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Biomethane production from anaerobic co-digestion and steel-making slag: A new waste-to-resource pathway

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**Biomethane production from anaerobic co-digestion and steel-making slag: A new
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Abstract

A proof of concept of using steel-making slag to upgrade biogas to biomethane is demonstrated in this study. Biogas is generated from the anaerobic co-digestion of sewage sludge and beverage waste. The CO₂ capture capacity of an alkaline liquor derived from the release of calcium from the steel-making slag is comparable to that of the commercial adsorbent monoethanolamine. Although only 5% of Ca in the steel-making slag was released to the alkaline liquor, 1 ton of steel-making slag could be capable of upgrading 10 m³ of biogas to over 90% methane content. The results also show that pH can be used as a surrogate parameter to monitor and control biogas upgrading. Further research to improve the release of calcium is essential for the acceleration of the weathering process of steel-making slag for subsequent construction applications.

Keywords: Biogas upgrading; Anaerobic co-digestion; Steel-making slag; CO₂ removal; monoethanolamine adsorption.

1. Introduction

Anaerobic digestion (AD) is a widely used technology for stabilizing organic waste as well as sewage sludge (SS) in wastewater treatment plants (WWTPs) (Sawatdeenarunat et al., 2016; Zhang et al., 2017). In recent years, the paradigm shift toward a circular economy has resulted in renewed interest in AD technology as a platform to recover resources from organic wastes. This can be achieved through anaerobic co-digestion (AcoD) of carbon-rich organic wastes and sewage sludge to produce biogas (Dhanya et al., 2020; Mata-Alvarez et al., 2014; Nguyen et al., 2019).

The produced biogas contains methane (CH_4 , 50-70% v/v), carbon dioxide (CO_2 , 30-40% v/v) and traces of water vapour, hydrogen sulphide (H_2S), ammonia and other gases. Biogas can be converted to electricity and heat by a combined heat and power unit to offset energy demands of the WWTPs. In addition to heat and electricity production, biogas can be upgraded to biomethane by removing CO_2 . Biomethane exhibits the same energy value as natural gas and can be fed to town gas grid or used as a transport fuel.

Several biogas upgrading technologies involving CO_2 removal have been available. These include physical scrubbing using water and polyethylene, chemical scrubbing using monoethanolamine, pressure swing adsorption, membrane separation and cryogenic separation (Baena-Moreno et al., 2019; García-Gutiérrez et al., 2016; Leung et al., 2014). However, the bottlenecks in terms of high energy and water consumption, difficulties in handling solvent, poisoning of adsorbents, and high investment and operational cost have been hindering the maturity of these technologies, especially in small-scale biomethane plants (Adnan et al., 2019). Hence, the discovery of a low-cost solution to capture CO_2 and produce biomethane is of particular importance.

A possible feedstock for CO_2 sequestration is industrial solid wastes (e.g. combustion residues, fly ashes and steel-making slag) which are generally alkaline and rich in calcium (Bacocchi et al., 2016; Huijgen and Comans, 2005; Ji et al., 2018). These wastes are abundant and widespread available in industrial areas, thus a low-cost material. Moreover, these materials tend to be much reactive for carbonation due to their chemical instability, thus reducing the energy consumption and costs of CO_2 sequestration (Huijgen and Comans, 2005).

Steel-making slag, a by-product from steel production, is a potential alkaline adsorbent for CO_2 capture from biogas due to the presence of free basic oxides, such as CaO and MgO in its chemical composition (Bacocchi et al., 2016; Chen et al., 2019; Heiderscheidt et al., 2020). Apart from the potential production of biomethane with low costs, the use of steel-

making slag for carbon sequestration brings other benefits. Firstly, accelerated carbonation of steel-making slag via carbon sequestration may be considered as a pre-treatment strategy to valorise this material prior to utilization in construction (Bacocchi et al., 2016). Due to its significant content of calcium and magnesium oxides, steel-making slag has a swelling property owing to weathering process when it exposes to moisture or rainwater. This property results in poor volumetric stability and low mechanic performance in construction applications (Bacocchi et al., 2016). Therefore, the weathering process of steel-making slag can be accelerated via CO₂ sequestration. Secondly, the use of steel-making slag for biogas upgrading can address environmental issues caused by the stockpile of steel-making slag in industrial areas or its discharge in landfill sites, and by the emission of CO₂ into the atmosphere. The leaching of alkaline materials during steel-making slag weathering into natural water bodies can be detrimental to the environment (Barca et al., 2014). CO₂ is a greenhouse gas and its increasing emission has been linked to global warming and climate change (Fan et al., 2019).

CO₂ sequestration by steel-making slag has been widely studied in recent years driven by greenhouse gas emission reduction and the development of circular economy in which re-use and recycling are favourable. The content of metal oxides and high alkalinity properties of steel-making slag confer a high potential CO₂ sequestration capacity (Bacocchi et al., 2009; Bonenfant et al., 2008; Ko et al., 2015). For example, Bacocchi et al. (2009) estimated a value of 140 m³ CO₂ adsorbed per ton of steel-making slag based on the total calcium content in steel-making slag. Ko et al. (2015) reported that CO₂ content in gas phase could affect positively the carbonation reactions with steel-making slag. However, these studies have only investigated the performance of steel-making slag using pure CO₂ gas from compressed gas cylinders. In addition, the configurations of steel-making slag giving the best CO₂ capture performance have not been indicated yet.

In this study, we demonstrated the proof-of-concept using steel-making slag to remove CO₂ for biogas upgrade from an AcoD system. Biogas production and quality as well as total solid removal were used to indicate the performance of AcoD. The release of alkaline material from steel-making slag and CO₂ sequestration capacity were examined and compared to a commercial CO₂ adsorbent. Possible measures to enhance the CO₂ removal capacity of steel-making slag were also discussed. This study thus provides insights to the development of a novel technique to simultaneously accelerate the weathering process of steel-making slag and upgrade biogas for biomethane production.

2. Materials and methods

2.1. Feed stocks and chemicals

Beverage waste was collected from a WWTP where it was co-digested with sewage sludge. This beverage waste is a mixture of soft drinks unsuitable for human consumption (e.g. out of date, contamination and damaged packaging) from a commercial waste collector in NSW Australia. The beverage waste was transported and stored in the WWTP prior to use for anaerobic co-digestion process. The storage environment (i.e. ambient temperature and atmospheric pressure) and intensive mixing condition ensure no remaining CO₂ gas from soft drinks in the beverage waste sample. Raw sewage sludge and digested sludge were also obtained from the same WWTP for daily experimental work and inoculating the anaerobic reactor, respectively. After collection, sewage sludge and beverage waste were stored at - 4 °C in the dark and used within 2 weeks.

