Cobalt nanoparticles to enhance anaerobic digestion of cow dung: focusing on kinetic models for biogas yield and effluent utilization

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Abstract
The impacts of Co nanoparticles (NPs) on the anaerobic digestion (AD) of cow dung were investigated using kinetic models (modified Gompertze, logistic, and first-order) and experimental measurements. The deviation between the predicted and measured data for biogas yield with modified Gompertze and logistic models were 0.66–2.26% and 1.43–4.19%, respectively. The addition of Co NPs (1–3 mg/L) improved the hydrolysis rate ($K$) value by 66.66–144% compared with the control. Furthermore, the fertilizer efficiency of effluent with Co NPs was comparable to that of commercial NPK compound fertilizer. The combination of kinetic models and experimental measurements can effectively quantify the impact of Co NPs on AD performance and provide an informed choice for industrial production.

Keywords Anaerobic digestion · Manure treatment · Cobalt nanoparticles · Methane production · Hydrogen sulfide · Effluent

1 Introduction
The global economic development in the current century had led to extensive use of fossil fuels. This extensive use of fossil fuels has led to enormous emissions of CO$_2$ as a final product of combustion. Moreover, the total generated solid waste and organic waste increases at an even higher rate, posing deadly environmental impacts upon improper treatment [28]. Nowadays, renewable energy sources based on biomass have become very important with a trend to partially replace fossil fuel consumption by transforming the organic waste into clean energy, such as the use of anaerobic digestion (AD) to convert organic waste such as animal manure [19], agricultural residues [46], food waste [16], sewage sludge [26], and different energy crops [37] into renewable energy in the form of methane (CH$_4$)–enriched biogas and effluent by the influence of microorganisms in the absence of oxygen [55].

AD involves four main steps: hydrolysis, acidogenesis, acetogenesis, and methanogenesis [32]. Hydrolysis is the first step in the AD process in which large polymers react with water to form smaller organic compounds such as glucose, fatty acids, and amino acids by the aid of fermentative bacteria. The second step is acidogenesis, in which smaller organics convert into volatile fatty acids (VFAs), alcohols, lactic acid, CO$_2$, H$_2$, NH$_3$, and H$_2$S under the action of acetogenic bacteria. The third step is acetogenesis, in which VFAs are transformed into acetate, H$_2$, and CO$_2$ via acetogenesis bacteria. The final step for biogas production is the methanogenesis, in which the acetate, H$_2$, plus CO$_2$ are converted into CH$_4$ and CO$_2$ by the aid of acetoclastic
methanogenesis (responsible for 70% of the methane produced in anaerobic digestion) and hydrogenotrophic methanogenesis (responsible for 30% of the methane produced in anaerobic digestion), respectively [29, 30].

In this regard, providing adequate nutrition and a stable operating environment for these microorganisms can ensure smooth digestion of organic waste by AD [23]. To provide more favorable conditions for the microorganisms present in the digester, trace elements as micronutrients have been added to the AD systems [6, 52]. Among them, Co has proven to be an important additive as a trace mineral for the growth of methanogenic bacteria during the AD process [10]. Co is essential for the degradation of methanol by methanogenic bacteria [42]. Furthermore, the use of Co is regarded as a key factor in the oxidation of acetate into CO$_2$ and H$_2$ leading to the hydrogenotrophic methanogens [47]; [40]. Abdelsalam et al. [1] investigated the impact of Co NPs (20 nm) on biogas and CH$_4$ production of cattle manure slurry via the batch AD system. Compared to the control (biogas, 33.0 L; methane, 16.8 L), the treatment of the substrate with 0.5 and 1 mg/L Co NPs increased both cumulative biogas production (36.5% and 64.12%, respectively) and CH$_4$ production (41.6% and 41.8%, respectively). These results agree with Zaidi et al. [53], who found that the use of 1 mg/L Co NPs during the AD of green microalgae increased biogas production by 9% compared to the control experiment. Moreover, the aforementioned additives reduce the lag phase time required to reach the peak production of biogas and CH$_4$. However, the addition of 2 mg/L Co NPs decreased both biogas and CH$_4$ production by 5.2% and 14.54%, respectively, compared to the control condition. A 29.0%, 26.05%, and 30.0% increase in CH$_4$ production were achieved from poultry litter treated with 1.4, 2.7, and 5.4 mg/L Co NPs, respectively [27]. In another study, the utilization of 1 mg/L Co NPs in AD has been studied in cattle manure as a substrate. There is an increase of 71.2% and 45.9% in biogas and CH$_4$ production respectively compared to control [1].

