BIOENERGY TRANSFORMATION OF PRESS MUD VIA ANAEROBIC DIGESTION USING IRON OXIDE NANOPARTICLES: AN ANALYSIS

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ABSTRACT

This study focuses on intensifying biogas production through anaerobic digestion of press mud with the addition of synthesized iron oxide nanoparticles at various doses (30 milligrams per liter, 60 milligrams per liter, 90 milligrams per liter, and 120 milligrams per liter) at 38°C in a laboratory-scale. The characterization of iron oxide nanoparticles was done using X-ray Diffraction and Fourier Transform Infrared Spectroscopy. Results revealed that the peak of biogas production reached 245 ml in the digester containing press mud with 90 mg/L of iron oxide nanoparticles. The kinetic modeling reveals that the modified Gompertz model and modified Logistic models fit excellently with the experimental curve of cumulative biogas production, with correlation coefficient ($R^2$) values ranging from 0.9969 to 0.9986 and from 0.9987 to 0.9995, respectively.

Keywords: Press Mud, Iron Oxide Nanoparticles, X-Ray Diffraction, FTIR, Biogas, Anaerobic Digestion.

INTRODUCTION

Anaerobic digestion is a series of four metabolic processes – hydrolysis, acidogenesis, acetogenesis, and methanogenesis that occur in the absence of oxygen and are facilitated by a diverse group of microorganisms. This process results in the biochemical conversion of biodegradable material. The initial stage of hydrolysis entails the fragmentation of intractable organic polymers, such as polysaccharides, proteins, lipids, and nucleic acids, into soluble monomers utilizing enzymes like amylases, proteases, and lipases. The sugars and amino acids created during the hydrolytic phase are fermented by bacteria called acetogens, which produce acetic acid, ammonia, hydrogen, and carbon dioxide. The methanogenic phase culminates in the transformation of the byproducts into methane and carbon dioxide through the actions of methanogens. Anaerobic digestion results in the production of biogas rich in methane (CH$_4$), a suitable fuel source. On the other hand, composting primarily yields CO$_2$, which cannot be used as fuel. Biogas is a renewable energy source that has replaced non-renewable fossil fuels in the production of heat and electricity. Additionally, the automobile industry has begun to produce vehicles powered by biogas. The generation of biogas has the potential of benefits both environmental and socio-economic aspects of society and farmers such as the creation of rural employment, thereby improving the economic level which reflects in the standard of living of rural communities. Press mud cake obtained as one of the residues from the sugar industry wastes are imposed directly into the agricultural fields. Press mud is a lignocellulosic biomass waste that has a rich potential source of biogas production. Lignocellulose primarily consists of cellulose, hemicellulose, and lignin. The cellulose and hemicellulose have an intimate combination with lignin which makes both difficult to biodegrade. Being Iron oxide nanoparticles are conductive...
materials, it invigorates the interspecies electron transfer directly in which the reduction of carbon dioxide to methane occurs with the gain of electrons by methanogenic microorganisms released from the oxidizing bacteria.\textsuperscript{14} Hydrolysis of complex organic material is perceived as the rate-limiting phase in anaerobic digestion leads to several researchers investigating the potential of Iron Oxide Nano Particles (IONPs) to enhance the hydrolysis as well as acidification and methanogenesis processes. This work investigates the effect of IONPs on the biodigestibility of the lignocellulosic press mud. Moreover, it extends to optimize the proper dose of iron oxide nanoparticles which intensifies the biogas production.

**EXPERIMENTAL**

**Material and Methods**

Fresh press mud from a nearby sugar industry was taken and sun-dried for a week. Then the impurities were manually removed and ground into a fine powder and stored for further use. Dried press mud was diluted with distilled water to create Total Solid content of 8%. Cow dung was made into a slurry (dilution ratio 1:1) to start up the anaerobic digestion process of press mud. For this study, a series of 1 L anaerobic digesters along with gas collectors were specially designed and manufactured.

**Synthesis of Iron Oxide Nanoparticles**

Iron (III) nitrate nonahydrate $[\text{Fe(NO}_3)_3 \cdot 9\text{H}_2\text{O}]$ (5 grams) was added to double distilled water resulting in a homogenous yellow-colored solution by constant stirring for an hour. To the metal nitrate solution, 50 ml of 2N sodium hydroxide was added drop by drop from the graduated burette with magnetic stirring turning the yellow-orange solution into a dark brown precipitate. The suspension was irradiated with ultrasound for 90 minutes using a laboratory model ultrasonic cleaner. After the ultrasonic irradiation, the suspension was filtered (0.45 m Nylon filter membrane) with double-distilled water until the pH level attained 7. The solids were calcinated in a muffle furnace at 450°C for 4 hours to get brown-colored nanoparticles. The yield of iron oxide nanoparticles was about 3.063 grams.

