operated at a mesophilic temperature ($37 \text{ }^\circ\text{C}$), solid retention time (SRT) of 15 d, and organic loading rate (OLR) of $1.42\text{--}2.00 \text{ kg VS/m}^3\text{-d}$, with separate biogas collection tanks for each reactor. Figure 1 shows the scheme of the pilot-scale reactors used for the experiment. The equipment was previously described in detail [31,32]. Each reactor was inoculated with anaerobic sludge from the mesophilic digesters at Öresundsverket. The reactors were fed once per day with 1.33 L of a mixture of primary and waste-activated sludge. In the first experiment concerning hydrogen sulfide reduction via addition of ochre, the doses were chosen at $5 \text{ g Fe}^{3+}/\text{d}$ and $2.5 \text{ g Fe}^{3+}/\text{d}$ in two of the reactors (corresponding to a molar ratio of 1.6 and $0.8 \text{ Fe}^{3+}/\text{S}^{2-}$, respectively). In the second period, involving the experiment for phosphates release control, the high and low doses were reduced to $1.5 \text{ g Fe}^{3+}/\text{d}$ and $0.75 \text{ g Fe}^{3+}/\text{d}$ respectively (corresponding to a molar ratio of 1.5 and $0.75 \text{ Fe}^{3+}/\text{P}_{\text{released}}$ respectively, where $\text{P}_{\text{released}}$ is $400 \text{ mg PO}_4\text{-P/L}$).

The pilot reactors were first operated continuously for 30 days to achieve steady state conditions and for the removal of the minor iron dose used at the full-scale installation. However, in order to avoid the transient phase in the results, the 30th day after the initial start-up was identified as day "1" in the data and the figures. The withdrawn sludge from the pilot scale reactors from day 26 was used as inoculum in the batch experiments. After a long period of operation, the hydrogen sulfide concentration in the biogas was still low, probably due to the low content of sulfates in the sludge feed. In order to provoke H_2S formation, sodium sulfate (Na_2SO_4) was added daily in all three reactors,

starting on day 28. The dosage of Na_2SO_4 in the reactors was increased gradually: 2 g Na_2SO_4 /day was added for 5 days, 4 g Na_2SO_4 /day for the next 10 days, and about 8 g Na_2SO_4 /day was added until the end of the experiment (day 52). The hydrogen sulfide concentration in the produced biogas quickly increased after the Na_2SO_4 addition, and then the first experiment with the ochre dose for hydrogen sulfide control started and ran for 3 days. After a short rest period for the reactors (from days 53 to 63), the second part of the experiment started, and the reactors were operated without ochre dosing for 20 days (from days 64 to 84). Then, they were operated with relatively lower doses of ochre for the phosphates release control until the end of the experiment.