Kinetic model fitting can identify optimal process variables including lag phase and hydrolysis constant. Moreover, it explores the biogas yield rate and potential of the AD process [22, 33, 49]. Considering the abovementioned advantages of kinetic model fitting, the effects of Co NPs on AD were investigated using both kinetic models and experimental measurements. Co NPs have been used in AD system and resulted in improved biogas production [2, 3]. However, the impact of Co NPs on the kinetic for biogas production and effluent utilization is not investigated, which is the key distinction from the present work. The following were the specific objectives of the study: (1) to determine the optimal concentrations of Co NPs on biogas and CH$_4$ production, H$_2$S mitigation, pH, volatile fatty acids (VFAs), and total alkalinity (TA) variation, total solids (TS) and volatile solids (VS) removal rates during AD of cow dung; (2) to predict the kinetic parameters (maximum biogas production rate and potential, lag phase, and hydrolysis constant) of biogas yield using the modified Gompertz model, logistic model, and first-order kinetic model; (3) to investigate the feasibility of effluent utilization by fertilizer analysis.

## 2 Materials and methods

### 2.1 Nanoparticle dispersion preparation

Co nanopowder was acquired from Nano research lab, Jharkhand, India. Stock solution of Co NPs was prepared by dispersing nanopowder into MilliQ water (Conductivity of 18.2 MΩ/cm at 25 °C). The stock was then ultra-sonicated at 20 kHz at 38 °C for 1 h to break aggregates and disperse Co NPs into the solution. To prevent photocatalytic and thermal reactions, the Co NP dispersion was kept in dark condition at 4 °C and used within 24 h of preparation [36].

### 2.2 Inoculum and substrate preparation

Anaerobic cow dung, which was used as an inoculum, had been cultured in a lab-scale batch bio-digester at mesophilic condition (33 ± 0.5 °C) for 30 days. Fresh cow dung was collected from the cattle farm of Odisha University of Agriculture and Technology, Bhubaneshwar, Odisha, India, which was used as a substrate in this study. The substrate was prepared by adding distilled water with fresh cow dung in a ratio of 1:1 on a weight basis. The substrate to inoculum was used in a ratio of 1:1 by volume basis was used (slurry) for each reactor. The main characteristics of the substrate, inoculum, and slurry used in this work are given in Table 1.

### 2.3 AD experiment design

The AD experiments were conducted in several identical 2000-mL digesters with a working volume of 1000 mL at mesophilic condition (33 ± 0.5 °C). Each digester contained inoculum

| Parameter                  | Substrate (cow dung + water) | Inoculum | Slurry (substrate + inoculum) |
|----------------------------|------------------------------|----------|------------------------------|
| TS (%)                     | 9.41 ± 0.32                  | 9.05 ± 0.42 | 9.30 ± 0.21 |
| VS (%)                     | 82.60 ± 1.7                  | 85.24 ± 1  | 83.30 ± 2                  |
| VFAs (mg/L)                | 4050 ± 32                    | 3300 ± 44  | 3750 ± 50                  |
| TA (mg/L CaCO$_3$)         | 4200 ± 73                    | 4500 ± 100 | 4300 ± 50                  |
| VFA/TA ratio              | 0.96 ± 0.01                  | 0.73 ± 0.01 | 0.89 ± 0.01                |
| pH                        | 6.45 ± 0.02                  | 7.14 ± 0.07 | 6.60 ± 0.05                |
(44.86 g dry matter), substrate (44.55 g dry matter), and varied amounts of Co NP additives depending on the test condition. The concentrations of Co NPs were 1 mg/L (0.06 mg/g VS), 2 mg/L (0.12 mg/g VS), and 3 mg/L (0.18 mg/g VS). The control digester only contained inoculum and substrate without Co NP additives. Each test condition was operated in triplicates. The gas vent on each digester was hooked to biogas collector unit for biogas collection and the volume of biogas produced was measured using a displacement method. For a more detailed description of the experimental devices, please refer to the previous articles [4, 5, 7]. The AD experiments were operated under batch mode for 30 days and terminated until daily biogas production was lower than 1% of the cumulative biogas production. Each reactor was shaken manually three times a day. The gas sample and liquid sample were taken.

