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Converting CO₂ from Biogas and MgCl₂ Residues into Valuable Magnesium Carbonate: a Novel Strategy for Renewable Energy Production.

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Abstract

In this work a novel strategy for bio-methane production and magnesium chloride waste valorization is addressed. The proposed process is a potential alternative path to the already existing biogas upgrading technologies by carbon dioxide mineralization into valuable magnesium carbonate. The main parameters affecting the precipitation efficiency (reaction time, reaction temperature, and molar ratio reactant/precipitator) are studied, leading to promising results which spark further investigation in this innovative route. Additionally the purity and the morphology of the obtained solid product was accurately analysed through different physicochemical characterization techniques such as Raman, X-Ray diffraction and Scanning electron microscope. The characterisation study reveals a mixture of Nesqueonite and Dypingite carbonate phases obtained in the process being the later the dominant phase in the resulting precipitate. Overall, the

results discussed herein confirmed the technical feasibility of this innovative strategy for synergizing carbon dioxide mineralization and renewable energy production.

Keywords

Carbon Capture and Utilization; Biogas Upgrading; Magnesium Carbonate Production; Waste Valorization; Bio-methane Production;

1. Introduction

The general concern about the unceasing increase of carbon dioxide (CO₂) emissions has led the research community to develop effective methods to capture this greenhouse gas [1]. Among these techniques, carbon capture and mineralization has emerged as a potential effective technology for small and medium CO₂ producers [2,3]. In this process, CO₂ reacts chemically with calcium (Ca²⁺) or magnesium (Mg²⁺) ions contained in minerals to form stable carbonates [4]. A plethora of studies dealing with CO₂ capture using minerals such as wollastonite [5,6] or serpentine [7,8] are available in literature. Unfortunately, the energy penalty of these processes due to expensive reprocessing stages [9], as well as their unfavorable life cycle assessment [10,11] limit the application of these methods. Nevertheless, such restrictions could be overcome by employing unused aqueous resources with high composition of Ca²⁺/Mg²⁺ such as brines or industrial residues [12–14], where the precipitation reaction is much faster than in a solid structure [15]. For instance, millions tons of magnesium chloride (MgCl₂) are obtained as wastes from potassium-based fertilizers production per year [12]. If these residues of MgCl₂ could be applied for CO₂ sequestration at assumable reaction conditions, a remarkable reduction of the carbon fingerprint could be achieved with a more favorable process economics. The direct carbonation of gaseous CO₂ into Mg²⁺ aqueous solutions has been proved to be technically limited at room temperature conditions since this reaction is not spontaneous under this environment [16,17]. This problem can be tackled by previously dissolving CO₂ in organic alcohols such as diisobutylamine, n-octanol,

ethanol or isopropanol among others [18–20]. Nevertheless, the cost associated to the utilisation of these chemicals make the overall economic balance insufficient for becoming a realistic option for industrial applications.

Biogas from the anaerobic digestion of biomass, which is roughly composed by 60% methane (CH_4) and 40% CO_2 , can be a potential industrial sector for the application of these novel techniques since the amount emitted of CO_2 fits in the emitters range. In this way, bio-methane would be obtained as valuable product with multiple applications [21–23]. In fact, several approaches for biogas upgrading to bio-methane production have been studied [24–26], since the upgrading process enhances the calorific value of bio-methane in comparison to biogas as well as increases the market price of the bio-methane [27]. Among the biogas upgrading technologies chemical absorption, physical absorption, pressure swing adsorption, membranes processes and cryogenic techniques have been regarded as potential solutions [28]. However, the main problem that these technologies face is their elevated operational and capital cost [29,30]. The future affordability of these processes relays on obtaining extra added value products that can be sold along with the obtained bio-methane. In this sense, we have based our work in obtaining valuable sub-products from carbon during biogas upgrading via chemical absorption. Therefore, the purpose of our work was to synergize carbon dioxide mineralization and biogas upgrading, since the amount and quality of the obtained carbonates would be attractive to the chemicals market. Figure 1 depicts the envisaged process for bio-methane and magnesium carbonate (MgCO_3) production from MgCl_2 wastes in a biogas upgrading plant.

