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Short review

Iron-containing clay and hematite iron ore in slurry-phase anaerobic digestion of chicken manure

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Abstract: It is shown in this review that addition of clay minerals and hematite iron ore can significantly enhance anaerobic digestion of chicken manure. Liquid-phase anaerobic digestion of chicken manure consumes a lot of fresh water and energy to keep waste as a suspension. Meanwhile, anaerobic digestion of chicken manure in clay slurry without stirring could minimize energy and water consumption because the initial acceptable content of organic solids can be increased. For example, this content can be increased from 5% (w v^{-1}) in suspension of chicken manure for liquid-phase anaerobic digestion up to 15% (w v^{-1}) in the slurry of chicken manure for slurry-phase anaerobic digestion than can save up to 13.3 L of water per kilogram of dry organic solids. The slurry-phase anaerobic digestion of nitrogen-, sulphur-, and fat-containing organic wastes can be enhanced using microbial reduction of Fe(III) in clay or in hematite iron ore. This is due to adsorption or precipitation of such inhibitors of microbial acidogenesis and methanogenesis as ammonium, sulphide, long-chain fatty acids, humic and fulvic acids with clay or ferrous ions. For example, maximum concentration of ammonium decreased from 11.4 g L^{-1} during liquid-phase anaerobic digestion to 1.4 g L^{-1} during slurry-phase process due to adsorption of ammonium ions on clay. Addition of iron-containing clay to slurry-phase anaerobic reactor removed dissolved sulphide totally due to its precipitation with ferrous ions that are produced by bioreduction of Fe(III) in clay. Slurry-phase anaerobic digestion enhanced with bioreduction of Fe(III) minerals is also more effective process in terms of environmental safety than widely used liquid-phase anaerobic digestion because of an absence of water supply and wastewater effluent.

Keywords: clay slurry; anaerobic digestion; organic waste; chicken manure; ferric bioreduction; ammonium adsorption

1. Introduction

Anaerobic digestion of the nitrogen-rich organic wastes such as chicken or pig manure is usually performed in practice as either solid-phase process with the content of solids about 60% (w v^{-1}) [1] or liquid-phase process with the optimum content of solids about 5% (w v^{-1}) [2]. The solid-phase process could be unstable because of not even distribution of the concentrations in the bulk of the matter, diffusion-limited mass exchange and production of process inhibitors due to the high content of organic waste, and potential penetration of oxygen into the porous solid matter [1,3,4]. The liquid-phase process, which is dominating among the practical commercial applications, requires a lot of fresh water to suspend organic waste and energy for liquid waste stirring. Additional technical problem of the liquid-phase anaerobic digestion is mechanical stirring or gas mixing in anaerobic digester, which are both complicated by instable pseudoplastic rheology of suspended organic waste [5]. Efficient liquid-phase anaerobic digesters including expanded granular sludge bed reactor, continuously stirred tank reactor, or sequencing batch reactor ensure high organic loading rates [6], but require a lot of water and energy. Therefore, it could be important to find new water- and energy-saving technology of anaerobic digestion of organic wastes in addition to the existing and widely using technologies.

The aim of this review was to find new effective ways for anaerobic digestion of organic waste to avoid problems of solid-phase and liquid-phase processes. The objectives of the review were related to enhancement of one type of organic waste, exactly to anaerobic digestion of chicken manure. These objectives were as follows: 1) determination of the parameters of slurry-phase process; 2) diminishing of the inhibiting effect of ammonium on anaerobic digestion using iron-containing clay; 3) evaluation of addition of iron-containing clay and/or iron ore for elimination of the inhibiting effects of sulphide, long-chain fatty acids, and humic acids on biogas production during anaerobic digestion of chicken manure.

2. Slurry-phase anaerobic digestion of chicken manure

A priori, wet organic waste can be mixed with clay producing slurry that could be digested without stirring in the simple underground construction. A soil or clay slurry usually contains up to 30–40% (w v^{-1}) of solids [7]. A slurry-phase anaerobic digestion ensures strictly anaerobic conditions due to oxygen consumption in the upper layer of slurry. There will be consumption of energy only for the mixing of waste and clay and no consumption of water in slurry-phase anaerobic digestion. Therefore, it is water-saving and low-cost biotechnology for utilization of organic wastes, for example chicken, pig, or cow manure, organic wastes of slaughterhouse, meat- or fish-processing plants.