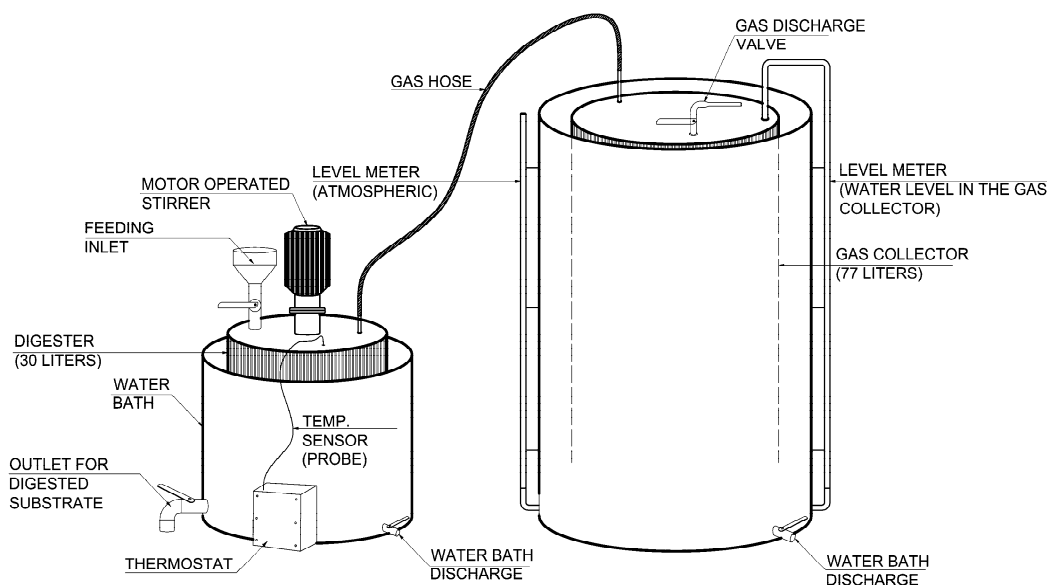


Figure 1. The schematic view of the pilot-scale equipment from [32]. Three identical reactors were used for the experiment.

2.2. Analytical Methods

The samples of primary activated and digested sludge from the batch and pilot-scale experiments were analyzed using HACH LANGE test tubes: LCK 320 for iron and LCK 049 for phosphate. The prepared tubes were analyzed with a HACH LANGE spectrophotometer (model DR 2800). All the samples stated above were centrifuged for 15 min at the speed of 10,000 rpm and filtrated through Munktell general purpose filter papers with a 6~10 μm pore size before further analysis. The TS and VS contents were measured according to standard methods. The alkalinity was measured according to the Swedish standard (ISO 9963-1:1994).

The methane production from the batch experiment was measured using a gas-tight syringe and gas chromatography (Varian 3800 Gas Chromatograph) equipped with TCD (thermal conductivity detector) and a column with dimensions of 2.0 m \times 1/8 inch \times 2.0 mm.

The composition of the produced biogas (methane, carbon dioxide, oxygen, and hydrogen sulfide (up to 2000 ppm)) during the pilot-scale experiment was measured using a portable gas-meter SEWERIN SR2-DO. The pH of the reactors was measured using a digital pH-meter (pH 3110 SET 2 incl. SenTiz[®] 41).

The volatile fatty acids (VFA) content of the samples was analyzed with gas chromatography using an Agilent 6850 Series GC System equipped with an FID (flame ionization detector) and a column with dimensions of 25 m \times 0.32 μm \times 0.5 μm .

3. Results and Discussion

3.1. Potential Use of Ochre

Ochre has a potential for reducing or preventing hydrogen sulfide formation in anaerobic digestion where iron deficit can enable such problems. Furthermore, the release of phosphorus during the anaerobic digestion of surplus sludge from plants with biological phosphorous removal can be prevented. However, it is necessary that the addition does not significantly influence the biogas production. Below, we present and discuss the experimental evidence for the potential.

3.2. Batch Experiment

The development of methane production in the batch experiments is shown in Figure 2 (the methane production from the inoculum has been extracted). The methane (CH_4) production with cellulose (reference substrate) was about 320 NmL $\text{CH}_4/\text{g VS}_{\text{in}}$ at the end of the experiment (after 24 days), which shows that the inoculum was functioning well (the theoretical potential for cellulose is 415 NmL $\text{CH}_4/\text{g VS}_{\text{in}}$) [29].

