Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2015, 7(9):353-359

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Effect of iron oxide nanoparticle in bio digestion of a portable food-waste digester

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ABSTRACT

Handling of wasted food product is a challenging task in municipal solid waste management. Dumping fast degradable material to landfills generates greenhouse gases as well as foul smell. Such biodegradable waste can be processed scientifically to obtain useful products. By utilizing these wastes in an anaerobic digester, biogas rich with methane gas (upto 60%) is generated and the residue slurry is used as organic fertilizer. It is the best means to deal with food/organic waste in rural as well as urban areas. Performance analysis of anaerobic digesters is reported in the literature since last few decades. Bio digestion involves slow chemical reactions. It is well reported in literature that high retention time makes this system less attractive. Additional iron content in the digestion process increases the production rate as it helps in reducing CO_2 to form CH_4. Increase in methane quantity increases the quality of biogas. Since pure iron may generate toxic free radicals in the system additional iron oxides powders are used. Generally nanoparticles catalyzes better than its bulk analogs. Bio degradable iron oxide nanoparticles produced by polyol method is added to the digester to enhance the rate of production.

Keywords: Bio Digestion; Food-waste; Iron Oxide Nanoparticles

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INTRODUCTION

Food waste is the least recovered materials in the municipal solid waste and is one of the most important materials to be reduced from landfills. Food that is disposed of in landfills decomposes to produce methane, a potential greenhouse gas that contributes to climate change. Both urban and rural area produces large amounts of food waste daily [1]. Till date a lot of biogas plants, all over India, are constructed in rural areas. But most of them are facing a lot of technical problems, like high retention time, consistent production of methane gas/day, and lot more. So it is very important to study all the physical parameters which affects the biogas production and to cut-off the technical problems that a system face.

Alvarez et al., (2000) has studied the different technology for anaerobic digestion of organic solid wastes [2]. Fundamentals (kinetics, modeling, etc.), process aspects (performance, two- and single-phase systems, wet and dry technologies etc.), digestion enhancement (with various pre-treatments), co-digestion with other substrates and its relation to composting technology are reported in detail. Corral et al., (2008) reported anaerobic digestion of dairy cow manure (CM), the organic fraction of municipal solid waste (OFMSW), and cotton gin waste (CGW) with a two-phase pilot-scale anaerobic digestion (AD) system [3]. They concluded that by comparing the single waste digestions with co-digestion of combined wastes, co-digestion results in higher methane gas yield. Dhamodharan and Kalamdhad (2014) described a review on pre-treatment and anaerobic digestion of food waste for high rate methane production [4]. Curry and Pillay (2012) investigated the feasibility of urban anaerobic digestion, presented few techniques for biogas estimation such as, ultimate analysis, yield from molecular formula analysis using a novel computer simulation technique, Anaerobic Digestion Model #1 (ADM1) [5].

The aim of this work is to study the physical parameters and find a way to increase the biogas production rate. Nanoparticles show better result than their bulks phase. It is reported in literature that a few metal oxide particle enhances the production and quality of biogas [6]. Iron oxides in nano-scale have exhibited great potential for their applications as catalytic materials, waste water treatment adsorbents, pigments, flocculants, coatings, gas sensors, ion exchangers, magnetic recording devices, magnetic data storage devices, toners and inks for xerography, magnetic resonance imaging, bio-separation and medicine. The new studies in this field suggest that using iron oxides nanoparticles in the digester can increase the rate of production of biogas from 40% to 200% (Casals et al., 2014) [7]. They used 100 ppm of 7 nm iron oxide nanoparticle and the biogas production increased by 180%. Mohapatra and Anand (2010) have reported on detail about synthesis and applications of nano-structured iron oxides/hydroxides [8]. The nano-structured iron oxides have been synthesized mostly by wet chemical methods which include precipitation at ambient/elevated temperatures, surfactant mediation, emulsion/micro-emulsion, electro-deposition etc. In this work iron oxide is selected as the catalyst to enhance the methane production rate in anaerobic digester. Since iron particles could be toxic, addition of iron particles directly may not be feasible [6]. Addition of Iron oxide nanoparticles will overcome the above stated problem.

EXPERIMENTAL SECTION

2.1. Anaerobic digestion

Anaerobic digestion is a method through which bio-degradable materials can be converted into useful energy. Here in anaerobic digestion, the conversion from useless materials to useful energy takes place in the absence of oxygen. The production of biogas was carried out in small digesters. The digester was made using normal 30 L plastic containers and marked as A and B (Fig. 1). They were additionally painted with black colour to avoid direct sunlight. Direct sunlight will facilitate formation of algae which converts anaerobic digester into aerobic digester [2]. Necessary attachments were made to take the gas out from the digester. The main part of the entire setup is as shown in the figure below. Water displacement method is used to collect the gas. The gas samples are collected in balloons and subjected for characterization.