For example, quantity of fresh water for the dilution of chicken manure from 15% to 5% (w v^{-1}) of organic solids before liquid-phase anaerobic digestion is 2 L of water L^{-1} of chicken manure or 13.3 L of water kg^{-1} of dry organic solids. This is the saving of water for slurry-phase anaerobic digestion of chicken manure in comparison with liquid-phase process. Additionally, there will be no wastewater effluent after slurry-phase anaerobic digestion because clay slurry could be used for the improvement of the texture of the sandy soil in arid area. So, saving of water and use of clay slurry after anaerobic digestion for sandy soil improvement could be especially beneficial for arid areas in developing countries [8]. Clay slurry-phase anaerobic digestion of chicken manure could be a low-cost treatment. It is known that cost of aerobic slurry-phase soil bioremediation is from $130 to $200 per cubic meter [7], so the cost of anaerobic clay slurry-phase treatment could be several times lower, approximately $20–30 per cubic meter, because there will be no need in aeration and average cost of clay is just about $75 per metric ton.

Technological comparison of liquid-phase and slurry-phase anaerobic digestions is shown in Table 1. Clay slurry-phase anaerobic digestion has a lot of other technological advantages over liquid-phase digestion that are described and analyzed below.

Table 1. Comparison of liquid-phase and slurry-phase anaerobic digestions of chicken manure.

Process characterization	Liquid-phase anaerobic digestions	Slurry-phase anaerobic digestions
Supply of fresh water for dilution before digestion	13.3 m^3 of water t^{-1} of dry manure	0
Supply of iron-containing clay	0	0.25 t of clay m^{-3} of chicken manure or 1.7 ton of clay per ton of dry manure
Wastewater effluent	13.3 m^3 of wastewater t^{-1} of dry manure	0
Mixing	Stirring of manure and water in the digestion tank	Mixing with clay in rotating drum reactor before digestion
Separation of solid and liquid wastes after digestion	Sedimentation tank or centrifuge	No need to separate. Clay slurry after digestion can be used for fertilization of sandy soil.

3. Removal of ammonium by adsorption with clay minerals during slurry-phase anaerobic digestion of chicken manure

The anaerobic decomposition of nitrogen-rich waste produces ammonium that is in equilibrium with free ammonia, which is strong inhibitor of methanogenesis [9,10]. For example, concentration of ammonium ions 4.8 g L^{-1} inhibited methanogenesis by 90% [11,12]. Meanwhile, concentration of ammonium during anaerobic digestion of non-diluted chicken manure was 6.0–6.5 g L^{-1} [2], from 2 to 16 g L^{-1} [11,12] and from 3 to 5 g L^{-1} during anaerobic digestion of the chicken manure in liquid-phase reactor [13,14]. Therefore, strong inhibition of methanogenesis at these conditions was observed.

There are known many physical and chemical methods for ammonia removal during anaerobic digestion of nitrogen-containing organic wastes [15,16]. The stripping of ammonia from recycled liquid [17], dilution of liquid with water [11], and technically complicated method with the recycle of biogas and the stripping of ammonia from liquid [11,18–21] can be used to remove up to 80% of the produced ammonia [18,20].

An adsorption of positively charged ammonium ions on negatively charged clay particles could be useful approach to diminish concentration of free ammonia. An average ammonium adsorption capacity of clay within 30 min at pH 7 is about 40 mg of ammonium g^{-1} of montmorillonite, vermiculite, bentonite, or zeolite [21–26]. Our unpublished data on sorption capacity of clay in the mixture of 5% (w v^{-1}) or 10% (w v^{-1}) clay in solution of ammonium chloride of 5000 mg of N–NH_4^+ L^{-1} showed that sorption capacity of bentonite or red argillite was 31–47 mg of N–NH_4^+ g^{-1} of clay and 11–15 mg g^{-1} N–NH_4^+ of clay, respectively. Ammonium adsorption rates for these clays were in average 20 and 6 mg of N–NH_4^+ g^{-1} of clay h^{-1}, respectively. It was shown that after addition of 3–10% (w v^{-1}) of bentonite the cumulative methane production from anaerobically digested chicken manure was increased from 161 in control to 302 mL of methane g^{-1} of chicken manure [27] and ammonia emission was reduced by 70% [28], probably due to adsorption of ammonium ions by clay. Increase of initial concentration of organic solids from 6% to 16% (w v^{-1}) decreased maxima of the rate of methane production probably due to increase of ammonium concentration (Table 2).