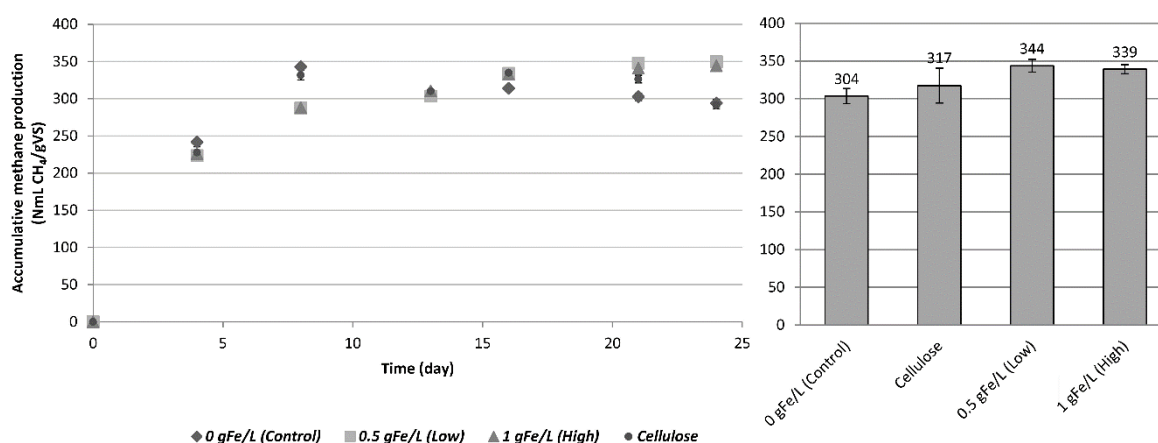


Figure 2. The bio-methane potential from the batch experiment for high and low doses of ochre as well as control reactor (no ochre was added). The average values of BMP presented in the figure above (right) are based on the last three measurements from the tests shown to the left.

The accumulated methane potentials for the control reactor and reactors with different concentrations of ochre (0.5 and 1 g Fe^{3+}/L) are almost similar with a slightly higher potential in the reactors with the ochre addition (around 340 NmL $\text{CH}_4/\text{g VS}_{\text{in}}$), which was about 10–15% higher than the methane potential from the control reactor (300 NmL $\text{CH}_4/\text{g VS}_{\text{in}}$). The ochre addition did not reduce the methane potential for any of the doses. This is in contrast to the previous studies, where the addition of ochre reduced the methane production by up to 50% [19].

At the end of the batch experiment, the released phosphate was found as shown in Figure 3.

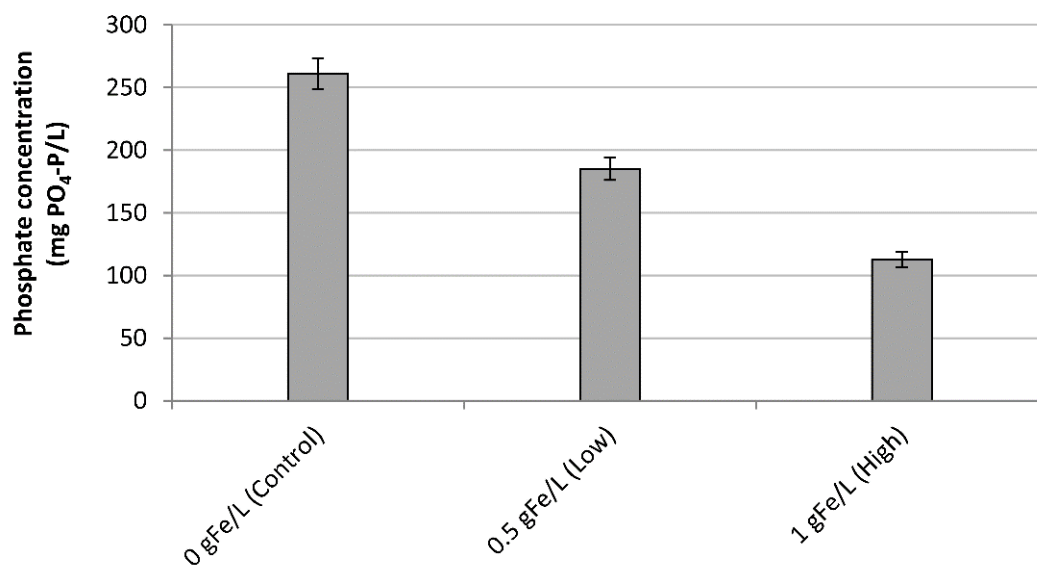


Figure 3. The PO₄-P concentrations measured in the batch reactors at the end of the batch experiments. The release constituted 261 mg PO₄-P/L in the control batch, while reductions of 29% and 57% were observed for the reactors dosed with 0.5 g Fe³⁺/L and 1 g Fe³⁺/L of ochre, respectively.