Fig 1: Portable food waste digesters

Two portable food waste digesters were built and the ingredients in the digesters are given in Table 1.

Table 1: Ingredients in digesters

Digester 1 (A)	Digester 2 (B)
Dairy cow manure: 2 kg Food waste: 6 kg Water: 10 L	
Iron oxide nanoparticle: 1.4 g	Nil

1.2. Synthesis of Iron Oxide Nanoparticles

There are various methods existing for the production of iron-oxide Nanoparticles. Basina et al., reported synthesis of biocompatible magnet iron oxide nanoparticles by modified polyol process for biomedical applications [9]. A detailed procedure to synthesize iron oxide nanoparticles has been laid out by Dozier et al., [10]. The synthesis is done using polyol process as described by Songvorawit et al. (2011) [11].

The synthesis is done by the reduction of ferric chloride using ethylene glycol. Here 2 g of ferric chloride (NICE) is reduced by 40 mL ethylene glycol and 0.1 ml 34% HCl under continuous stirring at 50-60 ^oC for about 24 hours. The solution is heated and stirred until the solution become brown. The nanoparticles are formed in the solution by slow reduction. Yellow brown colour solution turns dark brown after the reaction.

1.3. Separation of Nanoparticles

The separation of nanoparticles from the solution is done by centrifugation method. This is one of the easiest methods to separate particles which are immersed in solutions. Here the solution is kept in conical bottom test tubes, and due to the centripetal acceleration (occurred due to radial acceleration) the denser particles are settled down in the solution. Methanol (NICE) is used as diluent in 1:1 v/v ratio to facilitate the process [12]. Once it got settled down, the top part (the solution) was decanted out and the nanoparticles were moved to separate test tubes and washed well with ethanol to remove the impurities. Approximately 5-6 hours of drying at 100 ^oC, finally yields 0.7 g black powder of iron oxide nanoparticles.

1.4. Scanning Electron Microscopy

A scanning Electron Microscope is used to produce images of the sample by scanning it with a focused beam of light. This will give a high resolution image of the sample. This can be used to do structural studies of the particle.

1.5. Energy Dispersive X-Ray

EDX is a method used to find the chemical composition of the sample as well as for elemental analysis. Here this method is used to see the composition of the particles. It is one of the variants of X-ray fluorescence spectroscopy. EDX relies on the investigation of a sample through interactions between electromagnetic radiation and matter; it analyzes the X-rays emitted by the matter in response to being hit with charged particles. Its characterization capabilities largely depend on the fundamental principle that each element has a unique atomic structure, considering X-rays that are characteristic of an element's atomic structure to be identified uniquely from one another.

1.6. X-Ray Diffraction

XRD is a technique used to identify the phase of a crystalline material and is used for unit cell dimension calculation. The size of nanoparticle is calculated using the Scherrer Equation [12].

$$\tau = K\lambda/\beta Cos\theta \qquad (1)$$

Where, τ is the mean size of the crystalline; K is a dimensionless shape factor, with a value close to unity. The shape factor has a typical value of about 0.9, but varies with the actual shape of the crystallite; λ is the X-ray wavelength; β is the line broadening at half the maximum intensity (FWHM), after subtracting the instrumental line broadening, in radians. θ is the Bragg's angle.

1.7. Gas Analyzer

INDUS Model PEA205 is a class I gas analyzer equipped with a vacuum pump, can measure carbon monoxide (CO), carbon dioxide (CO_2)and Oxygen in percentage and hydrocarbons and Oxides of nitrogen in ppm. The probe which is attached to this system sucks the gases and then passes through a filter where the unwanted particles are filtered out. Then this is passed through the sensors where the analysis takes place.

RESULTS AND DICUSSION

3.1. Morphology of Nanoparticles

To characterize morphology of Iron oxide nanoparticles, SEM (scanning electron microscopy) is performed [13, 14]. SEM analysis is used to confirm the morphology of the synthesized iron oxide (IO) sample. The obtained results using scanning electron microscopy analysis clearly show that crystalline structure of the sample. From the literatures it is reported that the size of the Nanoparticles synthesized by polyol method can be of wide range, around 5 nm to 250 nm [12]. Since the sample was not washed completely, more discrete image could not be obtained. But from the SEM analysis we can say that the particle sizes varied from 50 nm to 200 nm. These particles can be used as a catalyst for bio-degradation.