2.4 Analytical methods and data calculation

The biogas volume was measured by the liquid displacement method; CH4 and H2S content were measured using a portable biogas analyzer (SR 2012, India). Every 10 days, TS, VS, and pH were determined. Standard procedures (Sect. 2540G) were followed to calculate TS% and VS% [14]; pH was measured using fisherbrand accumet XL600 pH/ISE/conductivity/DO benchtop meters. Before and after experiments, the total Co, K, and P were determined using an inductively coupled plasma optical emission spectrometer (ICP-OES, Perkin Elmer, Avio 200, USA). For Co, the effluent sample was prepared using nitric acid digestion standard procedures Sect. 3030F, APHA [13] which the K and P were prepared using nitric acid-hydrochloric acid digestion standard procedures Sect. 3030H, APHA [13]. The total C, N, S, and H were measured before and after experiments using a micro elemental analyzer with simultaneous CHNS determination (UNICUBE, Germany). After experiments, the characterization of organic material in the effluent samples (dry samples) was performed by Fourier transform infrared spectroscopy (FTIR, PerkinElmer spectrum, version 10.4.3., USA). The surface morphology and particle size characterization of Co NPs were carried out using a Carl-Zeiss Merlin II field emission scanning electron microscope (FESEM).

The cumulative biogas yield of each bio-digester was mathematically calculated, and the results were expressed as cumulative biogas yield per g VS added [56].

The VS removal efficiency was calculated by using Eq. (1) [11]:

\[
VS_{\text{removal efficiency}}(\%) = 100 \times \frac{VS_g - VS_d}{VS_d}
\]  

where VSg is volatile solids in substrate added (slurry) and VSd volatile solids in the effluent (after AD).

2.5 Kinetics analytical methods

2.5.1 Kinetics of biogas production

The calculation and comparison of biogas production kinetic during digestion of slurry with different Co NP concentrations were modeled via modified Gompertz model Eq. (2) [45] and logistic function model Eq. (3) [20]. This allowed the estimation of the lag phase time (λ, d), the maximum biogas potential production (Mmax, mL/g VS), and the maximum biogas production rate (Rmax, mL/g VS/d).

\[
M(t) = M_{\text{max}} \times \exp \left[ -\exp \left( \frac{R_{\text{max}} \times e}{M_{\text{max}}} (\lambda - t) + 1 \right) \right]
\]  

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

where \(M(t)\) cumulative biogas production (mL/g VS) at time \(t\) (30 days); \(M_{\text{max}}\) is the maximum biogas potential production (mL/g VS); \(R_{\text{max}}\) is the maximum biogas production rate (mL/g VS/d); \(\lambda\) is the lag phase (d); \(t\) is total digestion time (d).

2.5.2 Kinetics of slurry hydrolysis

The calculation and comparison of the hydrolysis rate constant (\(k\)) of slurry with different Co NP concentrations were modeled via first-order kinetic model Eq. (4).

\[
L_t = L_{\text{max}} \times (1 - e^{-kt})
\]

where \(L_t\) is cumulative biogas production (mL/g VS) at time \(t\) (30 days); \(L_{\text{max}}\) is the maximum biogas potential production (mL/g VS); \(k\) is the hydrolysis rate constant (d\(^{-1}\)); \(t\) is time (d).

To find out which model is closely matching with the experimental data, a second-order Akaike Information Criterion (AIC) test was carried out [39]. An AIC value can be positive or negative and the sign does not have a meaning since it can be changed using different units to express data. Models were compared by evaluating the difference between the AIC values in which the model with the smallest absolute value of AIC was taken as the most likely to be correct. The AIC value was calculated by using Eq. (5) [51].

\[
AIC = \begin{cases} 
\frac{N L_n^{\text{RSS} + 2n}}{N - n - 1}, & \text{when } \frac{N L_n^{\text{RSS} + 2n}}{N - n - 1} < 40 \\
N L_n^{\text{RSS} + 2n} < 40 
\end{cases}
\]
where \( N \) number of points; \( \text{RSS} \) residual sum of square; \( n \) number of model parameters.