3.3. Continuous Pilot-Scale Experiments

Figure 4 shows the development of hydrogen sulfide during the experimental period.

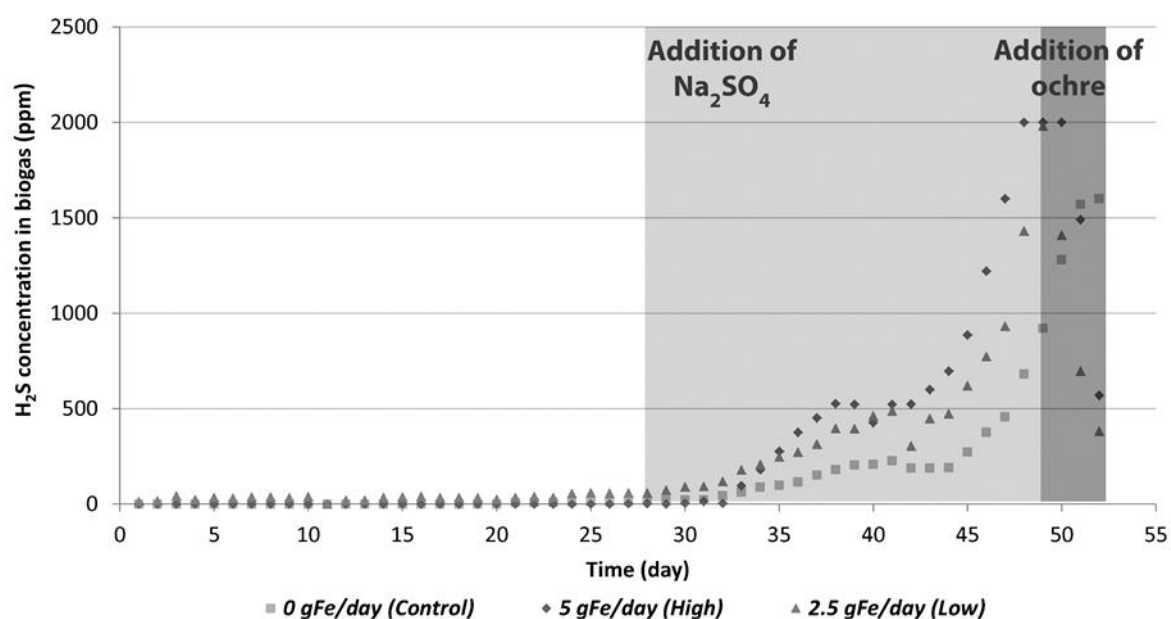


Figure 4. The hydrogen sulfide concentration in the produced biogas. Sodium sulfate started to be added in the reactors on day 28 of the experiment in order to provide sulfate as the substrate for the sulfate-reducing bacteria. The dosing of ochre started on day 49 in high (5 g Fe³⁺/day) and low (2.5 g Fe³⁺/day) reactors. No ochre was introduced in the control reactor.

In the start-up period, the H₂S concentration was low (<100 ppm), which was assumed to be the result of having a low sulfate content in the fed sludge. After the addition of sodium sulfate (Na₂SO₄) equally to all reactors (to provoke H₂S formation), the concentration increased very rapidly up to >2000 ppm before ochre was added. Both the high (5 g Fe³⁺/d) and low doses (2.5 g Fe³⁺/d) of ochre (corresponding to a molar ratio of 1.6 and 0.8 Fe³⁺/S²⁻, respectively), resulted in the immediate reduction of hydrogen sulfide (H₂S) concentrations (down to 570 ppm), while the control reactor