Analytical grade (>98% purity) monoethanolamine and NaOH were purchased from Sigma Aldrich (NSW, Australia). The solution of each chemical was prepared in 1 L bottle at 0.4 M concentration and used for CO₂ removal within 1 h of preparation. The concentration of 0.4 M was selected based on a preliminary testing to observe the saturation point over a short period (i.e. 4-5 days). This concentration was also selected as an intermediate value between the high practical concentration of commercial adsorbents (e.g. 5 M for monoethanolamine (Lv et al., 2015)) and the low concentration of Ca(OH)₂ produced from the steel-making slag as indicated in section 3.2.

The steel-making slag was obtained from an electric arc steel-making furnace (InfraBuild, Rooty Hill NSW 2766, Australia). The steel-making slag contained in weight 32% CaO, 32% Fe₂O₃, 16% SiO₂, 7% MgO, 6% Al₂O₃, and 6% MnO. The steel-making slag was washed with DI water to remove dirt and dried at 105 °C for 24 h. Then, the steel-making slag was crushed and sieved to obtain particle sizes of less than 0.6 mm.

2.2. Anaerobic co-digestion operation

A laboratory scale anaerobic co-digestion system was operated in this study (Figure 1). The system consisted of 28 L stainless steel conical reactor, a peristaltic hose pump (DULCO® Flex from Prominent Fluid Controls, Australia), a biogas counter (RITTER, MilliGascounter, Germany). On the biogas outlet line behind the gas counter, a three-way valve was inserted for the interchange of adsorbent solutions. One way was connected to the adsorbent bottle for the adsorption experiment, and another way was expected to be connected to a water bottle, which was identical to the adsorbent bottle, for solution interchange purpose. The volumes of liquid (i.e. adsorbent solution and water) in both these

bottles were the same (1 L). A water bath (Thermo Fisher Scientific, Australia) was used to maintain the reactor temperature at 35 ± 0.5 °C by circulating hot water from the heated bath through a rubber tube that was firmly warped around the reactor. The reactor and pipeline were insulated with two layers of polystyrene foam and aluminium foil.

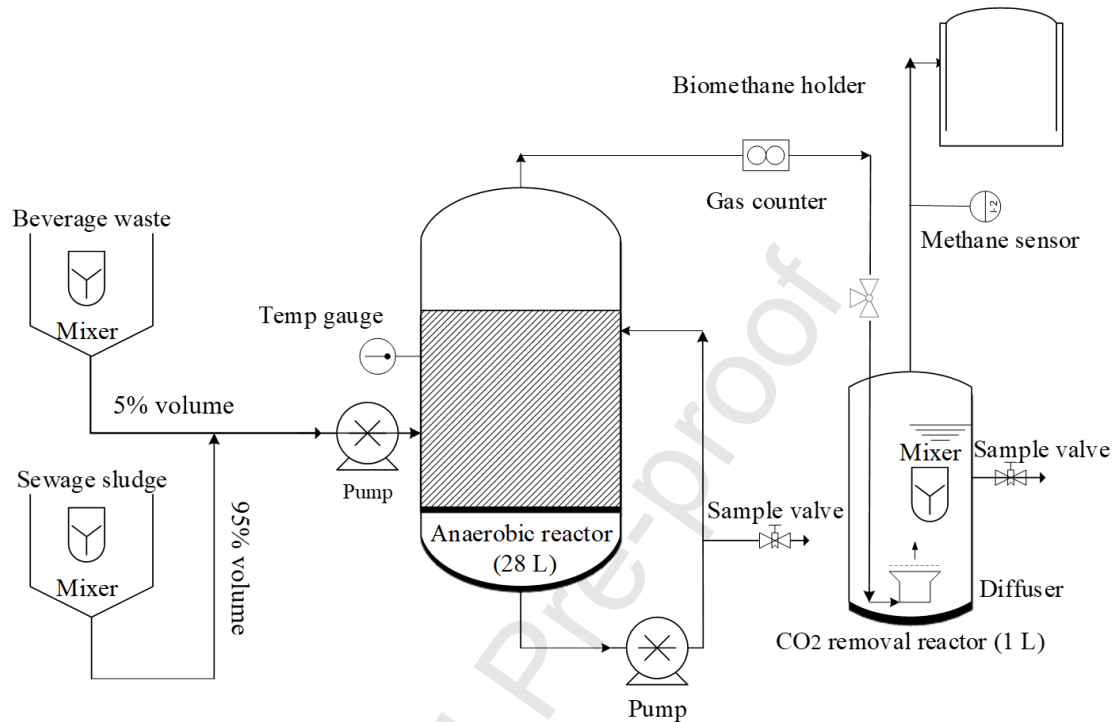


Figure 1. Schematic diagram of the anaerobic co-digestion set up and biogas upgrading line for this research.

The AcoD system was inoculated with 15 L of digested sludge. Thus, the active volume of the anaerobic reactor was only 15 L. Then, the digester was purged with N_2 gas for 10 min to remove residual oxygen. The digester content was mixed by the peristaltic hose pump. This pump was continuously operated to draw sludge from the bottom and return to the top of digester at 30 L/h (i.e. 36 turnover volumes per day).

The system was operated in a semi-continuous feeding. Each day, 750 mL of digestate was withdrawn and the same volume of substrate was then fed into the reactor, resulting in a sludge retention time of 20 days. The mono anaerobic digestion (AD) phase was operated for 30 days. Because the reactor has been acclimatised under the same condition, biogas production was stable throughout this experimental period. In this phase, sewage sludge was the only substrate. From day 31, the system was operated in AcoD mode and fed with a mixture of sewage sludge and beverage waste (95:5 %, v/v). The AcoD experimental phase

was operated for 90 days, during which the biogas upgrading experiments had been conducted since the biogas production was stable.

2.3. Preparation of steel-making slag liquor and in-situ alkaline release

To obtain the alkaline liquor, 400 g of steel-making slag was added to 1 L DI water and mixed continuously at 150 rpm and room temperature for 48 h. The equivalent steel-making slag mass per water volume ratio was therefore 0.4 (g/mL). pH and calcium ion (Ca^{2+}) concentration were measured at specific time intervals. After 48 h, steel-making slag was discarded to obtain the alkaline liquor (i.e. supernatant). The alkaline liquor was purged with N_2 gas, stored in an air-tight bottle, and used for CO_2 removal experiment in the following day.

CO_2 removal experiment was also conducted using in-situ alkaline release (instead of using the alkaline liquor, steel-making slag was added to DI water immediately before the CO_2 removal experiment). This is denoted as the in-situ experiment. In this experiment, 400 g of steel-making slag was introduced to the adsorption bottle containing 1 L of DI water. This mixture was immediately used for the adsorption experiment.

The ratio of calcium ion release from the steel-making slag into the liquor was calculated by the following equation:

$$x_{\text{Ca}^{2+}} = \frac{C_{\text{Ca}^{2+}} \times V_t}{m_{\text{slag}} \times \omega_{\text{CaO}} \times \frac{40}{56}} \quad (1)$$

Where: $x_{\text{Ca}^{2+}}$ is the releasing ratio of calcium ion; $C_{\text{Ca}^{2+}}$ is the concentration of Ca^{2+} in the liquor (mg/L); V_t is the total volume of the liquor (L); m_{slag} is the mass of the initial steel-making slag (g), and ω_{CaO} is the content of CaO in the initial steel-making slag (%).