### 2.6 Statistical analysis

FESEM was conducted to examine the surface morphology and structure of the Co NPs. Co NPs show irregular block particles with an individual size varying from 70 to 104 nm as shown in Fig. 1.

#### 2.7 Impacts of Co nanoparticles on biogas yield

An improvement of the startup of biogas yield was obtained when the substrate was exposed by 1, 2, and 3 mg/L of Co NPs as shown in Fig. 2. In particular, the addition of 1, 2, and 3 mg/L Co NPs enhanced the biogas yield startup by 23.0%, 53.1%, and 23.0%, respectively, as an average in the first 5th days of digestion period. The use of Co NPs reduces the time it takes to achieve peak biogas production. The highest daily biogas yield was attained with the 2 mg/L Co NPs.
NPs which yielded around 42.6 mL/g VS on day 6. However, the highest daily biogas production of control was achieved on day 19 and was 34.0 mL/g VS.

The presence of 2 mg/L Co NPs enhanced biogas yield to 676.5 mL/g VS, which is higher than the biogas produced by control, 1 mg/L Co NPs, and 3 mg/L Co NPs, which produced 589.2, 629.5, and 602.3 mL/g VS, respectively, as shown in Fig. 3. The statistical analysis showed that the presence of 1 and 2 mg/L Co NPs significantly increased cumulative biogas yield (p < 0.05) by 6.83% and 14.81%, respectively, as compared with control. However, there were no significant differences between cumulative biogas production with 3 mg/L Co NPs and control (p-value = 0.430). The use of Co NPs reduces the time it takes to achieve peak biogas production (Fig. 3). The control treatment produced 589.2 mL/g VS after 30 days of fermentation, while the Co NP treatment (2 mg/L) yielded 595.8 mL/g VS after 22 days of digestion, indicating that 22 days could be sufficient (HRT).

2.8 Impacts of Co nanoparticles on methane yield

The cumulative CH₄ production curves showed that adding 1 mg/L Co NPs to the substrate increased CH₄ yield to 33.3 mL/g VS, which is substantially higher (p < 0.05) than the CH₄ produced by control, 2 mg/L of Co NPs, and 3 mg/L of Co NPs, which produced 18.59, 29.07, and 28.75 mL/g VS of CH₄, respectively. The statistical analysis showed that the presence of 1, 2, and 3 mg/L of Co NPs improved the CH₄ yield by 79.12%, 56.37%, and 54.65%, respectively as compared to control (p > 0.05). Furthermore, no significant differences between CH₄ yield produced by the presence of 2 mg/L Co NPs and 3 mg/L Co NPs to the substrate were achieved (p-value = 0.857) as shown in Fig. 3.

The experiment finding agrees with Zandvoort et al. [54] who found that the optimal dosage is 0.8 mg/L Co. Moreover, our experiment showed that the maximum CH₄ yield was attended when the substrate was exposed with 1 mg/L Co NPs; this agrees with Abdelsalam et al. [1] who found that the presence of 1 mg/L Co NPs increased CH₄ yield by 86% in comparison to control condition (manure without NP additives). Furthermore, the enhancement of CH₄ in our results using 1 mg/L Co was consistent with findings of Qiang et al. [38], Demirel and Scherer [21], and Feng et al. [24], all of whom concluded that Co is an essential metal for methanogenesis because it serves as a metallic enzyme activator.

2.9 Effects of Co nanoparticles on hydrogen sulfide yield

The Co NPs significantly reduce the cumulative H₂S production (p > 0.05) for all concentrations tested compared to control, as shown from Fig. S2. The cumulative H₂S production of 1, 2, and 3 mg/L Co NPs were reduced by 15.38%, 13.20%, and 57.89%, respectively, compared to control. Furthermore, the highest H₂S removal efficiency was achieved with 3 mg/L Co NPs added and was 57.89%, while the 1 and 2 mg/L Co NP removal efficiency was 15.38% and 13.20%, respectively.

