EFFECT OF $CoCl_2$, $NiCl_2$ AND $FeCl_3$ ADDITIVES ON BIOGAS AND METHANE PRODUCTION

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ABSTRACT

Anaerobic digestion is a biological process used to convert organic wastes into biogas and a stable biofertilizer for agricultural applications as environmentally friendly products. The produced biogas is used as an alternative renewable energy source. The objective of this study was to investigate the effect of the additives $CoCl_2$, $NiCl_2$ and $FeCl_3$ on biogas and methane yield from fresh raw manure. A series of laboratory experiments using 2 L biodigesters were carried out in batch anaerobic mode. Each biodigester was fed with 1600 ml of slurry with individual addition of 1 mgL^{-1} $CoCl_2$, 1 mgL^{-1} $NiCl_2$ and 10 mgL^{-1} $FeCl_3$. All of the treatments were carried out by triplication for the statistical analysis purposes, and analyzed using MStat-C software v.2.1. The results showed that the highest biogas and methane production ($p<0.05$) were achieved with the addition of 1 mgL^{-1} $NiCl_2$ to the slurry, which were 507.9 and 279.3 ml g^{-1} VS, respectively; after 50 days of hydraulic retention time (HRT) compared with other additives. Furthermore, the biogas and methane production were in the order of $NiCl_2$>$CoCl_2$>$FeCl_3$ in comparison with the control. These results indicated that, the addition of aforementioned salts increased biogas yield by 1.44, 1.33 and 1.17 times the biogas yielded with the control, respectively. Moreover, the methane yield was increased by 1.55, 1.43 and 1.21 times the methane yielded with the control, respectively.

Keywords: *Anaerobic digestion, biogas, methane production, trace metals, additives, manure management, slurry treatment.*

1. INTRODUCTION

Anaerobic digestion (AD) is the most important techniques to convert organic waste into renewable energy in the form of methane (**Holm-Nielsen et al., 2009**).

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It's a widely used technique because it has several advantages, e.g. a low cell yield, a high organic loading rate, limited nutrient demands and low costs for operation and maintenance of the reactor system **(Wijekoon et al., 2011)**. Biomass energy, as a renewable and sustainable form of energy, is becoming more important due to its environmentally-sound and energy-saving production methods **(Berndes et al., 2003)**. It is expected that biogas will be a significant source of energy in the future to protect the environment, solve the pollution problem and to promote better health to agriculture and community. After animal excrement had been fermented in the biogas plant, it becomes a good quality and odorless substrate, which is better than fresh manure in improving the soil for the agriculture **(Ndegwa and Thompson, 2001)**. In Egypt, 18% of the agricultural wastes are used directly as fertilizer. Another 30% is used as animal food. The remainder is burnt directly on the fields or is used for heating in the small villages, using low efficiency burners **(El-Mashad et al., 2003)**. Manure (feces and urine) and slurry (manure with water) are not only treated anaerobically to produce biogas, but also aerobically to reduce harmful gaseous emissions **(Samer et al., 2014)**.

When organic matter such as food, plant debris, animal manure, sewage sludge and biodegradable portions of municipal solid waste - undergoes decomposition in absence of free oxygen, it normally generates a gas which consists of 40-70% methane, the rest being mostly carbon dioxide with traces of other gases **(Ferrer et al., 2011; Weiland, 2010)**. **Chen et al. (2008)** mentioned that, the mixture of CH_4 and CO_2 is not the only gas possible by anaerobic degradation of organic matter; particularly, methane is produced only if methanogenic bacteria are involved in the anaerobic decomposition.