2.4. Biogas upgrading experiments

Raw biogas from the anaerobic co-digestion was directly purged via a micro-diffuser at the bottom of the adsorbent glass cylindrical bottle. The adsorbent bottle (height and diameter of 33 and 6.2 cm, respectively) was placed on a magnetic stir at 150 rpm to mix the adsorbent solution and biogas bubbles for mass transfer maximization. The outlet biogas quality was recorded using a Lambda methane sensor (Lambda Laboratory Instruments). The pH of the adsorbent solution was measured every day by withdrawing 10 mL from sample valve (Figure 1). The experiment was terminated when no further changes in methane content were observed. Once one adsorbent lost its CO_2 removal capacity, another adsorbent was replaced for the test. It is noted that to minimize the interference to the AcoD system, during an interchange of the adsorbent solution, one idle gate of the three-way valve was connected to a water bottle as described earlier. Then, the three-way valve was switched to the water bottle.

In other words, biogas was aerated into the water bottle instead of the adsorbent bottle. The gas outlet of the water bottle was open to the air. The three-way valve was switched back to the adsorbent bottle for the next experiment once the new adsorbent solution had been installed. All CO₂ removal experiments were conducted in replicate.

2.5. Analytical methods

Biogas production was continuously recorded via the gas counter. Biogas composition was analysed using a portable GA5000 gas analyser (Geotechnical Instruments, UK) everyday (Nghiem et al., 2014). Total chemical oxygen demand (tCOD) was measured by using digestion vials (Hach, Australia) and Hach DR3900 spectrophotometer following the manufacturer's instruction. Alkalinity, total solids (TS), and volatile solid were measured weekly following the standard method 2320 and 2540, respectively. Digestate pH was measured every second day using a portable pH meter (Thermo Fisher Scientific, Australia). Ca²⁺ concentration in steel-making slag liquor was measured using an Inductively Coupled Plasma-Mass Spectrometry (Agilent 7900 ICP-MS).

The amount of CO₂ removed was measured using a gasometric system adapted from the Chittick apparatus (AOAC Official Method 923.02) (Huang et al., 2007). Briefly, the system contained two identical PYREX burettes (50 mL) connected to each other via a flexible tube (Figure 2). One burette (immobile burette) was connected to a glass bottle of HCl acid solution (2 M) that holds the de-absorbed reaction to release CO₂. On the line connecting the acid bottle and the immobile burette, a two-way valve was set up for pressure balance. The other burette (mobile burette) was open to the atmospheric and can be vertically slide up and down. HCl solution (2 M) was used to reverse carbonation of the absorbed solution for CO₂ release.

To prepare for CO₂ desorption measurement, the balancing valve was opened, and the two burettes were filled with 40 mL 2 M HCl solution. Liquid levels in these two burettes are identical. Then, 2 mL HCl solution (2 M) was placed into the acid bottle. The small adsorbent bottle inside the acid bottle was also filled up with 1 mL of the CO₂-adsorbed solution. The balancing valve was then closed and an air-tight lid was placed on the acid bottle.

Once the gasometric system was ready, the acid bottle was inverted allowing the adsorbent to mix in the acid. CO₂ gas released from the reaction pushed the liquid level in the immobile burette to a new position. The volume in the immobile burette was recorded as V_1 (mL). Next, the mobile burette was adjusted vertically until both burettes had the same liquid level. The volume of the immobile burette was recorded as V_2 (mL). The difference between V_2 and V_1 is the total volume of CO₂. The amount of CO₂ (in mole) adsorbed was calculated

using the ideal gas laws. CO₂ desorption measurement was repeated four times. The final amount of CO₂ absorbed was the mean value of four measurements. CO₂ loading of each adsorbent was calculated by dividing the mole of CO₂ absorbed to the total initial mole of the adsorbent.

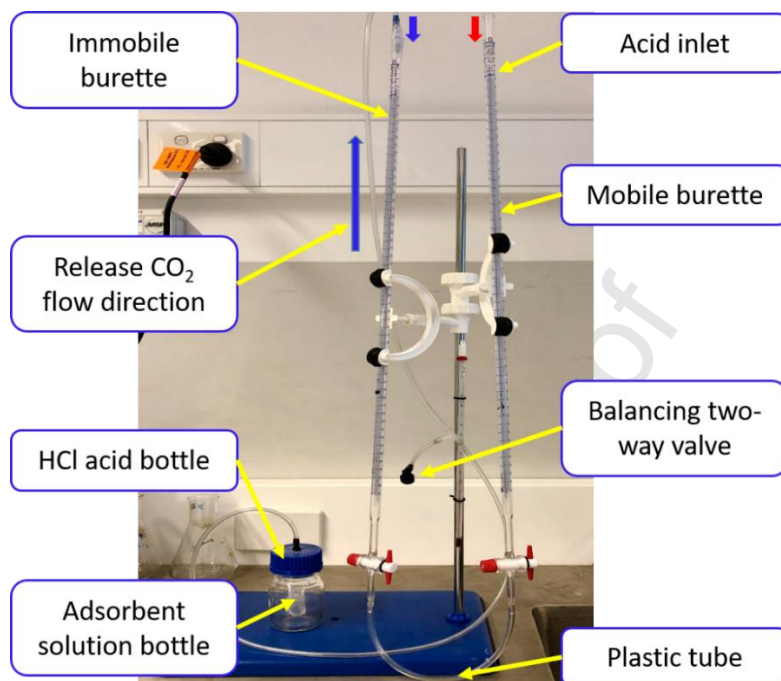


Figure 2. A photograph of the gasometric system to measure CO₂ adsorbent capacity of steel-making slag liquor.

3. Results and discussions

3.1. Anaerobic co-digestion performance

Co-digesting beverage waste at 5% by volume with sewage sludge led to an increase in organic loading rate and daily biogas production with no discernible influence on biogas composition (Table 1). The beverage waste in this study contains 4 times more COD content than sewage sludge. Importantly, almost all of this COD content is in soluble form and thus is readily transformable into biogas. The solid content in beverage waste is negligible and is exclusively in the form of volatile solid, thus it is also biodegradable (Table 2). As a result, the increase in biogas production from AcoD compared to mono-AD with only sewage sludge is as expected.

Of particular note, results in Table 1 provide evidence that AcoD can lead to a small but discernible synergistic effect that the increase in biogas production exceeds the increase in COD loading. In fact, the increase in COD loading due to AcoD was 15% (from 1.59 to 1.82 kg COD/m³·d) while the increase in biogas production was 30% (from 0.5 to 0.65 L/m³·d). The observed synergistic effect has been reported in several previous studies when sewage

sludge was co-digested with a highly biodegradable substrate such as food waste (Ma et al., 2019; Xie et al., 2017a; Xie et al., 2017b).