Table 2. Anaerobic digestion of chicken manure at different initial concentration of organic solids [13,14].

Concentration of organic solids, % (w v^{-1})	Maxima of the rate of methane production, normo L of CH_4 kg^{-1} of solids day^{-1}	Concentrations of produced ammonium, g L^{-1}	
		Initial	Final
6	17.0 ± 3.2	0.8 ± 0.2	2.4 ± 0.2
10	10.2 ± 2.4	1.4 ± 0.2	4.0 ± 0.3
16	6.1 ± 2.5	2.2 ± 0.3	5.0 ± 0.4

In average, the content of the elements in the dry chicken manure is as follows: C 35%, H 5%, O 30%, N 5.5%, and S 0.8% [11], so empirical formula of dry chicken manure is $CH_{1.648}O_{0.642}N_{0.133}S_{0.009}$. This formula can be used to calculate maxima of the anaerobic digestion products according to the Eq 1:

$$CH_{1.648}O_{0.642}N_{0.133}S_{0.009} + 0.371H_2O \rightarrow 0.493CH_4 + 0.507CO_2 + 0.133NH_3 + 0.009H_2S \quad (1)$$

According to this equation, production of methane, ammonia, and hydrogen sulphide per kg of dry chicken manure after its complete anaerobic digestion will be as follows: CH_4 420 L, NH_3 77 g, H_2S 11.8 g. NH_3 is in equilibrium with NH_4^+ depending on pH.

Calculations of the ratio of the chicken manure and clay could be done using data that concentration of ammonium during anaerobic digestion of chicken manure with the content of 20% (w w^{-1}) of solids could be up to 6.5 g L^{-1} [2]. To adsorb 6.5 g L^{-1} of ammonium, an addition of clay must be at least 162 g L^{-1}. In our experiments [13,14], clay-manure slurry was produced by mixing of 1000 g of red (montmorillonite) clay containing 7% (w v^{-1}) of iron and 25% (w v^{-1}) of water (=750 g of inorganic solids + 250 mL of water) and 3000 g of chicken manure with the content of organic solids 15% (w v^{-1}) (=450 g of organic solids in average + 2550 mL of water). It was inoculated with 300 mL of enrichment culture for anaerobic digestion enhanced with ferric bioreduction. In this case, the content of total solids, organic solids, and inorganic solids in slurry was in average 28%, 10.5%, and 17.5% (w v^{-1}). Enrichment culture for anaerobic digestion enhanced with ferric bioreduction was produced for 30 d of cultivation of 70 mL of clay-chicken manure slurry inoculated with 20 mL of anaerobic sludge of municipal wastewater treatment plant. Maximum rate of methane production in slurry-phase anaerobic digestion of the chicken manure was about 2.8 time higher than that in liquid-phase anaerobic digestion. Additionally, in the case of slurry-phase anaerobic digestion of chicken manure, there was no consumption of water and no wastewater effluent.

Fe^{2+} ions that are produced during bioreduction of iron-containing clay are further hydrolyzed forming insoluble positively, neutral, and negatively charged iron hydroxides, which are adsorbents of negatively and positively charged compounds [29–31]. Their ratio depends on the pH as shown in the Eq 2:

$$Fe^{2+} + x_1H_2O \leftrightarrow x_2Fe(OH)^+ + x_3Fe(OH)_2 + x_4Fe(OH)_3^- + x_5H^+ \quad (2)$$

Iron hydroxides are adsorbents of negatively and positively charged compounds, including phosphate [29–31]. In case of anaerobic digestion of organic wastes, bioreduction of ferric and precipitation of ferrous phosphate will prevent leaching of phosphate to environment from disposed clay slurry.