**Experimental Procedure**

Anaerobic digestion was performed in digesters with a working volume of 80% with press mud (8% Total Solids adjusted using distilled water) as feedstock with 10% v/v of cow dung as inoculum. To the press mud slurry, iron oxide nanoparticles viz., 30 milligrams per liter, 60 milligrams per liter, 90 milligrams per liter, and 120 milligrams per liter were incorporated as additives in the digesters labeled as N1, N2, N3, and N4 respectively. Each digester was buffered with Sodium bicarbonate to attain a pH value above 7. The anaerobic condition in the digesters was sustained by purging the headspace (20%) with nitrogen gas and maintaining an incubation temperature of 37°C. The digesters were shaken gently twice a day to ensure the uniformity of the press mud slurry phase. The biogas formed inside the anaerobic digesters get into the biogas collector and displaced an equal volume of water.

**Kinetic Modeling**

**Modified Gompertz model**

The Modified Gompertz equation, a non-linear regression model that is empirical, is an excellent fit for the bacterial growth curve.\textsuperscript{15,16} The exponential relationship between the population density and specific growth rate is demonstrated by the model.\textsuperscript{17,18} The modified Gompertz expression for cumulative biogas production has been represented as follows:

$$Y = A. \exp\{-\exp[R_{\text{max}}. e/A(\lambda - t) + 1]\}$$

In this equation, $Y$ represents the cumulative biogas yield after time t in ml/g, while $A$ stands for the biogas production potential in ml/g. The maximum biogas production rate is represented by $R_{\text{max}}$ (ml/g/day), the minimum time required for biogas production is represented by $\lambda$ (day), and the time taken for cumulative biogas yield is represented by t (days). The mathematical constant of Euler’s number is represented by $e$, with a value of 2.8712828.

**Modified Logistic Model**

The Logistic model (LM) fits the biogas production kinetics: The biogas production pattern includes a starting exponential increase followed by stabilization at the highest point.\textsuperscript{19,20} The Modified Gompertz
equation assumes that the biogas production rate is dependent on the amount of biogas generated thus far, the highest production rate, and the highest potential for biogas production. The Logistic equation underwent a modification and was applied in the following way:

\[ Y = \frac{A}{1 + \exp\left[4R_{\text{max}}/A(\lambda - t) + 2\right]} \]

The terminology of the terms is the same expressed in the above equation. To evaluate the kinetic parameters of the batch growth curve, The kinetic model of the first order, the revised Gompertz, and the adapted Logistic curve was fitted with the cumulative biogas production from press mud.

**RESULTS AND DISCUSSION**

**In-silico Analysis X-ray diffraction Analysis of Iron Oxide Nanoparticles**

An XPERT-PRO powder X-ray diffractometer was employed to evaluate the structural phase of Iron oxide nanoparticles, with a Cu radiation source and a current flux of 30 mA. The diffraction pattern of Iron Oxide nanoparticles (IONPs), obtained through X-ray diffraction, displays high-intensity peaks in the 20-70 angle range. The peaks in the X-ray diffraction (XRD) pattern of Iron Oxide nanoparticles are indexed to specific crystalline planes such as (0 1 2), (1 0 4), (1 1 0), (1 1 3), (0 2 4), (1 1 6), (0 1 8), (2 1 4), and (3 0 0) of nano-Fe crystalline. The sharp and strong diffraction reflection registered at \( \theta = 32.67^\circ, 35.13^\circ \) indicates that as-synthesized nanoparticles the formation of highly crystalline nanoparticles and the other peaks are found at 53.70º, 63.51º, 23.68º, 40.26º, 48.98º, and 61.96º respectively. These peaks confirm the formation of Fe₂O₃ nanoparticles.

![Fig.-1: (a) XRD pattern of Iron Oxide nanoparticles; (b) FTIR Graph of Iron Oxide nanoparticles](image)

The Average crystallite size was computed with a Full Width of Half Maximum (FWHM) at 20=35, it is found to be 44 nm. This result suggests that the crystalline structure possesses nanoscale dimensions. Indicating a potentially high surface-to-volume ration and enhanced material properties at this scale.

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FTIR Characterization of Iron Oxide Nanoparticles