The experiment results are higher than those of Hassanein et al. [27], who found that at 5.4 mg/L Co NPs, H₂S removal efficiency improved by 6.79%. This difference in results might be due to the difference in substrate type. These results indicated that Co NPs effectively mitigated the H₂S emissions in all treated bio-digesters. The possible reason for the mitigation of H₂S emission in this study is
the precipitation of metal sulfide [17, 48]. Insignificant differences between H₂S removal efficiency with 1 mg/L of Co NPs and 2 mg/L of Co NPs (p-value = 0.548).

2.10 Effects of Co nanoparticles on pH, volatile fatty acids, and total alkalinity

To begin with, the dynamic change in pH during AD reflected the impact of Co NPs on the AD process stability. The changes in pH have two stages as shown in Fig. S3. In the first stage (from the start of the experiment to day 20), pH showed a trend of increase. Furthermore, the highest pH value was recorded with 1 mg/L of Co NPs on day 20 and was 7.3.

The pH increase might be due to (i) VFAs in AD system are used and (ii) the reaction between Co and organic compounds in the medium which might lead to increase pH. From the abovementioned reaction, the substrate under AD will deprive of the hydrogen ions (H⁺) which will increase the pH of the substrate. Moreover, capturing CO₂ will prevent the formation of (H₂CO₃) inside the substrate which will increase the pH [12]. During the second stage (from days 20 to shut down), the pH decreases mainly because of VFAs cumulation [18].

The variation in volatile fatty acids (VFAs) concentration of 1, 2, and 3 mg/L Co NPs is shown in Fig. 4, and during the experimental period, VFAs have two stages. In the initial stage (during the first 20 days of digestion period), the VFAs concentration showed a sharp decrease trend for all Co NP additives with the highest VFAs degradation of 2800 mg/L with 2 mg/L Co NPs. This indicated that (i) after microorganisms adapted to the Co NP environment the Co NPs provided an effective electron donor to promote microbial metabolism; ii) the addition of trace elements such as Co might decrease the initial VFAs cumulation during the AD [15, 50].

In the final stage (during the last 10 days of digestion period), the VFAs concentration showed an increasing trend with all Co NP concentrations with the highest value of 4000 mg/L for 3 mg/L Co NPs. The increase of VFAs in the final stage might be due to the decrease in total alkalinity. During the final stage, the daily biogas production (Fig. 2) and pH value (Fig. S3) decrease might be due to the increase and accumulation of VFAs. Previous studies showed that the increase and accumulation of VFAs concentration resulted in a corresponding decrease in the pH value and biogas production [31, 41]. This indicates a relation between the pH, VFAs, and biogas production.

The total alkalinity (TA) showed a similar profile as pH (Fig. 5). The TA changes have two processes; before 20 days (from the start of the experiment to day 20), the TA showed an increasing trend. This indicated that the increase in TA of the substrate reflected a positive effect of Co NPs on consuming the VFAs. After 20 days (from day 20 to shut down), the TA showed a trend of decreases and this decrease might be because of the formation of VFAs [9].

In our results, the average TA concentrations when the substrate was exposed to 1, 2, 3 mg/L Co NPs and control were 4950, 4900, 4725, and 4475 mg CaCO₃/L, respectively. The increment of TA concentration was achieved with 1 mg/L Co NPs added. The TA concentration reflected the consumption of VFAs by methanogenic archaea [44] and consequently enhanced CH₄ production. These results indicate a relation between TA concentration and cumulative CH₄ production especially with 1 mg/L Co NPs added.

2.11 Effects of Co nanoparticles on total and volatile solids

The degradation of TS and VS are necessary to consider in evaluating the AD process stability. To begin with TS decomposition, Fig. S4 illustrates the TS content with 1,
2, and 3 mg/L Co NPs added in comparison with control. The TS content in all bio-digesters and control bio-digester showed a decreasing trend during the digestion period. Furthermore, the TS removal efficiencies of control, 1, 2, and 3 mg/L Ni NPs are calculated as 12.04%, 14.81%, 16.25%, and 14.81%, respectively.