(without ochre addition) still produced biogas with a high H_2S -content. It is important to note that sulfide concentrations below 1000 ppm in biogas are recommended in order to guarantee the safe use of the gas heater and a combined heat and power production [6,8,9]. However, volatile fatty acid (VFA) measurements (acetate and propionate) showed that the stability of the reactor with the high ochre dose was affected. The acetate level increased from ~ 50 mg/L (as COD) before addition, to levels ranging from 230–1700 mg/L after addition. This indicates that ochre in a high dose (5 g Fe^{3+}/d or 1.6 mole $Fe^{3+}/mole S^{2-}$) was inhibiting the acetate-utilizing microorganism. Previously, it was found that iron inhibits acetic acid conversion during the first 2–4 days of a high iron dose addition [33]. The dosing of ochre was stopped (from day 53), as was the feeding of sludge, to let the reactors recover.

After a short recovery period, the reactors were fed with sludge for 20 days (days 64–84) to eliminate the effect of the ochre dosing (H_2S -experiment): After this, a release of phosphates by up to 400 mg PO_4 -P/L in the sludge liquor was observed. As can be seen in Figure 5, the phosphate concentrations were at the same level in all three reactors, regardless of the previous ochre dosing in two of the reactors. It was also observed that the acetate concentration in the previously high-dosed reactor decreased at the same time. The dosing of ochre (days 85–100) resulted in lower phosphate concentrations in the sludge liquor compared to the control (without ochre dosing).

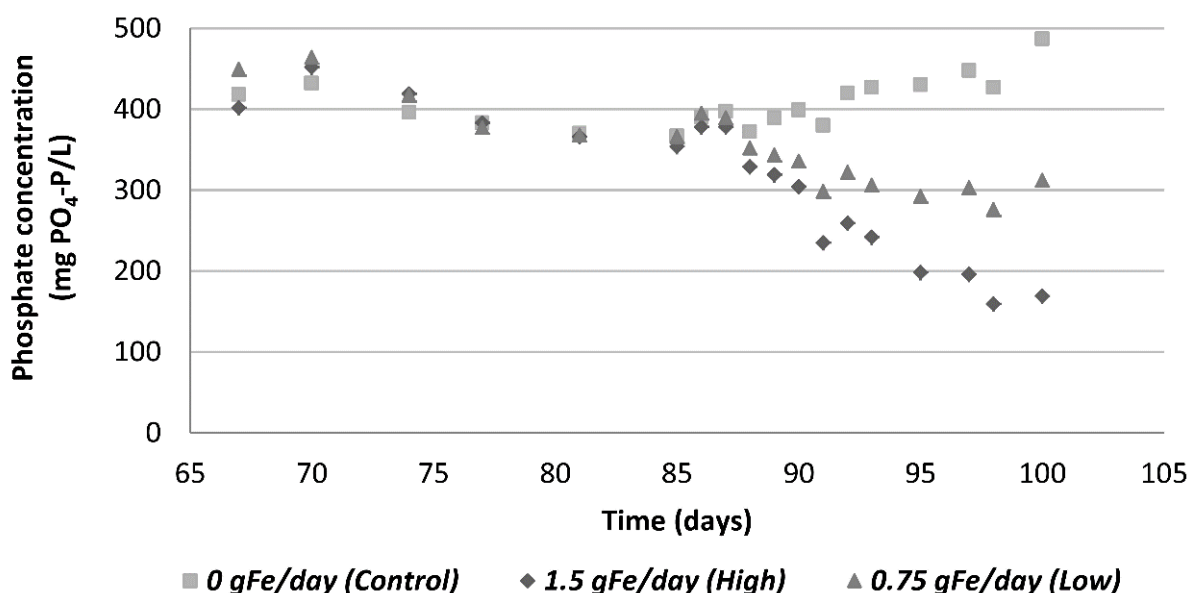


Figure 5. The dissolved phosphate concentrations (as mg PO_4 -P/L) in the continuously operated reactors. The dosing of ochre started on day 85 of the experiment and continued until day 100. The dosage was adjusted to 1.5 g Fe^{3+}/day and 0.75 g Fe^{3+}/day in the high and low reactors, respectively. No addition of ochre was introduced in the control reactor.