Methane content in biogas from AcoD was $66.0 \pm 2.7\%$ and was marginally higher than that from mono-AD with only sewage sludge. These results are in agreement with previous studies that have reported negligible changes or a minor increase in methane content in biogas from AcoD between sewage sludge and beverage waste compared to mono-AD (Isla et al., 2013; Wickham et al., 2018).

Table 1. Key performance indicator of anaerobic system with and without beverage waste addition (values indicated average \pm standard deviation of 20 samples).

Phase	Mono-AD	AcoD
Days	1 – 30	31 – 60
Organic loading rate (kg COD/m ³ ·d)	1.59 ± 0.20	1.82 ± 0.12
SS:BW ratio (% , v/v)	100:0	95:5
Biogas production (L/m ³ ·d)	0.50 ± 0.08	0.65 ± 0.15
CH ₄ content (%)	65.0 ± 3.6	66.0 ± 2.7
CO ₂ content (%)	40.0 ± 4.5	37.0 ± 6.2
H ₂ S (ppm)	921 ± 12	885 ± 18
tCOD removal (%)	60.2 ± 27.5	69.6 ± 7.9
TS removal (%)	44.3 ± 12.6	53.6 ± 11.6

A slight increase in removal efficiency of tCOD and TS was also observed in co-digestion experiment compared to the mono-AD (Table 1). This is attributed to the highly biodegradable organic content in the beverage waste as discussed above. These results were also consistent with the improvement of COD and TS removal at the full-scale AcoD at the WWTP where the sewage sludge and beverage waste were collected (in communication with the plant operators).

Table 2. Sewage sludge and beverage waste characteristics (values indicated an average \pm standard deviation of at least three samples)

Feedstock	tCOD (mg/L)	pH	TS (%)	Volatile solid (%)
Sewage sludge	31700 ± 2452	2.86	1.95 ± 0.20	1.76 ± 0.17
Beverage waste	125800 ± 1256	4.84	0.04 ± 0.00	0.04 ± 0.00

3.2. Steel-making slag liquor characterisation

When interacting with water, steel-making slag released calcium ions into the liquor solution, resulting in an increase in the solution pH (Figure 3). The alkaline level of the

obtained liquor increased to pH 11 within 12 hours after soaking the steel-making slag. Correspondingly, the Ca^{2+} concentration increased more than seven times to 3,500 mg/L. This phenomenon is attributed to the hydrolysis of calcium oxides in the steel-making slag that dissociated Ca^{2+} and OH^- ions into the aqueous solution, thereby increasing pH. The pH value of a saturated $\text{Ca}(\text{OH})_2$ solution is 12.4 (Athanassiadis and Walsh, 2017). The high steel-making slag liquor pH value of 11.7 suggests that the Ca^{2+} content is close to the theoretical value of saturated $\text{Ca}(\text{OH})_2$ solution.

At equilibrium, 1 g of steel-making slag could release 11 mg of Ca^{2+} to the alkaline liquor. Calcium oxide content in the steel-making slag based on an elementary analysis was 320 mg/g (section 2.1). Thus, according to Eq (1), at equilibrium, the amount of Ca^{2+} released to the alkaline liquor was only 5% of the total calcium in steel-making slag. This result could be explained by the hindrance to Ca release from calcium oxides of steel-making slag due to the rapid increase in pH of the liquor to the close theoretical pH of saturated $\text{Ca}(\text{OH})_2$ solution. In fact, further release of Ca can be stimulated by lowering the initial solution pH. Bang et al. (2016) observed 100% release of Ca to the aqueous phase by adding nitric acid and hydrochloric acid to the initial solution at 20% (w/v). Derived from the hypothesis that the ready availability of Ca^{2+} ions in the liquor and their in-situ release from steel-making slag might affect the efficiency of carbon sequestration, the CO_2 removal capacity of both the steel-making slag liquor and in-situ alkaline release was investigated.

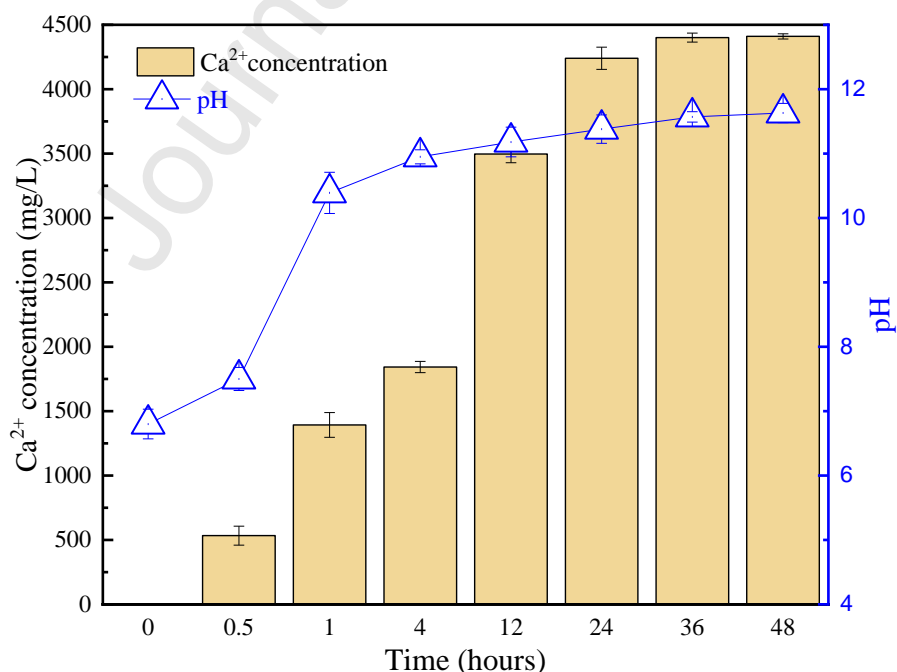


Figure 3. Changes in Ca concentration and pH of the alkaline liquor as a function of time due to calcium release from the steel-making slag (at room temperature (24 °C) and atmospheric

pressure). Values and error bars are the mean and standard deviation of two replicate experiments.

3.3. Biomethane production using steel-making slag in comparison with other adsorbents

The steel-making slag liquor was capable of removing CO₂ from biogas to achieve over 90% pure methane content. Within the initial experimental phase, the performance of the steel-making slag liquor was comparable to that of a NaOH solution and monoethanolamine which is a commercial CO₂ solvent. However, the adsorption capacity of the steel-making slag liquor decreased over time and the methane content dropped to 90% after 24 hour (Figure 4a). CO₂ removal by the steel-making slag liquor can be ascribed to the reaction between Ca²⁺ and CO₃²⁻ ions to form calcite at high pH as CO₂ purged into the adsorbent existed mainly in the form of carbonate (CO₃²⁻). Indeed, the presence of calcite was confirmed as white precipitate settled at the bottom of the adsorption bottle.

