Regular article

Innovative additives for chemical desulphurisation in biogas processes: A comparative study on iron compound products

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A B S T R A C T

Chemical desulphurisation with four iron compound additives in fermenting substrates for biogas production was studied in continuous 16 l laboratory anaerobic digestion tests. The experiments were performed to investigate the H_2S reduction in three phases including two dosing quantities. Subsequently, the supplementation was stopped. The removal efficiency (RE) increased to 37–51% towards the end of phase 1 and to 61–77% after phase 2. A significant difference in reaction time was measured at the start and at the end of supplementation. $FeCl_2$ showed the fastest response and the highest RE, especially in the first days after applying the treatment. FeOOH Type I and II also showed a high RE throughout the experiment and an additional depot effect was measured after stopping the supplementation, keeping the H_2S level lower for a period of at least 11 days. $Fe(OH)_3$ showed the lowest desulfurization effect.

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1. Introduction

Biogas has become an important ecological, resource-conserving and climate-neutral source of renewable energy in Germany. In the year 2012, biogas covered a proportion of 31.42 billion kWh (10%) on final energy consumption from renewable resources [1]. The production of biogas is based on various feedstock, such as agricultural and industrial residues, renewable energy crops or organic waste. Biogas is defined as a mixture of gases, 50–75% methane (CH_4), 25–45% carbon dioxide (CO_2), 0–20,000 ppm hydrogen sulfide (H_2S) and trace gases like nitrogen (N_2), oxygen (O_2), hydrogen (H_2) and ammonia (NH_3) [2,3]. The composition of biogas depends on the specific input substrate [4]. H_2S is formed during anaerobic fermentation of sulfate-containing feedstock [5] by reduction of inorganic sulfate through sulfate reducing bacteria in the digester [6]. The negative characteristics and effects of H_2S in the biogas, such as toxicity for humans and animals, as well as corrosion and process inhibition were discussed in detail by Nägele et al. [7]. To the contrary, sulfate is a highly valuable plant macronutrient [8] and its loss via H_2S in biogas is of economic and ecologic relevance in agriculture. Depending on the various pathways of biogas utilization, ranging from Combined Heat and Power (CHP) Units to biogas upgrading and gas grid

injection plants, different methods for desulphurisation in the biogas process have been developed and adapted [4,9]. Scientific literature provides various options to categorize the different approaches. Some authors categorize the technologies of biogas desulphurisation into internal and external methods [7]. Within the external purification methods, the H_2S in the gas phase is purified with biological, physical and chemical methods outside the digestion system (Fig. 1). The internal methods use the supply of ambient air into the gas phase of the digestion system or the desulphurisation in the digestate itself using iron compounds or a combination of both during digestion in the digester. There is no precise data available regarding the technologies, the number of biogas plants nor the combination of methods used for desulphurisation. The scarce data available, reports that approximately 90% of all biogas plants in Germany use the low cost method of ambient air injection (biological desulphurisation) into the gas headspace in the digester [10] to oxidize H_2S into elementary sulphur, sulfate-S or sulphite-S [11]. A significant disadvantage of this method is that due to the fluctuating H_2S contents, the dosage of air is often imprecise and leads to dilution of the biogas by inert gas (N_2) and remaining O_2 in the case of oversupply. This results in a lower biogas quality and affects the efficiency of biogas utilization, especially for biogas plants using upgrading technology. Furthermore, the oxidized product adheres to the surface of the digesters and pipes. This may lead to technical problems such as process failures if the sulphur crust is returned to the digestate and as a major drawback, it cannot be reused for plant nutrition. As the

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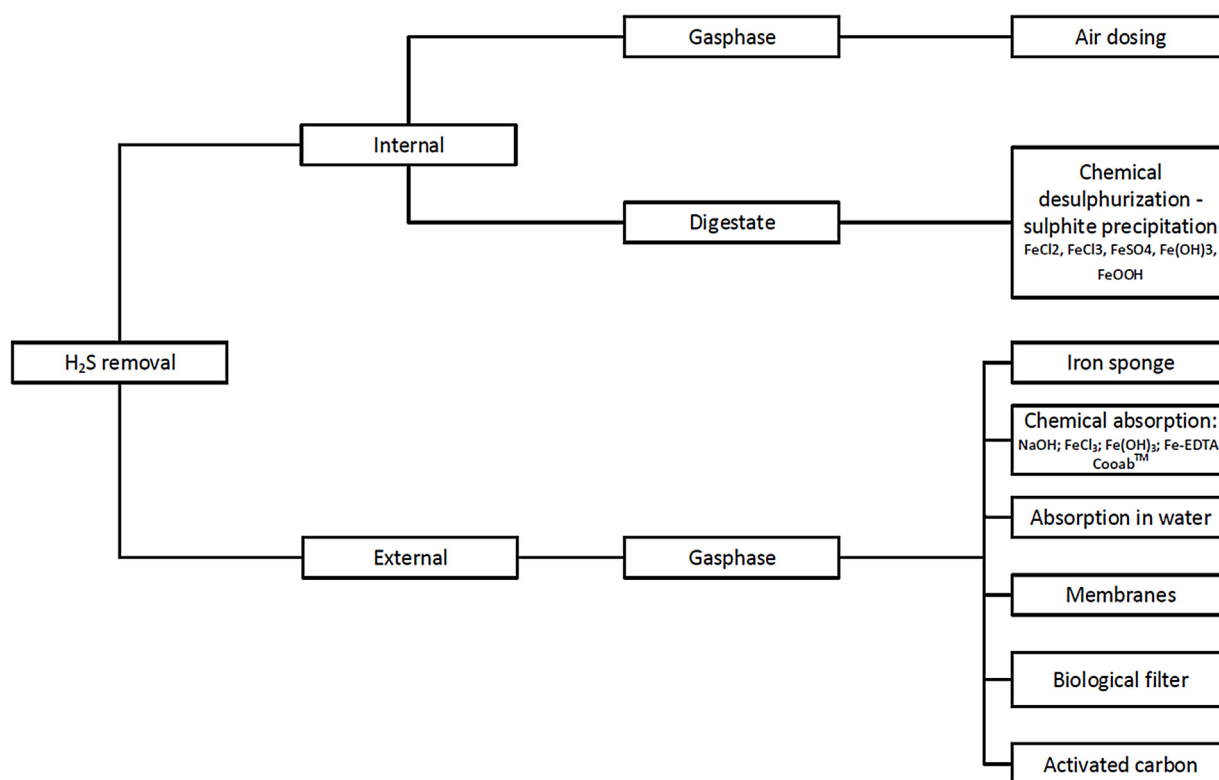 *E-mail address:* hajo.naegele@uni-hohenheim.de (H.J. Nägele).