Within a few days, the phosphate concentration levelled out to around 150 mg PO_4 -P/L in the reactor dosed with 1.5 g Fe^{3+}/d (1.5 mole $Fe^{3+}/mole P_{released}$). This can be compared to a level of around 300 mg PO_4 -P/L mg/L for 0.75 g Fe^{3+}/d (0.75 mole $Fe^{3+}/mole P_{released}$) and of around 450 mg PO_4 -P/L for the control.

The dosing of minor amounts of ochre can therefore be seen as a cheap method for significantly reducing the internal recycling of phosphate at treatment plants with enhanced biological phosphorus removal. Higher doses of ochre in continuous operation will increase the final sludge production by approximately 11–15%. The iron content in the sludge is expected to be high, around 40 – 50 g Fe/kg TS, which is similar to the iron content in sludge from wastewater treatments plants with chemical phosphorus removal [12,13,15,16]. Thus, the ochre dose should be optimized in order to keep the extra sludge production to a minimum, but even if the high dose is used the sludge production will in total be similar to that of plants with chemical precipitation.

4. Conclusions

We demonstrated the potential for using waste ochre instead of commercial iron to reduce hydrogen sulfide in biogas production and to reduce phosphate release into sludge liquor at WWTPs with enhanced biological phosphorus removal. This use will prevent serious problems in anaerobic digestion and will at the same time solve a significant waste problem resulting from the deposition of ochre from water treatment. However, in order to prevent the inhibition of the methane production process, small doses of ochre should be applied continuously, and the dosing should be optimized in order to reduce extra sludge production. In batch tests, the dosing of ochre (0.5 g Fe³⁺/L and 1 g Fe³⁺/L) showed no inhibition of the biogas production. With the addition of ochre, the accumulated methane potentials in the reactors were 10–15% higher than the methane potential from the control reactor. During the batch test, the phosphate release was reduced by 29% and 57% for the low and high doses, respectively.

During the pilot scale experiment, an immediate drop from 2000 ppm down to 570 ppm of the H₂S concentration in the biogas was seen after dosing with ochre at two different doses: 2.5 g Fe³⁺/d and 5 g Fe³⁺/d. However, the anaerobic conversion process in the reactor with the highest dose (5 g Fe³⁺/d) was inhibited by the ochre, resulting in high acetate concentrations (230–1700 mg/L).

In a second pilot scale experiment, ochre was dosed continuously in smaller amounts (1.5 and 0.75 g Fe³⁺/d) to avoid any inhibition while evaluating the phosphate precipitation. A reduction of phosphates in the sludge liquor (33% and 66% for the low and high doses, respectively) was obtained. The continuous dosing at the highest level that was used in this second test will increase the sludge production by 11–15%.

Author Contributions: S.Ö. came up with the basic idea of the project and developed it into experimental plans together with J.I.C.J. All authors participated in the detailed planning of the batch and pilot experiments. S.Ö. did the batch experiment with support from Å.D. and J.I.C.J., S.H. and H.K. did the main part of the pilot experiments with support from the other authors. S.Ö. evaluated the results together with all authors. She wrote the paper with significant input from all authors. All authors have read and agreed to the published version of the manuscript.

Funding: The Swedish Institute [Visby grant 00645/2010] and the Swedish Water & Wastewater Association funded the project.

Acknowledgments: NSVA (Öresundsverket WWTP) are acknowledged for providing sludge for the experiments and VA SYD (Sjölunda WWTP) for their help with practical problems at the pilot plant.

Conflicts of Interest: The authors declare no conflict of interest.

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