The AD consists of a series of microbial processes that convert organics to methane and carbon dioxide, and can take place under psychrophilic (<20 °C), mesophilic (25-40 °C) or thermophilic (50-65 °C) conditions, although biodegradation under mesophilic conditions is most common. It also enables higher loading rates than aerobic treatment and a greater destruction of pathogens **(Ravuri, 2013; El-Mashad et al., 2004)**. The process of AD is running at its optimum temperature range of 25 to 38 °C (mesophilic conditions), whoever temperatures in the range of 38 °C are greater stability of digestion process, easier to control and utilized in about 95% of all digesters **(köttner, 2003)**. Furthermore, a mesophilic digestion at 38 °C reportedly destroys 99.9% of pathogens **(Erickson et al., 2004)**. The pH value in the digester mixture should be kept within a desired range of 6.8-7.2 by feeding it at an optimum loading rate. Furthermore, during anaerobic digestion microorganisms utilize carbon 25-30 times faster than nitrogen. Thus to meet this requirement, microbes need a C:N ratio of 20-30:1 where the largest percentage of the carbon must be readily degradable **(Yadvika et al., 2004)**. Dry anaerobic digestion (>15% TS) has benefits over conventional anaerobic liquid digestion (<10% TS) because it reduces the volume of the reactor and wastewater, as well as producing a more easily transportable fertilizer **(Schäfer et al., 2006)**.

Other species of anaerobic microorganisms and different conditions, gases such as hydrogen and hydrogen sulfide may be generated instead of methane **(Diaz et al., 2010; Singh and Mandal, 2011)**. But methanogenic bacteria occur very commonly in nature and in most instances anaerobic digestion does result in the generation of the predominantly CH_4-CO_2 mixture which is widely referred as 'biogas' **(Abbasi et al., 2012)**.

Several studies have been carried out to increase biogas production by stimulating the microbial activity using various biological and chemical additives under different operating conditions. The use of additives in biogas plant could improve its performance significantly. The suitability of an additive is expected to be strongly dependent on the type of substrate **(Yadvika et al., 2004)**.

Trace metal elements are generally supplied to the influent of full-cale anaerobic bioreactors to maintain a good reactor performance, or process compensation must be made in either lower loading rates or lower treatment efficiency as a trade-off for non-ideality of nutrients **(Zhang, 2003)**. The trace metals required for the methane fermentation of various types of waste, such as starch **(Fang and Hui, 1994)**, cow dung **(Rao and Seenayya, 1994)**, methanol wastewater **(Fermoso et al., 2008)**, food waste **(Qiang et al., 2012)**, and a defined model that uses maize as the substrate (**Pobeheim et al., 2011**), have been studied using mesophilic digesters.

Microbial regeneration time is a function of the concentrations of nutrients present. Although ideal nutrients concentrations are not essential, lack of even a single trace metal may severely limit anaerobic conversion processes (**Zandvoort et al., 2002; Yue et al., 2007**). In practice, trace metals are also added in excessive amounts to full-scale installations to ensure the functioning of the treatment reactors. **Karlsson et al. (2012)** concluded that addition of trace elements improves the anaerobic digestion. Trace metals, such as nickel, cobalt and iron, have been shown to be stimulatory to anaerobic treatment of different types of wastewater (**Kida and Sonoda, 1993; Oleszkiewicz and Sharma, 1990**).

The effect of trace metal addition on the performance of bioreactors is an important study field in anaerobic biotechnology, as trace metals are involved in the enzymatic activities of acidogenesis and methanogenesis (**Kida et al., 2001**).

The objective of this study is to investigate the effects of trace metals such as $CoCl_2$, $NiCl_2$ and $FeCl_3$ on biogas and methane production from livestock manure using lab scale batch system. The results of this research will be used as a guideline for studying the effect of using metallic nanoparticles to enhance biogas production and methane yield.

2. MATERIALS AND METHODS

2.1. Fresh manure

The fresh raw manure was collected randomly from cattle holding pen unit located in the Western Farm of the faculty of agriculture, Cairo University, Giza city, Egypt.

2.2. Slurry preparation

The collected raw manure was homogenized by mixer for 30 minutes with 50% distilled water to obtain slurry (7-9% Total solids). Then, the biodigesters were fed with 1600 ml of the slurry.