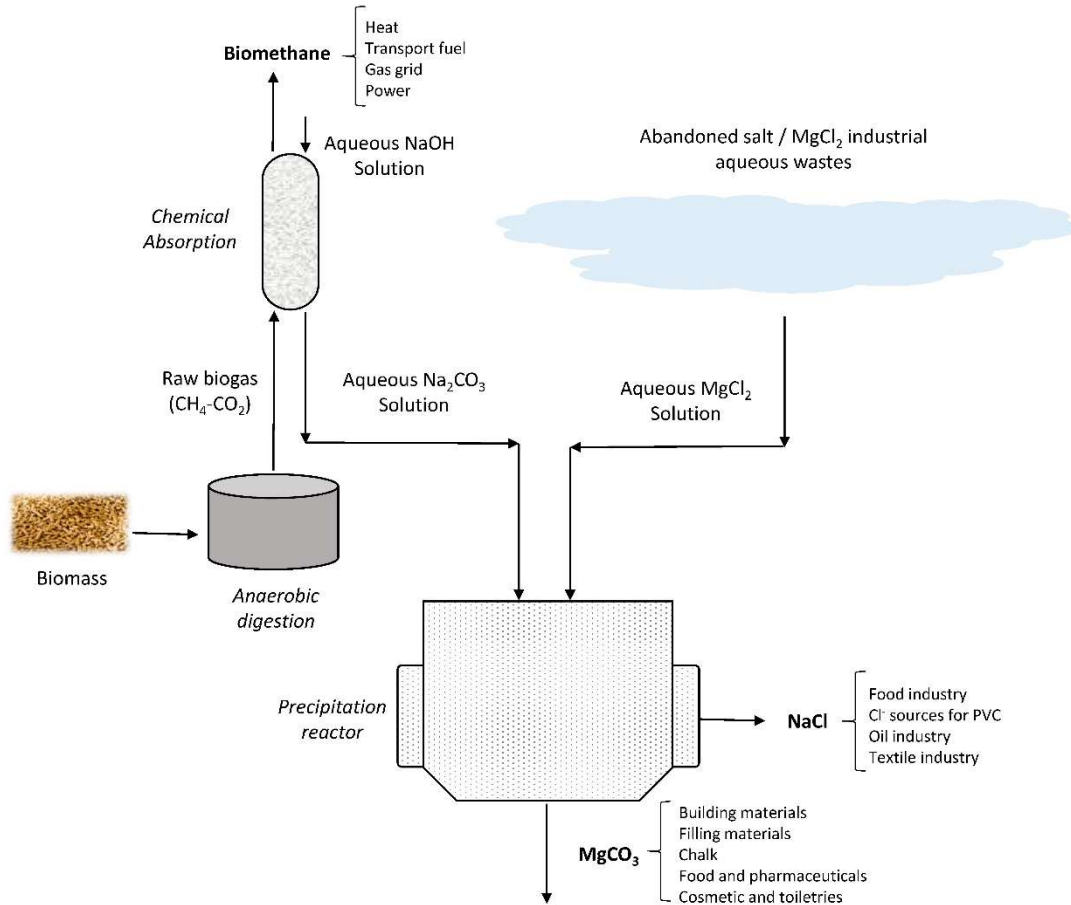
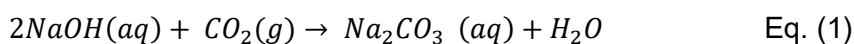
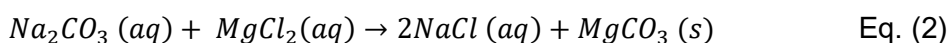


Figure 1. Novel process for bio-methane and $MgCO_3$ production through CO_2 and $MgCl_2$ waste valorization.

In this process first the biogas produced in the anaerobic digestion is directly introduced in a packed tower where the chemical absorption of CO_2 with $NaOH$ takes place (equation 1). This reaction has been proved by several authors to guarantee high capture efficiencies of more than 90% [26,31,32]. Sodium carbonate (Na_2CO_3) is obtained as product of this reaction, which can be employed as an aqueous solution to mineralize CO_2 in a carbonate structure. In this way, there is no need of a previous dissolution stage, avoiding the utilization of organic alcohol compounds which makes the process more expensive.