Fig. 1. Overview on common desulphurisation methods, classified into internal and external methods (adapted from [3] and [8]).

injection is imprecise and leads to a fluctuation in H_2S content in the biogas, a final cleaning step is necessary, which is often carried out with activated carbon filters. With a growing number of plants producing biomethane from biogas for grid injection, there is a need for technologies without air injection. Desulphurisation of biogas after the digestion process in separate systems avoids the drawbacks of desulphurisation in the gas phase during digestion, but the facilities needed are technically demanding and require high maintenance and increased costs. Chemical desulphurisation in the digestate during digestion is a method that avoids the drawback of the other methods as it is easy to apply, binds the sulphur in the digestate as iron sulfide (FeS) and does not introduce any diluting substances into the gas. Hence, the formation of H_2S is suppressed and the negative impacts of H_2S in the biogas are avoided. Iron compounds such as iron(III) oxide-hydroxide ($Fe(OH)_3$) and iron(II) chloride ($FeCl_2$) are well-known agents used in biogas processes [4]. The market offers a wide range of products and iron compounds that differ considerably from each other. As new products are entering the market, the aim of the presented lab-scale study was to compare four iron compound products for H_2S removal in digestion processes and to examine the biological process parameters of the fermenting substrates. The substrates used for digestion were based on manure from animal husbandry and renewable energy crops. To the authors knowledge, there are no publications available in scientific literature that present results for other products than iron salts (e.g. $FeCl_2$) for H_2S removal during digestion in the fermenting substrate.

2. Materials and methods

2.1. Anaerobic digestion test

A continuous biogas test (CBT) with 15 horizontal stainless steel digesters each with a net volume of 16 L was used according to the VDI Guideline 4630 [12]. The inoculum used was a fermenting sub-

strate of a mesophilic operating full-scale biogas plant, fed on a mixture of 35% liquid manure from cattle and pig and 65% renewable energy crops (60% grass silage, 30% maize silage, 10% ground grain). Each digester was fed with 15 kg of inoculum. The input substrates were fed into the reactor on the front side via an inlet and stirred with an electric driven reel agitator in intervals of one minute agitations followed by a three minute break. On the rear side, the digested substrate was taken out via an overflow valve [12]. The process was heated up to 40 °C by a water bath and a circulation thermostat connected to a heating system surrounding the drum. The biogas was continuously released from the top end of the digester and passed through a gas wash bottle into a storage bag. A gas measuring unit automatically analysed the gas quantity (Höntzsch FA MS40, Germany), as well as the content of CH_4 and CO_2 (D-AGM Plus, Sensors Europe, Germany) and H_2S (Membrapor H_2S/S-5000-S, Switzerland). The measurements were carried out once a day. The 15 digesters were fed similar to practical conditions at an organic loading rate of 2.5 kg organic dry matter (oDM) per cubic meter (m^3) digester volume per day, resulting in a hydraulic retention time (HRT) of 60 days. According to the chemical compositions and process restrictions mentioned, the standard daily feed was calculated at 147.00 g fresh material of the substrate mixture (37% maize silage, 37% grass silage and 26% laying hen manure) and 120.00 g fresh material of separated liquid substrate from the secondary digester of the full-scale biogas plant. The solid material was pre-treated in a cross-flow grinder for 15 s [13].

2.2. Investigated iron compounds

In this study, market available additives iron(III) oxide-hydroxide (FeOOH) (Type I), iron(III) hydroxide ($Fe(OH)_3$), iron(II) chloride ($FeCl_2$) and a newly developed innovative product iron(III) oxidehydroxide (FeOOH) (Type II) were tested (Table 1). The FeOOH (Type II) has a 10-times higher surface (approximately 150 m^2 g^{-1}) compared to Type I and therefore another reaction time and quality