2.3. Samples and slurry analysis

The chemical composition of fresh manure and slurry samples were determined using the standard methods (**EPA, METHOD 1684, 2001**). The analysis of total solids (TS), volatile solid (VS) and ash were carried out using muffle furnace (Ney Tech, Vulcan D-550, York, USA). The pH value and the temperature were measured using a pH meter (Jenway 3520, Staffordshire, UK), as shown in Table (1).

Table (1): Chemical composition of fresh manure and slurry.

Parameter	Fresh manure	Slurry
TS (%)	14.8	7.16
VS (%)	11.67	5.85
VS (% from TS)	82.24	81.28
Ash (%)	2.51	1.34
Organic carbon (% from VS)	47.7	47.15
Total Nitrogen (%)	1.83	1.96
C:N ratio	26:1	24:1
pH value	6.13	5.85

2.4. Chemical additives

The following chemicals were used as additives to enhance the anaerobic processes; Cobalt chloride hexahydrate ($CoCl_2.6H_2O$, crystallized 99%, Fluka), Nickel chloride hexahydrate ($NiCl_2.6H_2O$, crystallized 99.9%, Fluka) and Ferric chloride hexahydrate ($FeCl_3.6H_2O$, granulated 99%, Riedel-de Haën)

2.5. Experimental set up

A batch anaerobic system was designed, according to the design guidelines and parameters developed by **Samer (2010 and 2012)**, and implemented in the previous study of **Abdelsalam et al. (2015)**. The main experiment tools consist of: biodigester, temperature control and biogas measurement. A 2-liter wide neck reaction Pyrex flask (Scilabware, FR2LF, Staffordshire, UK) was used as biodigester, plugged with tightly Teflon cap, equipped with step motor (5 rpm) for mixing the substrate for 1min every hour **(Keshtkar et al., 2003)** and gas outlet connected to biogas holder and measurement (in ml), through water trap to reduced water vapor as shown in Fig.1.

In order to withdraw samples or to enable pH value measurements without interrupting the anaerobic conditions of the system, a plastic tube with long of 12 cm and a diameter of 2 cm was fixed in a hole in the cap and immersed in the substrate. The temperature was controlled using a thermostatic water bath (Raypa, BAD-12, Barcelona, Spain) and maintained at 37±0.3 °C.

The volume of biogas was measured by liquid displacement method using ultra clear polypropylene graduated cylinder (1000 ml, ± 10 ml, Azlon) connected to gas outlet by 6 mm plastic hose at its base and placed upside down in another polypropylene cylinder (2000 ml, Azlon) filled with water. Methane (CH_4) and carbon dioxide (CO_2) percentages were measured using portable gas analyzer (Geotech, GA2000, Warwickshire, UK). The recorded data were downloaded from the gas analyzer to PC using Gas Analyzer Manager Software (GAM, version 1.4.0.12) in the form of Excel Worksheet.

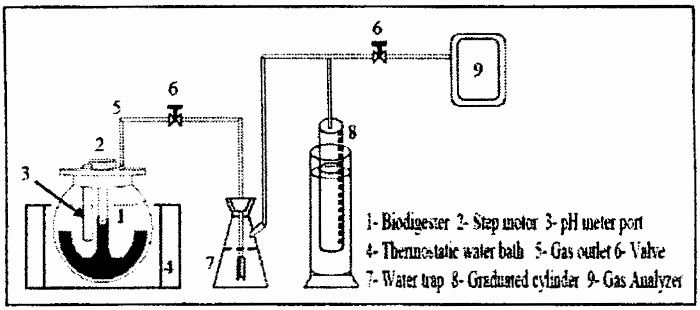

Fig. (1): The schematic diagram of experimental laboratory set up (Abdelsalam et al., 2015).