From the image (Fig. 2) it is confirmed that the sample contains various sizes of nanoparticles. Similar results on SEM analysis of IO nanoparticles have also been reported in the literature. However, the nanoparticle synthesis might also be controlled by using additional stabilizer like PVP (poly-vinyl pyrrolidone) and varying concentration of Cl^- ions in the solution [12].

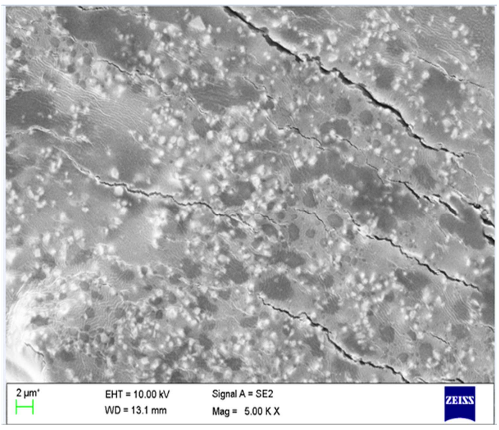

Fig. 2: SEM Image of Iron oxide nanoparticles

Energy-dispersive X-ray spectroscopy (EDS or EDX) is an analytical technique used for the elemental analysis or chemical characterization of a sample. Initially, trace amount of chlorine is detected because the nanoparticle prepared was not washed completely with methanol/ethanol. This ends up in impure sample in which there is unreacted chloride salt. Once we further wash the sample with ethanol the amount of impurities will get reduced and the amount of chlorine could not be detected.

3.2. X-Ray Diffraction pattern

The XRD pattern of nanoparticles prepared by the polyol process is shown in the Fig. 3. The XRD is used to characterize the crystal structure. X-ray diffraction pattern is similar to that reported in literature [15]. Miller indices are almost same as that in reported literatures. So it is suggestive of the synthesized nanoparticles being pure crystalline iron oxide nanoparticles only.

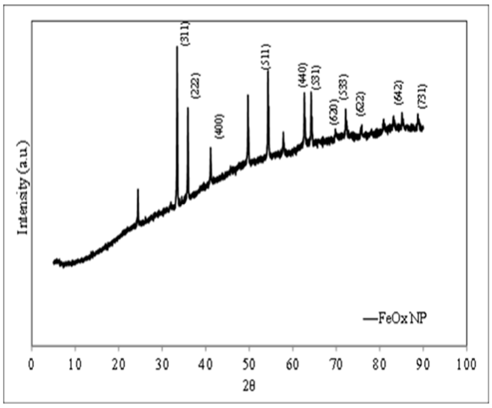

Fig. 3: XRD pattern of Iron oxide nanoparticles

The XRD pattern is further analyzed to find the particle size of iron oxide NPs. Particle size is calculated using Sherrer equation, individually choosing the peaks from XRD pattern.

Table 2: Particle size chart

Bragg's angle, 2θ	Particle size
24.4°	56 nm
33.4°	20 nm
35.8°	7 nm
41.2°	16 nm
49.6°	8 nm
54.3°	11 nm
57.8°	16 nm
62.6°	33 nm
64.2°	7 nm

The Table 2 shows the particle size with respect to the peaks appeared in the XRD graph. In the initial point the Scherrer value is 4 nm. But the corrected value is 56 nm which is so much high than the original value. As a result we took 56 nm as the real value. From these results the average particle size is ~20 nm. However nanoparticle synthesis in a large scale, produces bigger size of particles [12] hence overall size range should be ~50 nm.

3.3. Biogas Production

The pH of the system is studied and was found to be very low. It is measured to be 4 in digester A and 4.3 in digester B, just after a week because of oily food waste from the hostel canteen was added. According to literature report it is found that the pH should be in the range of 6.7 to 7.5. So the next step is to increase the pH value to 7 [16,17]. The easiest method to increase the pH value is by adding sodium bi-carbonate salt and urea granules. The addition of sodium bi-carbonate helps to increase the pH to ~7. The biogas production started after 75 days in digester B. Yield was also noticeably less even after 75 days. However, the average room temperature during this time was 25-30 ^{o}C. The gas is collected in large balloons for further testing. The biogas production is very slow in temperature ~25 ^{o}C [18]. In order to obtain a fast production the temperature should be maintained at 30-35 ^{o}C. This is the temperature at which the system can give its best results. But maintaining such temperature may need additional heating which will consume grid power hence brings down the overall system efficiency. If the environment temperature drops, the retention time increases.