NaOH could maintain the CO₂ removal efficiency for a longer period (50 hours) in comparison to the steel-making slag liquor. This phenomenon is due to the difference in the alkaline strength of these solutions. The concentration of Ca²⁺ ions in the liquor that was derived from the dissolution of Ca(OH)₂ was approximately 4,400 mg/L (Figure 3), corresponding to 0.11 moles of Ca(OH)₂, significantly lower than that of NaOH (0.4 moles).

Both steel-making slag liquor and in-situ alkaline release are capable of removing CO₂ from biogas, but the steel-making slag liquor showed better performance (Figure 4b). However, the lifespan of the steel-making slag liquor (72 hours) until loss of CO₂ removal capacity was double that of in-situ alkaline release (36 hours). In in-situ alkaline release, the aeration of CO₂ in biogas led to decrease in pH, thereby encouraging the release of Ca, but the rate of release was slow. The decline in pH of in-situ alkaline release (Figure 6) is unfavourable for CO₂ adsorption. When pH decline outweighed the benefits from the slow release of Ca in in-situ alkaline release towards the carbonation process, the efficiency of adsorption process decreased significantly. Further research to find out how to maximize the release of Ca and maintain high pH at the same time is needed to enhance the CO₂ capture performance of using the steel-making slag.

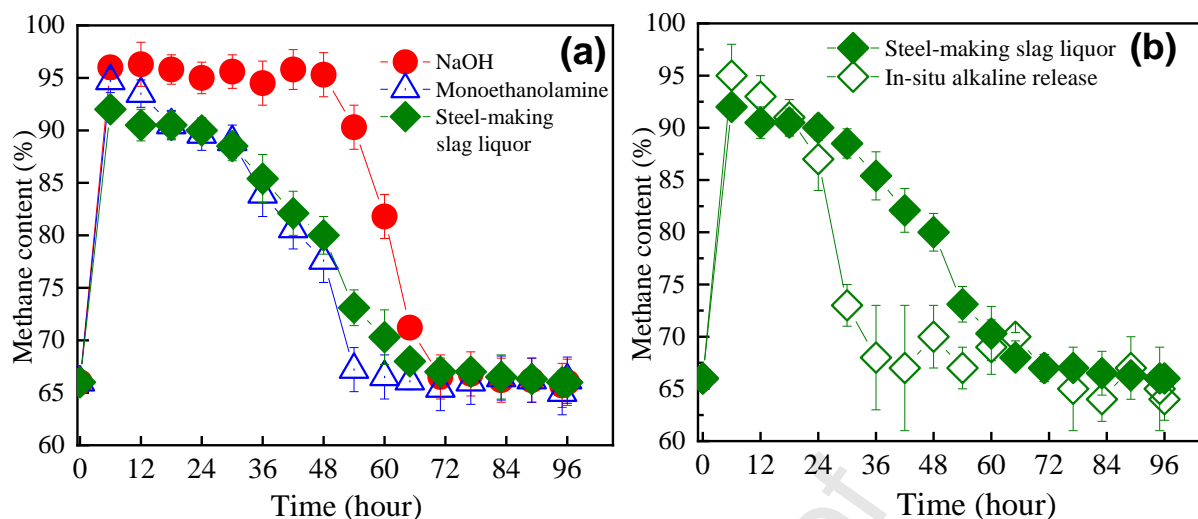


Figure 4. The methane content in biogas after CO₂ removal as a function of time by the steel-making slag liquor and other commercial adsorbents (a), and in-situ alkaline release (b). Values and error bars are the mean and standard deviation of two replicate experiments.

3.4. CO₂ capture capacity of steel-making slag liquor

To compare the CO₂ capture capacity of different adsorbents, CO₂ loading that indicated the mole of CO₂ adsorbed per mole of adsorbent was used. Overall, the actual amounts of CO₂ adsorbed into all adsorbents were lower than the theoretical values that were obtained based on the stoichiometric ratio of the reaction between CO₂ and the adsorbents (1:1) (Figure 5). This result could be explained by the inefficient adsorption of CO₂ at unfavourable pH conditions since the pH of adsorbents decreased over time (Figure 6), and by the possible competitive adsorption between CO₂ and other acidic gases (i.e. H₂S) in biogas (Table 1). Indeed, H₂S was not detected in biogas after adsorption process.

The results demonstrate that the steel-making slag liquor has a similar CO₂ adsorption capacity comparing to monoethanolamine, but markedly lower than that of NaOH (Figure 5). Ca(OH)₂ is a weaker alkaline than NaOH. The CO₂ adsorption capacity of monoethanolamine in this study (0.53 mol CO₂/ mol monoethanolamine) is in agreement with the previous study (Lv et al., 2015) and similar to that of the steel-making slag liquor. The CO₂ removal capacity of the steel-making slag liquor was 4 m³ CO₂ per ton of initial steel-making slag, corresponding 10 m³ biogas used. In this study, the calcium leaching process has not been optimised and the efficiency is only 5%. With research to improve the calcium leaching efficiency to 100%, 1 ton of steel-making slag can then process 200 m³ of biogas.

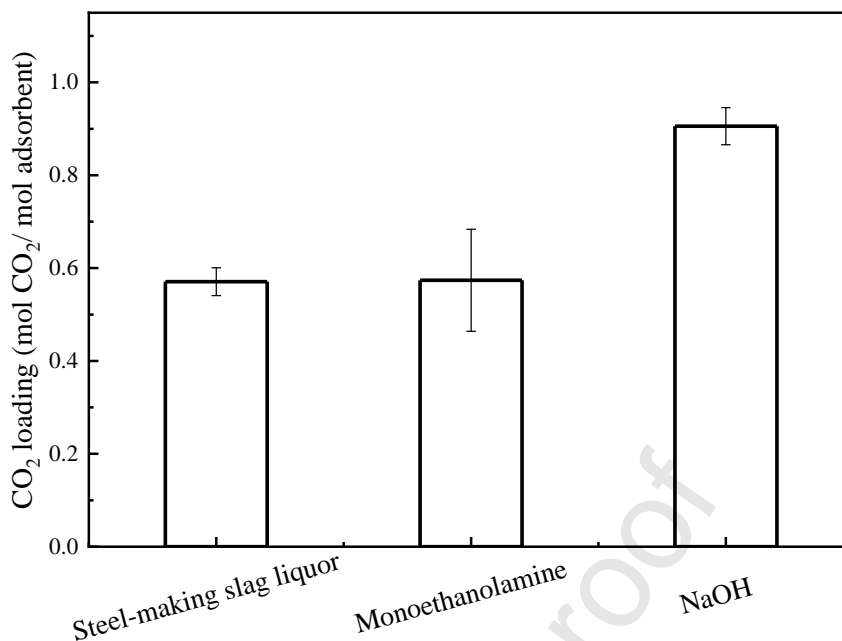


Figure 5. Comparison in values of CO₂ loading towards using different adsorbent solutions. It is noted that CO₂ loading towards using steel-making slag liquor was calculated based on the mole of Ca released. Values and error bars are the mean and standard deviation of two replicate experiments.