The clay slurry after anaerobic digestion could be used as soil fertilizer and enhancer of the sandy soil texture. Clay adsorbs potassium ions [32] of the chicken manure, so clay slurry after digestion and bioreduction of iron is enhanced with ammonium, potassium and phosphate. Our calculations show that clay after slurry-phase anaerobic digestion can contain about 1% of potassium, 0.5% of phosphorus, and 2% of nitrogen. Therefore, this clay slurry could be used as a soil amendment to enhance fertility of soil.

4. Removal of sulphide during methanogenesis due to bioreduction of Fe(III)

The sources of hydrogen sulphide in anaerobic digestion are sulphur-containing aminoacids and bioreduced sulphate. Methanogenesis was inhibited by 50% at the concentration of 184–354 mg of H_2S L^{-1} [33,34]. In our experiments on anaerobic digestion of the chicken manure in liquid-phase reactors, the concentration of hydrogen sulphide was 212 mg L^{-1} [13,14], which is in the range of inhibiting levels for methanogenesis.

Hydrogen sulphide is not only inhibitor of methanogenesis but also dangerous substance for human health [7]. During the agitation or mixing of swine manure in a deep pit storage system the concentration of hydrogen sulphide was observed at levels exceeding 300 mg m^{-3} of air inside the barn [35]. Meanwhile, hydrogen sulphide concentrations of 300–450 mg m^{-3} of air can result in conjunctivitis and respiratory tract irritation after 1 h, and concentrations of 750–1050 mg m^{-3} of air can result in collapse in 5 min [36].

Probably, the best option to avoid inhibition of methanogenesis by sulphide is its precipitation using ferrous ions produced by bioreduction of Fe(III) of clay or iron ore [29,37,38] that is going by the Eq 3:

$$Fe^{2+} + S^{2-} \rightarrow FeS\downarrow \quad (3)$$

To ensure this reaction, iron of iron-containing clay or hematite iron ore, mostly Fe_2O_3, must be reduced to soluble ferrous ions by iron-reducing bacteria. Electron donor for bioreduction of ferric could be organic acids, preferably acetate [29,39]. Bioreduction is going according to the Eq 4:

$$8\ Fe^{3+} + CH_3COOH \rightarrow 8\ Fe^{2+} + 8\ H^+ + 2\ CO_2 + 2\ H_2O \quad (4)$$

Acetate is the major product of acidogenic fermentation of carbohydrates of organic waste.

The most available source of iron for this process can be iron of clay or the powder of hematite iron ore. The content of iron in clay minerals is 29% in nontronite, 18% in glauconite, less in other minerals, and some portion of iron in natural red clay is in the form of ferric (hydr)oxides [40]. Ironrich bentonites can contain up to 7.5% (w w^{-1}) of iron [41]. From the stoichiometry of the Eq 3, addition of clay that contains 15% of iron (equal to 2.7 mmol of Fe g^{-1} of dry clay) can precipitate 86 mg of sulphide g^{-1} of dry clay. Calculations from Eq 1 showed that the concentration of H_2S for slurry-phase fermentation with 15% of organic solids can reach 1.77 g L^{-1}. This concentration is above inhibitory level. However, addition of 25% (w v^{-1}) of clay with 15% of Fe(III) for slurry-phase anaerobic digestion of chicken manure can remove 3.2 g L^{-1} S^{2-}, so the final concentration of sulphide will be zero due to precipitation of sulphide with dissolved Fe^{2+}. Clay that contains 10% of iron can precipitate 57 mg of sulphide g^{-1} of dry clay and addition of 25% (w v^{-1}) of this clay for slurry-phase anaerobic digestion of chicken manure can remove 1.42 g L^{-1} S^{2-}, so the final concentration of sulphide will be 0.35 g L^{-1} S^{2-}, which is in inhibitory concentration range. Thus, only clay with sufficient content of iron could be used to ensure concentration of H_2S lower than inhibition levels. If the content of iron is not sufficient, iron ore dust, ferric chloride or ferric hydroxide can be used as addition to clay slurry.