Normally biogas production occurs from biomass to biogas as follows [6]:

Biomass $\rightarrow$ Sugars $\rightarrow$ Acids $\rightarrow$ Acetate $\rightarrow$ CH_4+CO_2

Sodium bicarbonate and urea is used in order to control the pH of the system and cow manure is used as the microbial seed which helps to produce sufficient amount of micro-organisms, which helps in the conversion process. Several reaction leads to formation of methane (CH_4) from acetates where a catalyst like iron oxide may be of help.

3.4. Effect of Iron Oxide Nanoparticle

The effects of nanoparticles are studied here. 1.4 g of IO nanoparticles is added to the digester A. Though Casals et al., added 100 ppm nanoparticles to enhance the yield, here the waste and environment are different. Small 1 L plastic cans were filled with proportional mixture of cooked rice, cow manure, 10 mL of acetic acid, (sodium bi-carbonate to adjust pH) and 40, 60, 80 and 100 ppm of iron oxide nanoparticles kept at exact 35 ^{o}C. Within a month all the cans except the 40 ppm can starts yielding gas hence we concluded that 70-80 ppm of nanoparticle will be sufficient to yield biogas. Thus the biogas production started after 60 days in digester A. Yield was also comparatively high and both the digesters continuously yield gas even after 75 days at room temperature.

The total retention time taken for digester B is more than 2 months at room temperature whereas in case of digester with iron-oxide the retention time is less. It is seen that the retention time is within 2 months only. Also the amount of gas produced is different. In normal digester we collected almost 3 to 4 balloons (~4 L at 1 atm) whereas with catalyst, we were able to collect almost 7 to 8 balloons (7 L at 1 atm). So it can be seen that the catalyst helps to reduce the retention time as well as it helps in increasing the quantity as well [19]. Iron ions help in reducing CO_2 to form CH_4 in presence of hydrogen [6,7].

Su et al., reported that zero valent iron particle enhances the biogas production and it was supported by the Xiu et al. [20,21]. Su et al., added 0.1% 20 nm iron particles to the anaerobic digester. Xiu et al., claimed inhibition of dechlorination by iron nanoparticles enhances methane production. However, Yang et al., did not find any improvement in bio digestion after adding iron particle in sludge from Columbia waste water treatment plant [22].
It is important to study the composition of the biogas. A normal flue gas analyzeris used to detect CO and CO_2 in the biogas. Here we used INDUS 5-gas analyzer model PEA205 to find the amount of carbon dioxide present in the collected gas thus to assume that the amount of unburned hydrocarbons can be methane.

Table 3: The reading from the 5-gas analyzer

Digester without Iron Oxide NPs		Digester with Iron Oxide NPs	
CO_2	40%	CO_2	35%
CO	0.005%	CO	0.002%

Flue gas analyzer is able to detect the amount of CO_2 and CO. Normally a biogas will have a small amount of H_2S in it. Mostly the amount varies from 0.1 % to 1%. Since it is very small the amount of H_2S can be neglected [6]. Similarly the amount of CO in biogas is found to be very less and neglected. The remaining part can be assumed as mixture of mainly methane, small quantity of nitrogen and moisture.

From the Table 3 it is clear that the amount of hydrocarbon is varying when we used iron oxide NPs as there is a small reduction in the amount of CO_2. This shows that there is an increase in methane production when we used iron oxide NPs. So it is clear from this that the addition of IO nanoparticle can increase the rate of biogas production. Also it is seen that the addition of NPs reduced the total retention time for the biogas production. Almost 25% reduction in retention time is there during the experimental studies.

CONCLUSION

The biogas production can be a way of organic waste management. Production of biogas from food waste is successful though the retention time for this was very high. Food waste causes a reduction in the pH value. Addition of urea, sodium bi-carbonate helps to maintain the pH in the range of 6.5 to 7.5. It took almost 3 months to produce the biogas whereas with catalyst the retention time decreases to 2 months at room temperature.

Equipped with a temperature control system and by addition of catalyst during the process quality as well as quantity of gas can be improved.

Iron oxide nanoparticle can be a good catalyst to serve this purpose. The synthesis of Iron oxide nanoparticles is simple by polyol method. The nanoparticles should be washed several times after separation by centrifuge by methanol and ethanol to remove the impurity.

The SEM and EDX analysis shows that the synthesized nanoparticles were having required sizes. The particle sizes varied near ~50 nm.

Also it shows that the nanoparticles were similar to NPs reported in literatures. XRD graph shows that the NPs were very similar to standard iron-oxide characteristics.

It should be noted that the addition of 70-80 ppm of iron oxide NPs also improved the quantity as well as quality of biogas production. Digester with iron oxide nanoparticle has lesser CO_2 content in it.

Acknowledgements
Authors are thankful to the Department of Material Science, Indian Institute of Science, Bengaluru for SEM and XRD facility.

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