3.5. Solution pH as an indicator of biogas quality

The observed correlation between methane content and pH of the sorption solution in Figure 6 suggests that pH could be used as a surrogate parameter to monitor and control CO₂ removal. As the adsorption capacity of the solution was depleted, the solution pH decreased. Thus, pH measurement can be used to determine when to replace the steel-making slag liquor. For steel-making slag liquor, over 90% methane content in upgraded biogas can be achieved when the solution pH is above pH 9 (Figure 6). A similar result can be observed when the release of alkaline was examined in-situ (i.e. alkaline release from steel-making slag and CO₂ removal occur simultaneously). In practice, it is envisaged that treated effluent can be used to produce the alkaline liquor. After CO₂ adsorption, the treated effluent can be discharged into the environment or beneficially reused without further treatment.

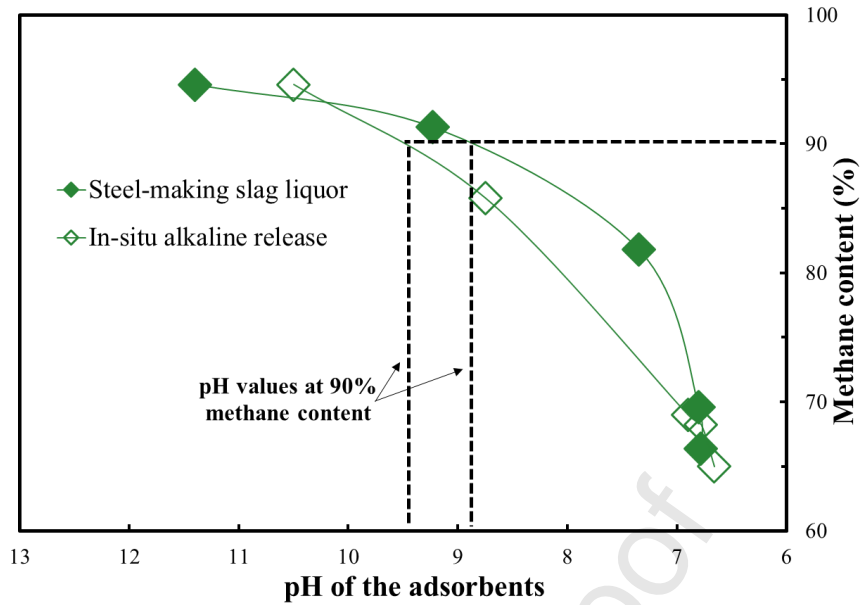


Figure 6. Changes in methane content in biogas as a function of pH during the biogas upgrading experiment.

4. Conclusion

This study demonstrates the proof of concept of using steel-making slag to upgrade biogas to biomethane. Biogas was obtained from the anaerobic co-digestion of sewage sludge and beverage waste. The release of calcium from the steel making resulted in an alkaline liquor that has similar CO₂ removal performance when comparing to the commercial adsorbent monoethanolamine. In addition, the values of CO₂ loading on steel-making slag alkaline liquor and monoethanolamine were significantly lower than the theoretical stoichiometric values and that of NaOH (strong alkaline) solution. This result suggests the possibility of further process optimisation for a higher CO₂ removal efficiency. Indeed, only 5% of CaO in steel-making slag was released into the alkaline liquor in this study. Even at this low calcium release efficiency, 1 ton of steel-making slag can be used to upgrade 10 m³ of biogas to over 90% methane content. The process of CO₂ adsorption to the alkaline liquor can be monitored by measuring the solution pH, thus, providing a low cost and reliable supporting index for process control. Further research to increase the efficiency of calcium release is required to ensure that steel-making slag is fully weathered for subsequent beneficial reuse (e.g. road base construction).

5. Acknowledgement

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Author contribution

Minh T Vu: Conceptualization, experimental work, drafting the first version, editing.

Luong N. Nguyen: Conceptualization, experimental work, reviewing, editing.

Kang Li: CO₂ adsorption experiment, reviewing.

Md Abu Hasan Johir: Experimental work, reviewing.

Andrea Fontana: Conceptualization, steel making slag characterisation, reviewing.

Long D. Nghiem: Supervision, planning, conceptualization, experimental work, reviewing, editing

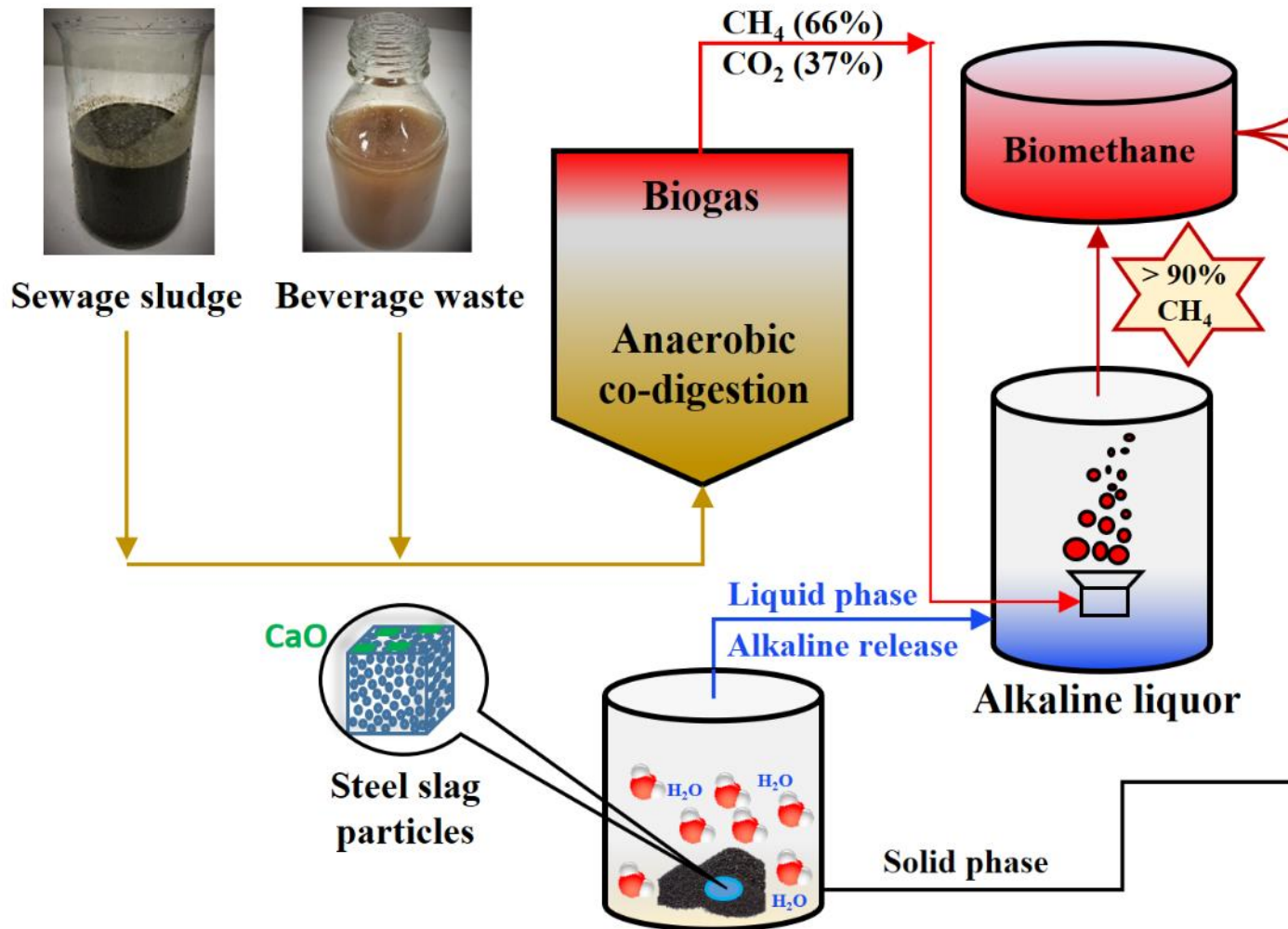
Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Journal Pre-proof