2.6. Experimental design

A series of laboratory experiments using 2 L biodigester; with 10% headspace of biodigester **(Samer, 2010)**, were implemented in this study and operated in batch anaerobic mode to investigate the effects of $CoCl_2$, $NiCl_2$ and $FeCl_3$ on biogas and methane production. Each biodigester was fed with 1600 ml of slurry, and 1 mgL^{-1} $CoCl_2$, 1 mgL^{-1}, $NiCl_2$ and 10 mgL^{-1} $FeCl_3$. These concentrations were selected based on previous research conducted by **Qiang et al. (2013)**.

All treatments were carried out in three replicates for the statistical analysis purposes, and analyzed using Least Significant Difference (LSD, MStat-C software v.2.1.) at a significance level of $p<0.05$, where the superscript different letters means there is a significant differences among all treatments.

The performance of each biodigester was assessed with respect to cumulative volume of biogas produced and corrected according to standard pressure and temperature (STP; 760 mm Hg, 0 °C) **(Hansen et al., 2004)**.

3. RESULTS AND DISCUSSION

3.1. The influence of trace metals on biogas and methane production

3.1.1. Biogas

The generally accepted view is that trace metals are necessary for the microorganisms. Previous researchers have reported that iron, cobalt and nickel were able to stimulate methanogenes. An improvement of the startup of biogas production was observed when the slurry was treated with 1 mgL^{-1} $CoCl_2$, 1 mgL^{-1}, $NiCl_2$ and 10 mgL^{-1} $FeCl_3$. Furthermore, the lag phase was reduced and the biogas production reached 346.7, 426.7 and 473.3 ml biogas in the first day, respectively. However, the control lasted for 8 days to produce 360 ml biogas as shown in Fig. 2. Our results in agreement with **Krongthamchat et al. (2006)** who reported that the addition of 0.1 mgL^{-1} $CoCl_2$, 0.1 mgL^{-1}, $NiCl_2$ and 1 mgL^{-1} $FeCl_3$ reduced the lag phase of digester sludge.

The cumulative biogas production curves confirm that the aforementioned additives significantly increased ($p<0.05$) the biogas production to 43,823.3; 47543.3 and 38570 ml of biogas, respectively. This compared with the control which produced 33006.7 ml biogas as shown in Fig. 3.

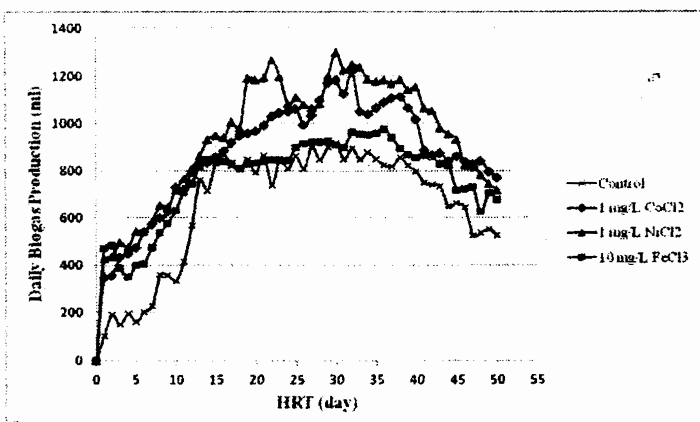

Fig. (2): Daily biogas production affected by trace metals additives.

On the other hand, Fig. 4 illustrates the specific biogas production for each additive. The highest significant value of specific biogas production ($p<0.05$) was observed for the slurry treated with 1 mgL^{-1} $NiCl_2$ which was 507.9 ml Biogas g^{-1} VS. This results agrees with **Gustavsson et al.**

(2013) who stated that nickel concentrations in digester substrates improves biogas production by increasing methane yield and maintaining process stability. Furthermore, our results in agreement with **Demirel and Scherer (2011)** observed that feedstock containing 0.11-0.25 mg Ni kg^{-1} stimulates biogas generation.