In this work our proposal is to mineralize CO₂ via precipitation reaction with an aqueous MgCl₂ solution which may come from wastes, according to equation (2). This process allow us to transform wastes in high value MgCO₃ with multiple applications in food and pharmaceutical industries or as construction material [14]. Additionally, NaCl is obtained as a valuable by-product with a variety of commercial applications [33].



Since the chemical absorption stage has been previously addressed showing outstanding results [34,35], this work focus on the precipitation reaction between Na₂CO₃ and MgCl₂. The effect of temperature, molar ratio and reaction time on MgCO₃ precipitation are investigated, as well as the main physicochemical characteristics of the solid obtained by means of Raman, XRD and SEM. This paves the way for further by-product valorization in order to achieve more economical and sustainable biogas upgrading plants. Furthermore, this study could be of interest for scaling-up bio-methane production plants in the near future as key facilities to facilitate the transition towards low-carbon societies relaying on renewables sources of energy. In addition, this study is called to be an inspiring contribution for renewable energy sector.

2. Materials and Methods.

2.1 Materials

MgCl₂ and Na₂CO₃ employed in this work were provided by PanReac-AppliChem (pure-grade or pharma-grade, 99% purity).

2.2 Experimental Procedure and Physicochemical characterization

The precipitation experiments were carried out in a 600 mL beaker whose temperature was controlled using an isothermal water bath. 100 mL of both synthetics Na₂CO₃ and MgCl₂ solutions were prepared with the chemicals mentioned before. Na₂CO₃ concentration was set at 20 mg/L as a typical value reached after the absorption stage,

according with previous references in this area [31,36]. Notwithstanding, the value of $MgCl_2$ concentration was varied as one of the main parameters studied as explained below. Once the reaction was finished under the conditions imposed, the product solution was duly filtered and separated for analysis. During the experiment the solution was electromagnetically stirred at a constant speed of 1,000 rpm. A Trison instrument was used and data was logged for temperature and, in order to agree with the carbonates pH range (8-11), it was measured by the same instrument. The precipitation efficiency was defined as the amount of $MgCO_3$ obtained divided by the maximum $MgCO_3$ that could be obtained stoichiometrically. This parameter was calculated for every test in order to compare the influence of the different studied variables. The parameters values were chosen according to similar studies as well as to compare the results with previous studies of our team [35,37,38]. Thereby, Temperature (T) reaction was set at $50^\circ C$, molar ratio (R) at 1.2 mol Mg/Na_2CO_3 , and Reaction Time (RT) at 30 minutes. These values were considered as standards and they were varied one by one to study their individual effect on the precipitation reaction. The matrix of experiments done in this paper is available in Table 1.

Table 1. Matrix of experiments carried out.

Test	Standard	RT1	RT2	RT3	RT4	T1	T2	T3	T4	R1	R2	R3	R4
Time (min)	30	120	60	45	15	30	30	30	30	30	30	30	30
Temperature ($^\circ C$)	50	50	50	50	50	70	60	40	30	50	50	50	50
R	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.5	1.3	1.1	1

The solid obtained by filtration was dried at $105^\circ C$ and physicochemically characterized by means of Raman spectroscopy, XRD and SEM. As there are many types of $MgCO_3$ structures, first Raman was employed to ensure a carbonate phase reached and afterwards, XRD and SEM were useful to distinguish among the different structures of $MgCO_3$ as will be later explained in details. Raman measurements of the powders samples were recorded using a Thermo DXR2 spectrometer equipped with a Leica DMLM microscope. The wavelength of applied excitation line was 532nm ion laser and

50x objective of 8-mm optical was used to focus the depolarized laser beam on a spot of about 3 μm in diameter. A JEOL JSM6400 operated at 20 kV equipped with energy dispersive X-ray spectroscopy (EDX) and a wavelength dispersive X-ray spectroscopy (WDS) systems was used for the microstructural/chemical characterization (SEM with EDS and WDS). X-ray diffraction (XRD) analysis was completed by an X'Pert Pro PAN analytical instrument. The 2θ angle was increased by 0.05° , with a 450 time per step over a range of $10\text{-}90^\circ$. Diffraction patterns were then recorded at 40 mA and 45 kV, using Cu K α radiation ($\lambda=0.154$ nm).