Figure-1 (b) depicts the FT-IR spectrum of hematite Fe$_2$O$_3$ nanoparticles, in the range of 400-4000 cm\(^{-1}\). The two characteristic bands at 440 cm\(^{-1}\) and 527 cm\(^{-1}\) indicate the presence of Fe$_2$O$_3$ nanoparticles. Another two peaks of the FTIR spectra at 3434 cm\(^{-1}\) and 1637.23 cm\(^{-1}\) show the H$_2$O molecules adsorbed on the surface of Fe$_2$O$_3$ nanoparticles. The structure of Fe$_2$O$_3$ nanoparticles has a rhombohedral lattice of hematite due to the Fe-O vibration attributed to the peaks at 440 cm\(^{-1}\) and 527 cm\(^{-1}\). A significant increase in the biogas volume was obtained with the addition of IONPs. Figure-2 to Fig.-5 depicts the entire scenario of Anaerobic Digestion by Iron oxide Nanoparticles. The biogas age starts from the very most 1st day itself in the digester with the addition of 120 mg/L of IONPs proceeded by the remaining digesters on the 2nd day of the biochemical transformation of press mud. It was seen that the elevation of biogas began around the following 17 days of the anaerobic process. The biogas altitude lies on the 21st day with 30 mg/L, correspondingly 60 mg/L shows on the 22nd day, 90 mg/L shows on the 19th day, and 120 mg/L shows the 17th day of the entire anaerobic retention period. The extreme biogas creation was 245 ml achieved with the addition of 90 mg/L of iron oxide nanoparticles to the press mud and this was increased by about 39.02% higher in comparison with biodigester contained just press mud (i.e., Control). After that, the biogas production falls off on the 35th day and the 38th day in the digesters with the addition of 30 mg/L and 60 mg/L respectively whereas the biogas declined on the 33rd day with the addition of 90 mg/L as well as 120 mg/L. Correspondingly, the highest daily biogas production obtained from the digesters (30 mg/L), (60 mg/L), and (120mg/L) were 193.2, 234, 218.6 ml respectively.

Fig.-2: (a) Daily Biogas Production from Press Mud with the Addition of Iron Oxide Nanoparticles; (b) Cumulative Biogas Production from Press Mud with the Addition of Iron Oxide Nanoparticles

Moreover, the highest cumulative biogas yield through the anaerobic digestion of press mud with the addition of 90 mg/L IONPs was found to be 3787.5 ml in 32 days. The remaining doses of IONPs viz., 30mg/L, 60mg/L, and 120mg/L were found to be 3043.8, 3709, and 3138 ml respectively. The improved performance of biogas digesters was due to the release of Fe$^{2+}$ ions on the dissolution of IONPs into the slurry. The released iron ions can be adsorbed by the anaerobic microorganisms for their growth. The addition of IONPs led to the biodegradation of press mud and consequently increase the biogas volume. There is an insignificant difference in the highest biogas yield from the press mud with concentrations of 60 mg/l and 90 mg/l IONPs added.

Fig.-3: Comparison of Daily Biogas Production from Press Mud with the Addition of Iron Oxide Nanoparticles
IRON OXIDE NANOPARTICLES

However, the bacterial activity can be affected by the excessive concentration of IONPs resulting in a decline in biogas production with a concentration of 120 mg/L than that of 90 mg/L. As shown in Fig.s, the coefficient of determination (R\(^2\)) was higher for the modified Logistic model (0.9987-1.9995) and the modified Gompertz model (0.9969-0.9986). The biodigester N4 (120 mg/L) had the highest correlation coefficient (R\(^2\)) value of 0.9986 in modified Gompertz model whereas the biodigester N2 (60 mg/L) had 0.9969.
the lowest R² value of 0.9969. In the modified Logistic model, the highest correlation coefficient (R²) value of 0.9995 was obtained for the digester N2 (60 mg/L) and N4 (120 mg/L) whereas the least correlation coefficient (R²) value of 0.9889 was obtained for the biodigester N3 (90 mg/L). Hence, the modified GM fitted well with the experimental biogas production than the modified LM for biogas production from press mud with the addition of Fe₂O₃ nanoparticles.

CONCLUSION
The IONPs prepared by the ultrasonication method were used as an additive with different concentrations (30, 60, 90, and 120 mg/L) to enhance the anaerobic digestion of press mud. The optimal dosage of IONPs was 90 mg/L yielded 3787.5 ml as cumulative biogas and the highest biogas value of 245 ml. Fe₂O₃ nanoparticles enhanced the generation of acetate which provides a suitable substrate for methanogenesis. Thus, iron oxide nanoparticles promote the mechanism to produce hydrogen and methane in the anaerobic digestion of press mud. Furthermore, Fe₂O₃ nanoparticles have a larger surface area to release more Fe²⁺ ions and act as electron acceptors as well as electron donors, thus favoring the conversion of products formed in the acetogenesis into methane and carbon dioxide. Therefore, more biogas was produced after Fe₂O₃ nanoparticles were added to the press mud, which stimulated the activity of methanogens. These results revealed that low concentrations IONPs (30, 60, 90 mg/L) and greater doses over 120 mg/L decreased the number of microorganisms (Bacteria and Archaea) and activity of important enzymes. Improved biogas production can be attributed to the bio-stimulating effects of IONPs (Fe₂O₃) on the methanogenic activity of anaerobic digestion of press mud.

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CONFLICT OF INTERESTS
The authors declare that there is no conflict of interest.

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