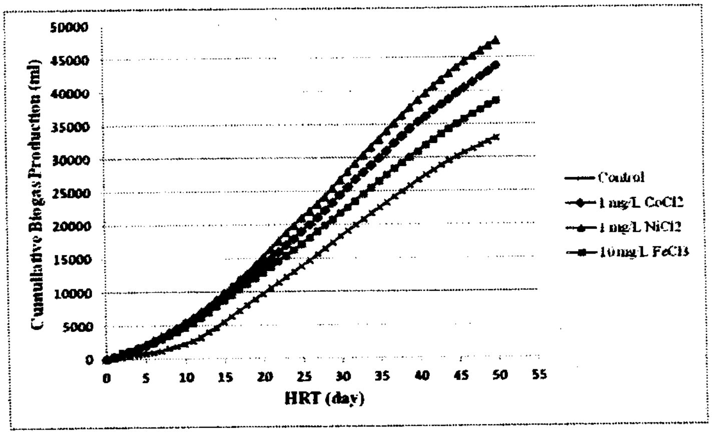

Fig. (3): Cumulative biogas production affected by trace metals additives.

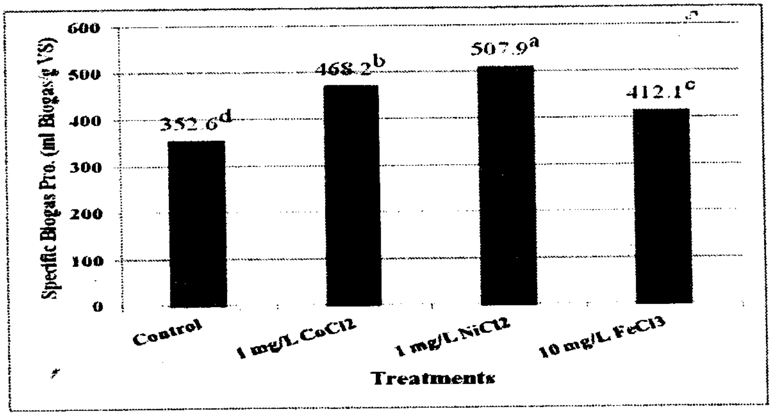

Fig. (4): Specific biogas production affected by the addition of trace metals ($p<0.05$).

3.1.2. Methane

All additives of trace metals have a clear stimulating effect on methanogenic activity during the start up of the anaerobic process in comparison with the control. Furthermore, average CH_4 % with the addition 1 mgL^{-1} $NiCl_2$ to slurry yielded the highest CH_4 % which was 22.41% of CH_4 during the start up from day 1 to 5 of the experiment compared with the addition of 1 mgL^{-1} $CoCl_2$, and 10 mgL^{-1} $FeCl_3$ which yielded 10.28 and 7.01% of CH_4, respectively as shown in Fig. 5 ($p<0.05$). Moreover, the addition of 1 mgL^{-1} $NiCl_2$ to slurry yielded the highest CH_4 % which was 51.8% as an average during 50 days of HRT. These results agree with **Uemura (2010)** who showed that nickel is the most important trace element for the anaerobic digestion of the organic fraction of municipal solid waste. Additionally, our results are in line with **Qiang et al. (2013)** who concluded that, the addition of 10 mgL^{-1} Fe, 1 mgL^{-1} Co and 1 mgL^{-1} Ni to the thermophilic digester led to success AD during 30 days of HRT.

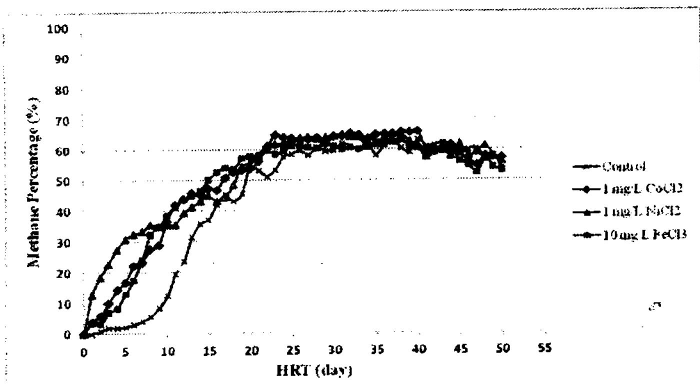

Fig. (5): Methane percentage affected by the addition of trace metals.