3. Results

3.1 Precipitation results

As discussed above, one of the main targets of this study is to characterize the influence of the reaction parameters in the precipitation efficiency of the carbonate precipitation reaction. In order to establish the trends of the precipitation efficiencies upon variation of the parameters considered as the most influencing, the experiments were done in three level for each of them as indicated in Table 1. Figures 2, 3, 4 and 5 depict the results obtained in our experiments by the variation of temperature, molar ratio and reaction time.

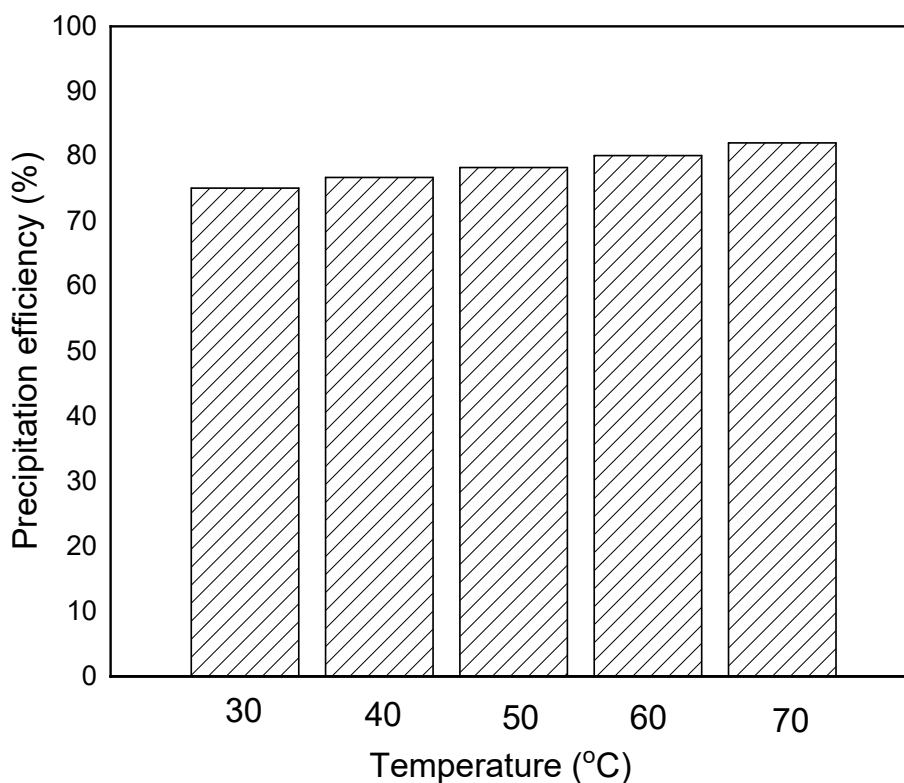


Figure 2. Influence of a temperature on precipitation efficiency. Tests carried out at $t=30\text{min}$ and $R=1.2$.

Figure 2 reveals the trends of the precipitation efficiency when varying the reaction temperature. In agreement with previous works, this trend seems to be positive and the precipitation efficiencies are quite similar than those observed employing organic alcohols as CO₂ carriers [39]. This is a very important fact as the market price of our reactants is quite low compared to that of the organic alcohols typically employed in this process. The precipitation efficiency for 30°C was 75.13% which means that good results can be obtained at room conditions, what is an important advantage respect to current ongoing industrial processes for CO₂ mineralization. Increasing the temperature from 30°C to 50°C is not worthy inasmuch only a 3% of improvement is obtained. However, there is a remarkable increase from 75.13% to 82.07% when rising up the temperature from 30°C to 70°C. Thus, an increase of more than double the initial temperature value

would be necessary for a substantial improvement of the overall precipitation efficiency. Even under the maximum temperature tested in our experiments this process is much more feasible in terms of energy consumption compared to traditional methods. Nevertheless, this parameter needs to be optimized since 50°C can be easily obtained by means of renewable energies whereas 70°C would be a more challenging situation to be achieved exclusively using sustainable resources.