Figure 6 shows the VS content under different concentrations of 1, 2, and 3 mg/L Co NPs compared to control. During the experimental period, the VS content curve showed a similar profile. The VS removal efficiencies of control, 1, 2, and 3 mg/L Co NPs are calculated as 11.55%, 12.16%, 11.85%, and 10.66%, respectively. The change in TS and VS content with the addition of Co NPs indicated that Co nanoparticles enhanced the degradation of organic matter by improving the capacity of methanogenic archaea to degrade organics.

2.12 Effects of Co nanoparticles on the characterization of organic material and chemical composition of the effluent

The characteristic vibrations of the chemical bonds and chemical functions are detected by using the FTIR method. The profile of the FTIR spectrum of effluent when the substrates exposed to 1, 2, and 3 mg/L Co NPs compared to control is shown in Fig. 7. The main absorption peaks identified according to the literature were (i) O–H stretching of the carboxylic and alcoholic group at about 3450 cm\(^{-1}\); (ii) C–H stretching of the aliphatic at about 2900 cm\(^{-1}\); (iii) –COO\(^-\) stretching of the carboxylic acid at about 1600 cm\(^{-1}\); (iv) C–O stretching of the carbohydrate at about 1100 cm\(^{-1}\) [8, 25]. The addition of different concentrations of Co NPs presented a change in the intensity and shift of peaks.
compared to the control peak. In particular, the strong peak around 1100–950 cm\(^{-1}\) observed in the spectrum corresponding to the C–O stretching of the carbohydrate.

The decrease in intensity of this band in the spectrum of the treated sample reflects the decreased carbohydrate. For example, the presence of 1 mg/L Co NPs had the lowest intensity of the C–O band compared to other treatments (2 and 3 mg/L Co NPs) and control. These results indicated that (i) the presence of 1 mg/L Co NPs might be enhancing the methanogenesis communities to decompose the carbohydrate with the formation of VFAs and consequently enhanced CH\(_4\) production; (ii) this indicates a relation between the highest cumulative CH\(_4\) production and the FTIR spectrum of effluent with 1 mg/L Co NPs added.

The effect of different concentrations of Co NPs on the chemical composition of the digestate is observed in Table 2. The presence of Co NPs increased sulfide content. Sulfide content increased by 3%, 3.6%, and 12.12% with 1, 2, and 3 mg/L Co NPs added compared to control, respectively. The presence of 3 mg/L Co NPs decreases the H\(_2\)S production by 57.89% as shown in Fig. S2 compared with control.

The possible reason for the mitigation of H\(_2\)S emission and increased sulfide content in the effluent in this study is the bioavailability of organic matter and sulfate in the AD stimulates the growth of SRB, which reduce sulfur to sulfide as a terminal electron receiver from a wide range of elements, such as H\(_2\), ethanol, formate, succinate, pyruvate, and lactate [35]. In this context, Co NPs effectively mitigated the H\(_2\)S emissions by killing SRB, directly absorbing the sulfur in the digestion, or altering the contaminating elements through a specific biochemical process [43].

### 2.13 Fertility evaluation of effluent containing Co NPs

The total nutrient (NPK) content of the digestate with 1, 2, and 3 mg/L Co NPs are 5.32%, 4.68, and 4.63%, respectively, as shown in Fig. 8. Since the total nutrient content of all Co NP concentrations was close to 5%, they can be used in combination with an artificial compound fertilizer. After dewatering, digestates were dried to obtain a high-quality organic compound fertilizer. NPK organic compound fertilizer can improve the physical and chemical characteristics of soil effectively, promoting the formation of soil aggregate structure and enhancing the activation of soil nutrients.