The maximum daily methane production was observed with the addition 1 mgL^{-1} $NiCl_2$ to slurry, which yielded more than 700 ml CH_4 starting from day 21 to 40 of HRT, while the other additives were unable to yield as high as the 1 mgL^{-1} $NiCl_2$ additive except that the addition of 1 mgL^{-1} $CoCl_2$ lasted for day 31 to 40 to yielded more than 700 ml CH_4 as shown in Fig. 6.

Fig. 7 illustrates the cumulative methane production curves which proved that the addition of 1 mgL^{-1} $CoCl_2$, 1 mgL^{-1} $NiCl_2$ and 10 mgL^{-1} $FeCl_3$ to the slurry increased the methane production to 23,994.37; 26,139.39 and 20,346.42 ml CH_4, respectively, while the control yielded only 16,811.35 ml CH_4.

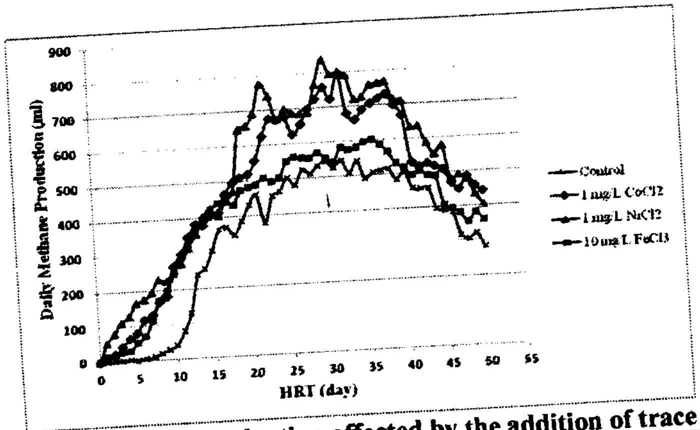

Fig. (6): Daily methane production affected by the addition of trace metals.

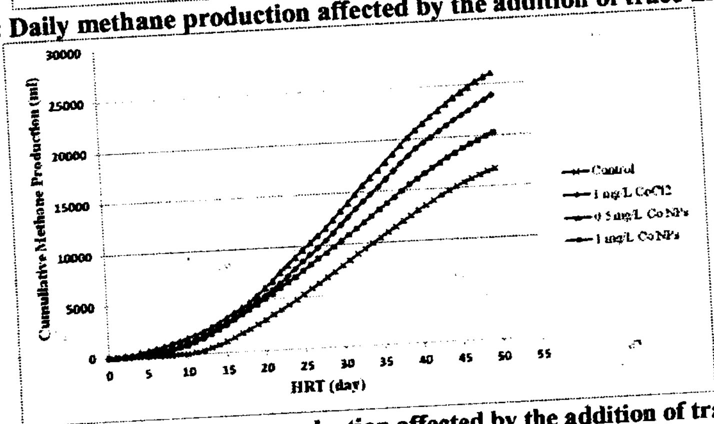

Fig. (7): Cumulative methane production affected by the addition of trace metals.

The specific methane production with the addition of 1 mgL^{-1} $CoCl_2$, 1 mgL^{-1} $NiCl_2$ and 10 mgL^{-1} $FeCl_3$ to the slurry compared with the control were illustrated in Fig. 8.