Graphical Abstract



Highlight

- Proof of concept using steel-making slag liquor to remove CO₂ from biogas
- Ca²⁺ released from steel-making slag captured CO₂ via carbonation process
- Steel-making slag liquor achieves similar CO₂ removal compared to monoethanolamine
- pH can be used as a surrogate parameter to monitor the CO₂ removal process

Journal Pre-proof

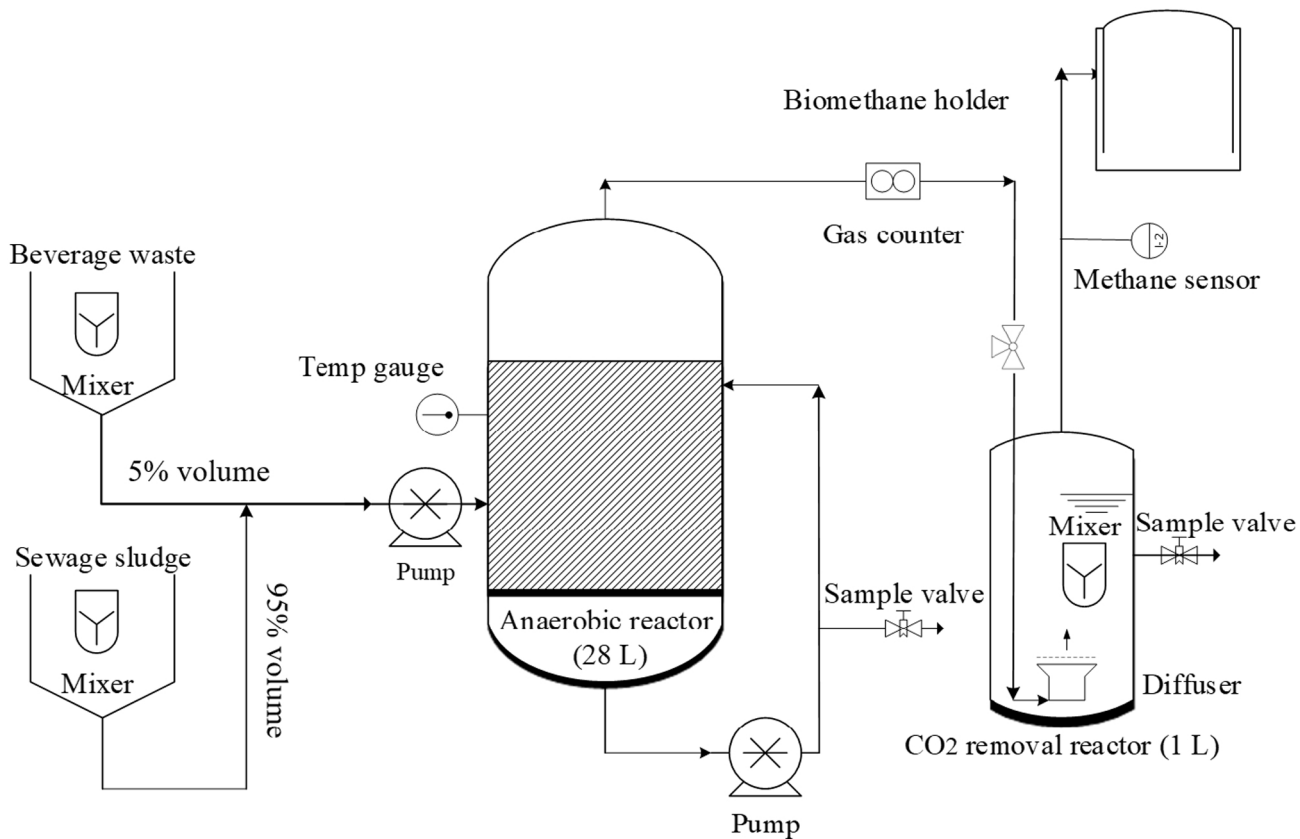


Figure 1

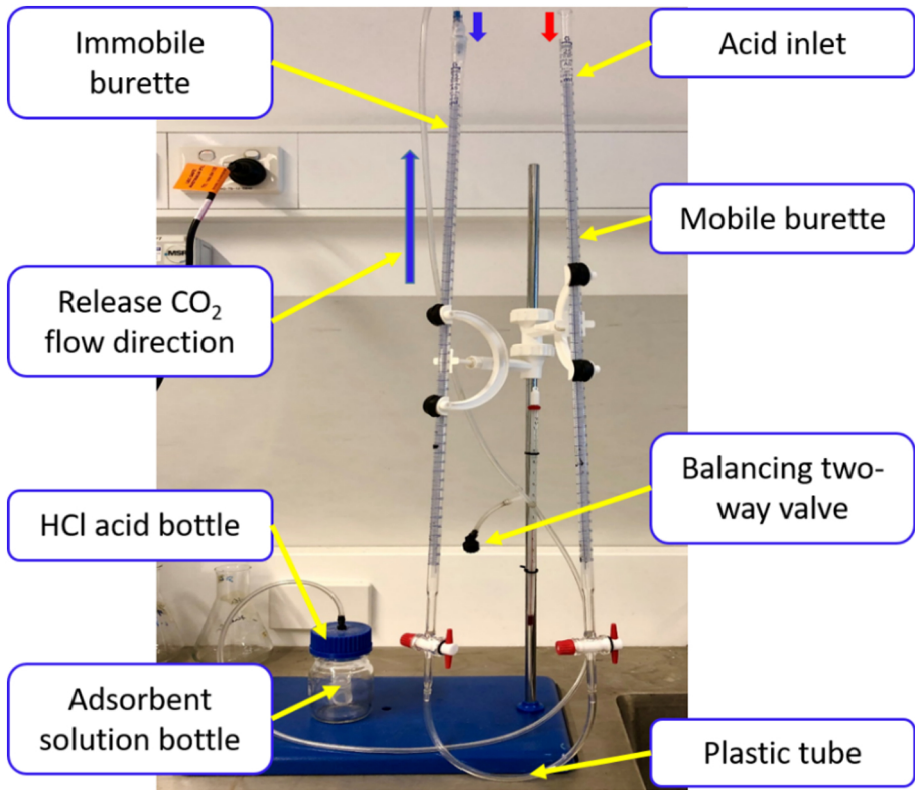


Figure 2

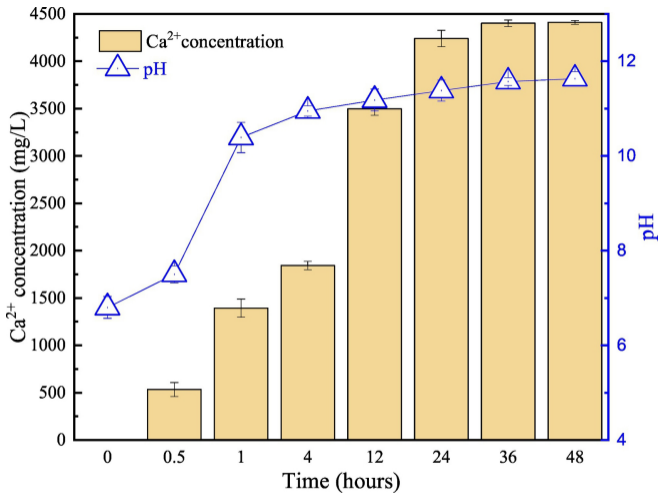


Figure 3

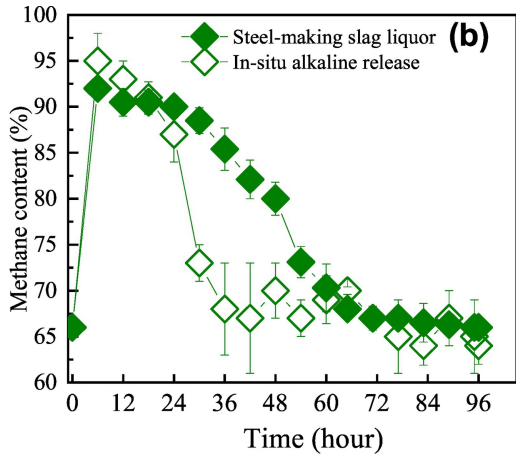
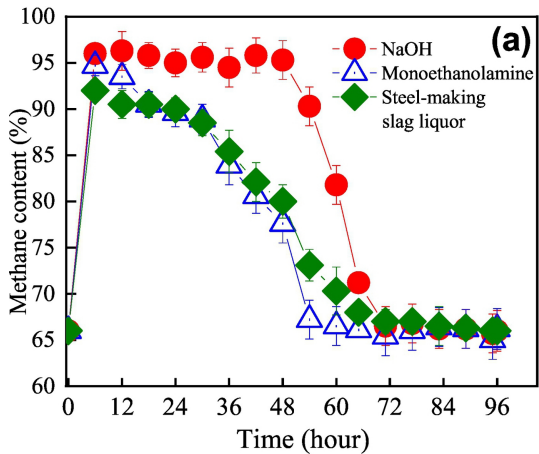


Figure 4

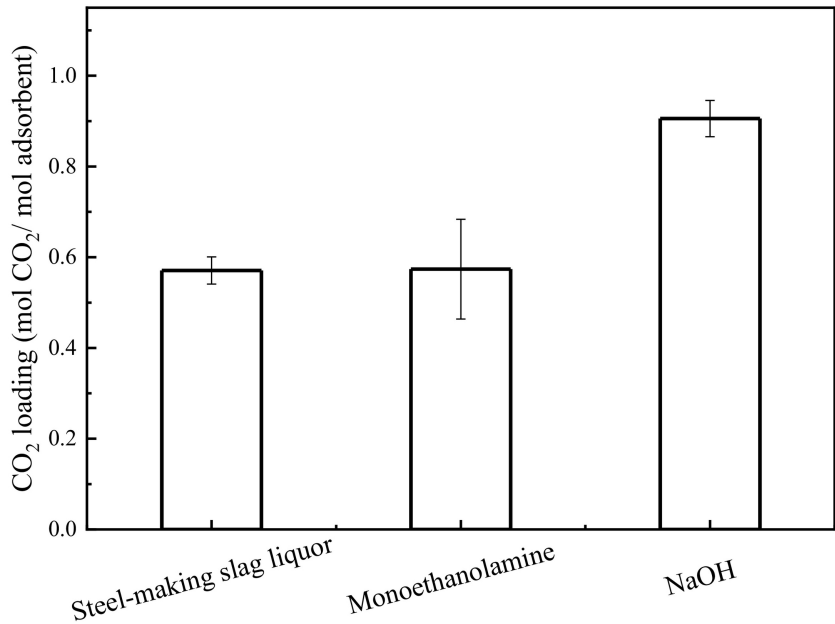


Figure 5

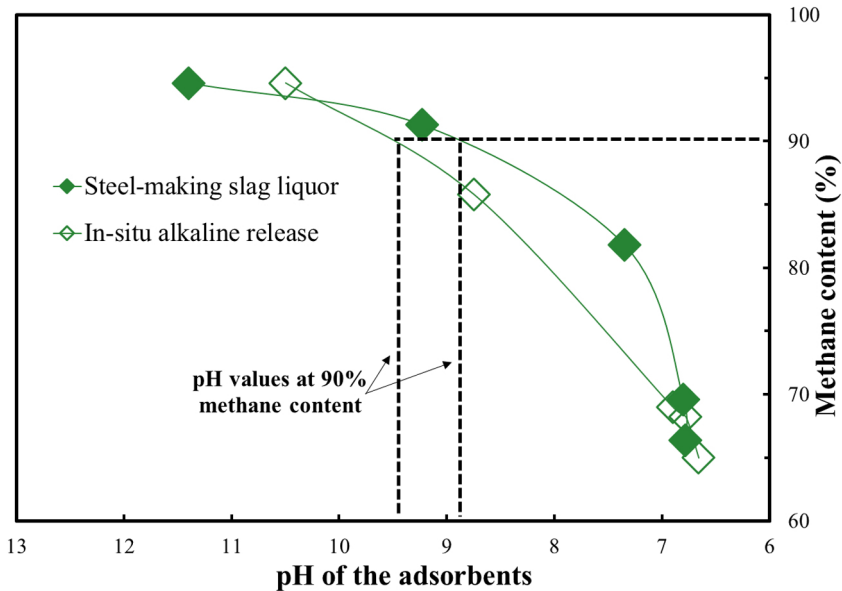


Figure 6