| Table 2 Chemical composition of the effluent with different concentrations of Co NPs |
|-----------------------------------------|-----------------|-----------------|-----------------|-----------------|
| Element | Before digestion | After digestion | | |
| | Slurry | Control | 1 mg/L Co NPs | 2 mg/L Co NPs | 4 mg/L Co NPs |
| C % | 39.63 | 40.91 | 40.27 | 40.27 | 41.03 |
| H % | 5.93 | 40.91 | 40.12 | 40.12 | 39.80 |
| S % | 0.31 | 0.33 | 0.340 | 0.342 | 0.373 |
| Fe % | 0.18 | 0.20 | 0.18 | 0.24 | 0.19 |
| Ni % | 7.4*10\(^{-4}\) | 8.2*10\(^{-4}\) | 0.041 | 7.4*10\(^{-4}\) | 1.1*10\(^{-3}\) |
| Co % | 8.8*10\(^{-4}\) | 2.0*10\(^{-4}\) | 8.8*10\(^{-4}\) | 2.7*10\(^{-3}\) | 2.3*10\(^{-3}\) |
It is clear that the crops require much less water when NPK organic compound fertilizer is used, and the chronic water shortage problem in the area can be solved. Thus, the AD digestate with the three Co NPs can be used to produce the NPK organic compound fertilizer, which is beneficial for plant height, root length, root diameter, and dry weight [34].

### 2.14 Cost analysis from Co nanoparticle input

Cost analysis was performed to investigate the effect of Co NPs on CH$_4$ production. The cost calculation is based on the amount of CH$_4$ produced (L) from 1 L of substrate. As shown in Table 3, the highest net profit was attained when the substrate was treated with 1 mg/L Co NPs and was 1.05 USD over the control. Additionally, concentrations of 2 and 3 mg/L Co NPs achieved net profit of 0.73 and 0.71 USD, respectively, over the control. These results indicated that not only the supplementation of bio-digesters with Co NPs boosted CH$_4$ production, but also gained more profits from the commercial aspect of view. Therefore, Co NPs might represent a sustainable and economic approach to enhancing CH$_4$ from anaerobic digestion of cow dung.

2.15 Kinetic analysis of biogas yield

The results obtained from the modified Gompertz and logistic function models are presented in Tables 4 and 5, respectively. The comparison of experimental and predicted biogas production by 1, 2, and 3 mg/L Co NP additives and control is shown in Figs. 9 and 10. While using the modified Gompertz model, the presence of 1, 2, and 3 mg/L Co NPs improved maximum biogas production rate ($R_{\text{max}}$) by 14.29%, 26.80%, and 4.60%, respectively, compared to control. Moreover, the addition of 1, 2, and 3 mg/L of Co NPs shortened the lag phase ($\lambda$) and was 1.24, 0.59, and 0.89 days, respectively, compared with control (1.58 days).

Similarly, for logistic function model, the maximum biogas production rate ($R_{\text{max}}$) for the control, 1, 2, and 3 mg/L Co NPs were 28.69, 32.23 (12.33% increase), 34.58 (20.52% increase), and 29.47 (2.71% increase) mL/g VS/d, respectively. Also, the presence of 1, 2, and 3 mg/L Co NPs shortened the lag phase ($\lambda$) and was 1.90, 0.95, and 1.55 days, respectively, compared with control (2.43 days). It is identified by both the kinetic models that Ni NPs had improved the biogas production rate and shorten the lag phase. The results for Akaike Information Criterion (AIC)
Table 4 Parameters of modified Gompertz model at different concentrations of Co NPs

| Kinetics parameter                  | Treatments          | Control    | 1 mg/L Co NPs | 2 mg/L Co NPs | 3 mg/L Co NPs |
|------------------------------------|---------------------|------------|---------------|---------------|---------------|
| $R^2$                              |                     | 0.998      | 0.998         | 0.997         | 0.998         |
| $M_{\text{max}}$ (mL/g VS)         |                     | 663.9 ± 10.37 | 664.86 ± 7.29 | 695.86 ± 8.27 | 647.92 ± 8.26 |
| $R_{\text{max}}$ (mL/g VS/d)       |                     | 27.35 ± 0.51 | 31.26 ± 0.56  | 34.68 ± 0.81  | 28.61 ± 0.54  |
| $\lambda$ (d)                      |                     | 1.58 ± 0.19 | 1.24 ± 0.17   | 0.59 ± 0.21   | 0.89 ± 0.18   |
| Predicted biogas yield (mL/g VS)   |                     | 593.13 ± 13.74 | 620.67 ± 19.15 | 661.50 ± 18.08 | 596.58 ± 19.39 |
| Measured biogas yield (mL/g VS)    |                     | 589.2 ± 13.65 | 629.50 ± 19.43 | 676.50 ± 18.50 | 602.30 ± 19.58 |
| Difference between measured and predicted biogas yield (%) | | 0.66 | 1.42 | 2.26 | 0.95 |
| AIC                                |                     | 135.88     | 134.00        | 151.31        | 134.80        |