Many anaerobic bacteria are able to reduce Fe(III) in clay minerals thus producing dissolved Fe(II) [40,42,43]. Different organic compounds, even xenobiotics, can be used as electron donors for ferric bioreduction [38]. Actually, an addition of not only iron-containing clay, but other iron-containing substances such as iron ore, iron hydroxide, ferric or ferrous chloride can significantly enhance anaerobic digestion of organic wastes probably due to elimination of inhibitory effect of sulphide and long-chain fatty acids on methanogenesis [29,38,44,45]. To initiate growth of iron-reducing bacteria in the mixture of red clay and chicken manure during slurry-phase anaerobic digestion it could be inoculated by the mixture of iron-reducing bacteria from the previous cycles of anaerobic digestion enhanced with ferric bioreduction.

The concentration of total Fe(II) increased almost linearly during anaerobic digestion of organic matter. The maximum Fe(II) production rate was 58 ± 3 g of ferrous ions m^{-3} d^{-1}. It was shown in our triplicate-performed experiments [38] that the rate of methanogenesis linearly depended on the molar ratio of Fe/S in slurry of clay and chicken manure (Figure 1).

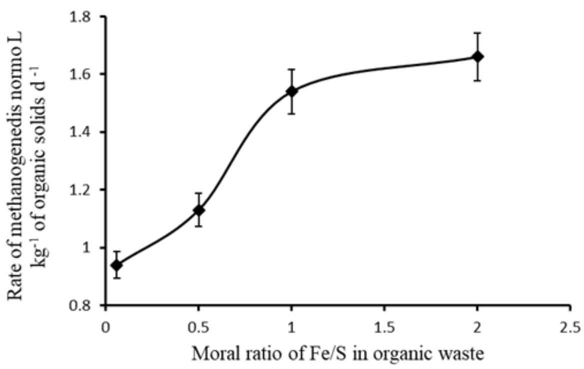

Figure 1. Effect of the molar ratio of Fe/S in slurry of clay and chicken manure on the average rate of methanogenesis for 14 d.

Average concentration of sulphide after 40 d of liquid-phase anaerobic digestion was 200 mg L^{-1}, while in slurry-phase anaerobic digestion it was only 2 mg L^{-1}. It was shown in our experiments [13,14] that it was almost no sulphide in slurry when the content of iron in clay was sufficient to bind sulphide (Figure 2). Probably, slurry-phase anaerobic digestion enhanced by Fe(III) bioreduction could be suitable for all organic wastes with high content of organic sulphur or sulphate.

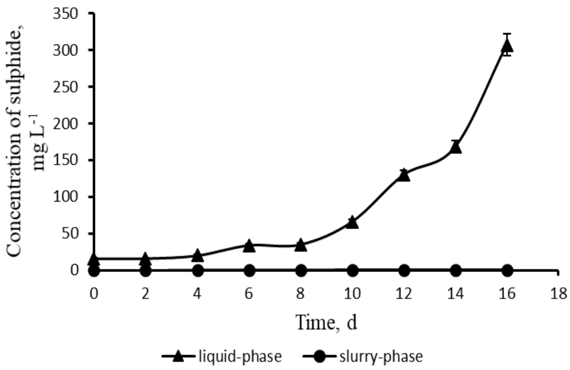

Figure 2. Concentration of sulphide in liquid-phase (triangles) and slurry-phase enhanced with bioreduction of iron (circles) anaerobic digestion.

5. Removal of long-chain fatty acids during methanogenesis due to bioreduction of Fe(III)

Wastes of vegetable oil refinery, fish processing, slaughterhouse, wool scouring, and dairy production contain lipids, which are hydrolyzed to long-chain fatty acids (LCFA) and glycerol during anaerobic digestion. It is well known that salts of LCFA are inhibitors of both acidogenic fermentation and methanogenesis because these substances are surfactants damaging integrity of cell membrane [11].

Addition of dissolved ferrous/ferric salts diminished the inhibitory effect of LCFA because of the precipitation of LCFA as iron salt. Precipitation of LCFA with either added ferrous salt [37], or soluble ferrous ions produced by bacterial reduction of Fe(III) [29,38,39,44] could be used following the Eq 5:

$$2RCOO^{-} + Fe^{2+} \rightarrow (RCOO)_2Fe\downarrow \quad (5)$$

For example, degradation of stearic acid, one of model compound of LCFA, was improved for 10 d in the presence of divalent iron by 150% [44,46]. Iron ore or even iron-containing clay can be applied even for anaerobic degradation of vegetable oil. The methane production was increased 1.5 times as compared to control without clay addition. COD removal efficiency was 98%, 80% and 77%, when iron was added to ensure the ratio of 20, 40, and 80 mg of Fe mg^{-1} of COD, respectively. Acetic and propionic acids were accumulated in the methanogenic reactors and inhibited methanogenesis when either iron was not present or COD/Fe ratio was higher than 20. However, no accumulation of soluble acetic and propionic acids was observed when the mass ratio of COD/Fe was below 20. So, presence of iron(II) significantly improved anaerobic digestion of the lipid-containing wastes [44–46]. It is known an application of ferrous for the combination of Fenton's oxidation together with anaerobic digestion of oily wastes [47]. However, hydrolysis of vegetable oil and precipitation of ferrous salts of produced long-chain fatty acids after bioreduction of Fe(III) in clay or iron ore could be more effective technology.

Anaerobic digestion enhanced by iron bioreduction could be used also for digestion of activated sludge on municipal wastewater treatment plants. Hydraulic retention times in the anaerobic digester, augmented with an iron-reducing microbial consortium and ferric (hydr)oxide, can be decreased from 20 to 10 d [48]. An addition of 1.25% (w v^{-1}) ferric chloride to the anaerobic digester of activated sludge removed sulphide and volatile organic sulphur compounds from biogas [49]. An addition of goetite (ferric oxide) promoted anaerobic digestion of algal biomass and methanogenesis [50]. There are other numerous examples of positive effect of the ferric bioreduction on anaerobic digestion [51–53]. Therefore, the interactions between the biogeochemical cycles of phosphorus, sulfur and iron were studied and modeled for improvement of anaerobic digestion process [54].

An additional benefit of slurry-phase anaerobic digestion enhanced by Fe(III) bioreduction could be also elimination of inhibition of acidogenesis and methanogenesis by humic and fulvic acids [55–57]. These compounds with negatively charged COOH and OH groups could be precipitated by cations of Fe^{2+} and $Fe(OH)^{+}$ or due to the formation of Fe^{2+} bridges between negatively charged humic acid and clay particles [58,59].

6. Conclusions and recommendations

Slurry-phase anaerobic digestion of chicken manure enhanced by microbial reduction of Fe(III) in iron-containing clay or hematite iron ore could be useful in practice, especially in arid regions of developing countries because of such advantages over liquid-phase digestion as absence of water consumption and wastewater effluent as well as faster and bigger production of methane. An addition of clay, containing sufficient quantity of Fe(III), can eliminate inhibition of anaerobic digestion by ammonium, sulphide, long-chain fatty acids, and probably humic acids. However, economic benefits of slurry-phase anaerobic digestion of the chicken manure depend on the local availability and costs for iron-containing clay, iron ore powder, water supply and wastewater treatment.

Commercial applications of iron bioreduction in anaerobic digestion of organic wastes are protected by the patent of USA 7393452 "compositions and methods for the treatment of wastewater and other waste" [60]. The proposed schematics of the process for anaerobic slurry-phase anaerobic digestion of chicken manure enhanced by bioreduction of Fe(III) is shown in Figure 3. However, combination of clay slurry-process and ferric bioreduction was not studied yet in full scale, so this review is aiming to initiate these studies and potential applications.

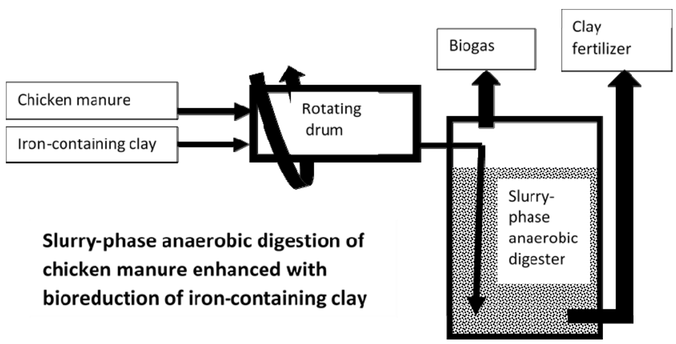

Figure 3. The schematics of the clay slurry-phase anaerobic digestion enhanced by ferric bioreduction.

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Conflict of interests

The authors declare no conflict of interest.

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