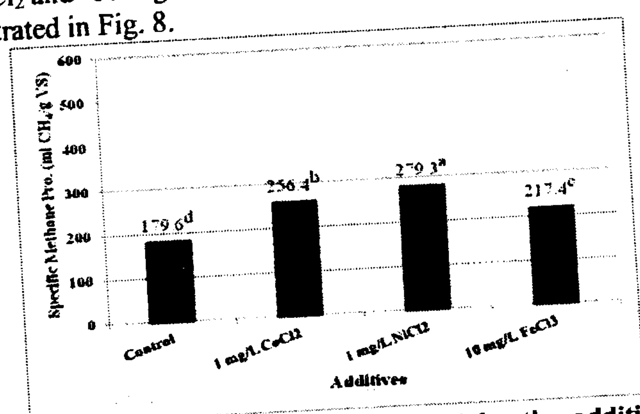

Fig. (8): Specific methane production affected by the addition of trace metals ($p<0.05$).

The highest significant value ($p<0.05$) of specific methane production observed with the addition of 1 mgL^{-1} $NiCl_2$ and was 352.8 ml CH_4. g^{-1} VS, respectively.

3.2. The influence of trace metals on decompose of total and volatile solids

Anaerobic digestion can only partially decompose the organic fraction due to the limitation of digestion time. Volatile solid reduction is frequently used as a parameter to characterize the performance of anaerobic sludge digestion **(Arnaiz et al., 2006)**. Considering the analysis of the organic matter showed that the highest decomposition of TS and VS were observed when the slurry was treated with 1 mgL^{-1} $NiCl_2$ at the end of the experiment which were 5.73 and 4.2%, respectively as shown in Figs. 9 and 10. Our results on the degradation of organic matter with the addition of Fe NPs agree with **Irvan (2012)** who reported that, the degradation rate of total solid and volatile solid increase with the addition of trace metals such as Fe.

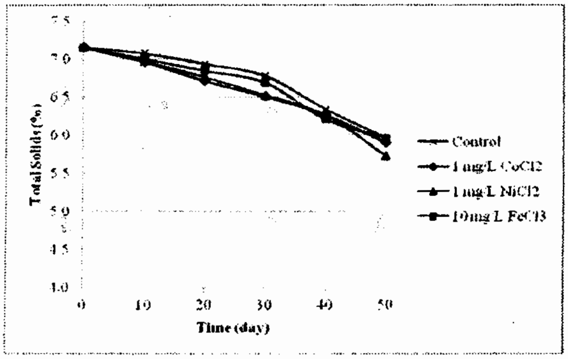

Fig. (9): Total solids (TS) affected by the addition of trace metals.

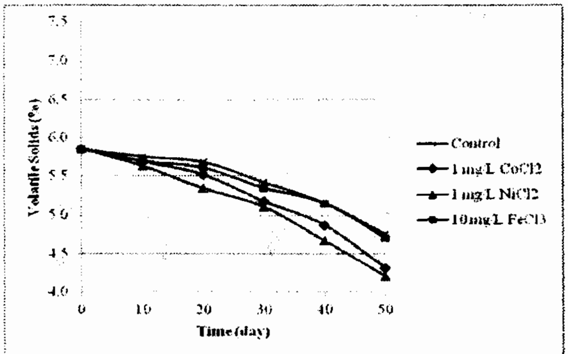

Fig. (10): Volatile solids (VS) affected by the addition of trace metals.

Tables 2 and 3 summarize the overall mean performance of biogas and methane production affected by the addition of 1 mgL^{-1} $CoCl_2$, 1 mgL^{-1} $NiCl_2$ and 10 mgL^{-1} $FeCl_3$ to the slurry during 10 time intervals of 50 days of HRT.

Table (2): Mean performance of biogas production affected by the addition trace metals during different time intervals within HRT.