$M_{\text{max}}$, maximum biogas potential yield; $R_{\text{max}}$, maximum biogas yield rate; $\lambda$, lag phase; $R^2$, correlation coefficient; AIC, Akaike’s Information Criterion

Table 5 Parameters of logistic function model at different concentrations of Co NPs

| Kinetics parameter                  | Treatments          | Control    | 1 mg/L Co NPs | 2 mg/L Co NPs | 3 mg/L Co NPs |
|------------------------------------|---------------------|------------|---------------|---------------|---------------|
| $R^2$                              |                     | 0.996      | 0.996         | 0.991         | 0.995         |
| $M_{\text{max}}$ (mL/g VS)         |                     | 603.56 ± 8.62 | 620.12 ± 7.01 | 660.19 ± 9.88 | 600.42 ± 8.02 |
| $R_{\text{max}}$ (mL/g VS/d)       |                     | 28.69 ± 0.74 | 32.23 ± 0.85  | 34.58 ± 1.35  | 29.47 ± 0.84  |
| $\lambda$ (d)                      |                     | 2.43 ± 0.28 | 1.90 ± 0.26   | 0.95 ± 0.39   | 1.55 ± 0.30   |
| Predicted biogas yield (mL/g VS)   |                     | 580.8 ± 13.45 | 607.12 ± 18.73 | 649.29 ± 17.75 | 584.22 ± 18.99 |
| Measured biogas yield (mL/g VS)    |                     | 589.2 ± 13.65 | 629.50 ± 19.43 | 676.50 ± 18.50 | 602.30 ± 19.58 |
| Difference between measured and predicted biogas yield (%) | | 1.43 | 3.68 | 4.19 | 3.09 |
| AIC                                |                     | 157.08     | 158.41        | 183.81        | 161.15        |

$M_{\text{max}}$, maximum biogas potential yield; $R_{\text{max}}$, maximum biogas yield rate; $\lambda$, lag phase; $R^2$, correlation coefficient; AIC, Akaike’s Information Criterion

Fig. 9 The comparison of experimental and predicted biogas production by using modified Gompertz model with different concentrations of Co NPs.

[Diagram showing cumulative biogas yield over time for different treatments]
test for the modified Gompertz and logistic models are shown in Tables 4 and 5. The modified Gompertz model has a lower Akaike Information Criterion (AIC) value which is indicating that it is a better model to use in this case.

The hydrolysis of organic materials was evaluated using first-order kinetic model to obtain the hydrolysis rate constant ($K$) and $R^2$ in Eq. (4) and Table 6. In general, the model was well fitted to the experimental results, with coefficient of determination (0.991–0.993). Compared with the $K$ value of control treatment, the presence of 1, 2, and 3 mg/L Co NPs enhanced the cow dung hydrolysis rate by 72.22%, 144%, and 66.66% as compared to control. The biogas production data well fitted with the modified Gompertz model ($R^2 = 0.997–0.998$) and logistic function model ($R^2 = 0.991–0.996$).

### 3 Conclusions

The performance of AD of cow dung was significantly enhanced by adding Co NPs. The addition of 2 mg/L Co NPs resulted in the highest biogas production (14.81%). Modified Gompertz model had a better fit with the particle biogas production than logistic function model. The addition of Co NPs (1–3 mg/L) enhanced the hydrolysis rate ($K$) value by 66.66–144% as compared with control. Effluent with Co NPs showed remarkable fertility (4.63–5.32%). Combining kinetic models and experimental measurements can be an optimal strategy for evaluating the impacts of Co NP additives on AD. In the future, this study can open up a new avenue for the use of effluent-containing NPs as fertilizer.

### Supplementary Information

The online version contains supplementary material available at [https://doi.org/10.1007/s13399-021-02002-x](https://doi.org/10.1007/s13399-021-02002-x).

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### Data availability

The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

### Declarations

**Ethical approval** Not applicable.

**Consent to participate** Not applicable.

**Consent to publish** Not applicable.

**Competing interests** The authors declare no competing interests.
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