HRT (day)	Biogas production, ml			
	Control	1 mgL^{-1} $CoCl_2$	1 mgL^{-1} $NiCl_2$	10 mgL^{-1} $FeCl_3$
(1-5)	159.3	412.7	476.0	419.33
(6-10)	296.0	614.0	629.3	526.00
(11-15)	658.0	810.7	864.7	794.67
(16-20)	829.3	936.0	1060.0	829.33
(21-25)	826.7	1035.3	1170.0	857.33
(26-30)	876.0	1095.3	1146.0	920.00
(31-35)	865.3	1099.3	1215.3	946.67
(36-40)	825.3	1078.7	1166.7	908.00
(41-45)	708.0	867.3	998.7	820.00
(46-50)	557.3	815.3	782.0	692.67
Mean	**660.1**	**876.5**	**950.9**	**771.4**

(LSD = 12.59, $p<0.05$)

Table (3): Mean performance of methane production affected by the addition trace metals during different time intervals within HRT.

HRT (day)	Methane production, ml			
	Control	1 mgL^{-1} $CoCl_2$	1 mgL^{-1} $NiCl_2$	10 mgL^{-1} $FeCl_3$
(1-5)	2.2	44.8	109.1	27.69
(6-10)	21.3	172.9	216.4	159.32
(11-15)	202.9	363.0	354.8	360.57
(16-20)	380.3	481.6	526.3	456.92
(21-25)	453.1	642.0	718.0	510.27
(26-30)	520.5	692.9	734.2	561.79
(31-35)	523.5	710.9	768.4	576.32
(36-40)	505.9	706.3	744.4	561.67
(41-45)	430.7	521.3	597.9	478.51
(46-50)	322.1	462.3	458.2	374.55
Mean	**336.3**	**479.8**	**522.8**	**406.8**

(LSD = 9.798, $p<0.05$)

4. CONCLUSIONS

According to the results of this study, it can be concluded that:

1. The addition of trace metals such as Cobalt, Nickel and Iron improve the startup of anaerobic digestion.
2. The trace metals additives can increase the degradation of organic matter by stimulating the methanogenic activity.
3. Methane percentage was increased with the addition of trace metals.
4. The statistical analysis indicated that the biogas production increased with the addition of trace metals by the order Ni>Co>Fe.
5. The statistical analysis of the results of methane production shows the same behavior of biogas production.
6. The addition of 1 mgL^{-1} $NiCl_2$ to slurry produced the highest specific biogas and methane production.

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الملخص العربي

تأثير إضافة $CoCl_2$، $NiCl_2$ و $FeCl_3$ علي إنتاج الغاز الحيوي والميثان

عصام عبد السلام[1] ، محمد سامر[2] ، محمد علي عبد الهادي[3]، حلمي السيد حسن[4] ، يحيي بدر[4]

يعد التخمر اللاهوائي عملية بيولوجية تستخدم لتحويل المخلفات العضوية إلى غاز حيوي وأسمدة حيوية متوازنة للإستخدامات الزراعية كمنتجات صديقة للبيئة. وفي هذا السياق، يعتبر الغاز الحيوي الناتج أحد مصادر الطاقة المتجددة.

ويهدف هذا البحث إلي دراسة تأثير إضافة أملاح كلوريد الكوبلت ($CoCl_2$)، كلوريد النيكل ($NiCl_2$) و كلوريد الحديديك ($FeCl_3$) على إنتاج الغاز الحيوي و الميثان من روث الماشية. أجريت التجارب المعملية بالوحدة التجريبية للغاز الحيوي بالمعهد القومي لعلوم الليزر - جامعة القاهرة باستخدام مجموعة من الهاضمات الحيوية (مخمرات) بحجم كلي للمخمر الواحد ٢ لتر بنظام تشغيل الدفعة الواحدة. حيث تم تغذية كل مخمر بحجم ثابت ١٦٠٠ مللتر من روث الماشية بنسبة مادة جافة كلية (TS) ٧,١٦% مع إضافة الأملاح سابقة الذكر ١, ١ و ١٠ مليجرام/لتر, علي الترتيب. وقد أجريت هذه التجارب باستخدام ثلاثة مكررات و ذلك بغرض التحليل الإحصائي بإستخدام برنامج (MStat-C software v.2.1).

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