Comparing with previous similar studies in terms of temperature, our innovative process has proved to be more feasible due to the higher efficiencies obtained. For instance at 30°C our precipitation efficiency was 75.13% while less than 70% was obtained in a similar study with organic alcohols as solvent [12]. Morene et al also performed comparable experiments at ambient temperature using steel slags as precipitator agent [38]. They obtained around 60% of equivalent efficiency which again reflects a poorer precipitation capacity compared to our results. Air pollution control residues were employed in [40], obtaining 65.1% efficiency for 55°C whereas in our work 78.28% precipitation efficiency was obtained at 50°C with MgCl₂ residues. In summary from the temperature perspective (and ultimately energy savings in the process) there are obvious advantages of our approach over previously reported strategies.

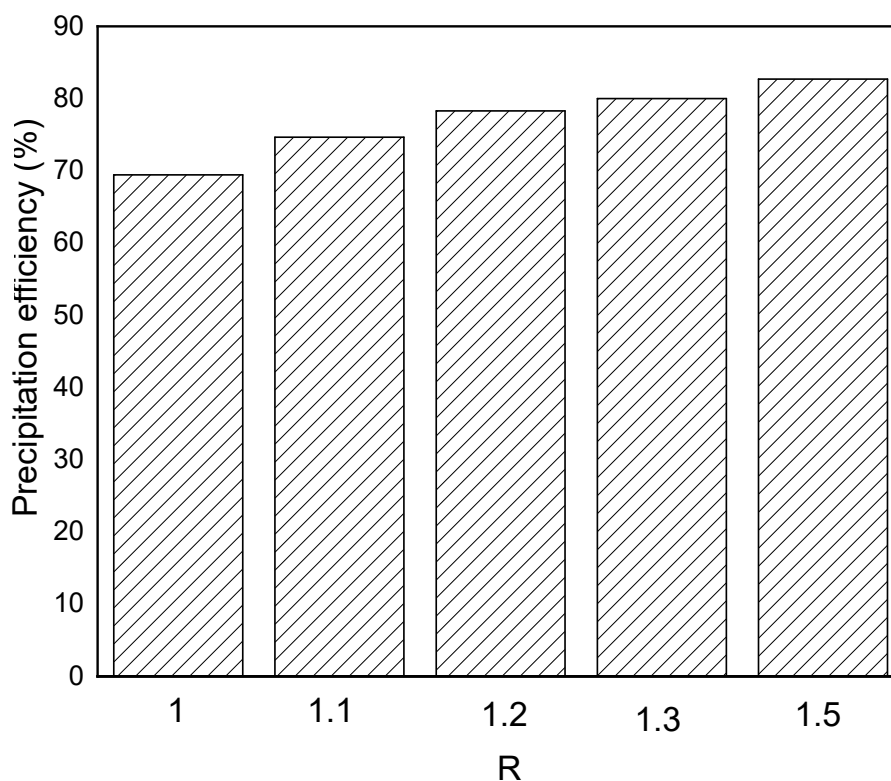


Figure 3. Effect caused on precipitation efficiency by R variation. Tests carried out at $t=30$ min and $T=50^{\circ}\text{C}$.

Figure 3 shows again a positive trend of precipitation efficiency regarding the variation of molar ratio. This could be due to a major proportion of chloride ions enhancing their reaction with sodium and thereupon providing more free carbonates which triggered the precipitation of MgCO_3 . Interestingly, the molar ratio indeed has a stronger effect than reaction temperature in the precipitation efficiency. This wide difference can be observed when increasing the R value from 1 to 1.2, where the precipitation efficiency was enhanced from 69.44% to 78.28%. When an R value of 1.5 was tested, 82.70% precipitation efficiency was obtained. This last increase did not show to be as effective as the first one since less than 4% of enhancement was achieved. Moreover, upon this value a higher chloride concentration in the NaCl solution would be obtained. This could

unbalance the pH of the solution making necessary a pre-treatment before employing it in a potential industrial process thus increasing the overall running cost.

Similar studies varying parameters equivalents to R also showed positive trends upon incrementing R value [12,20,37]. Organic alcohol N235 was used as solvent and showed around 45% efficiency with molar ratio equal to 1. At 1.5 molar ratio little more than 60% was obtained [12]. In our work almost 70% was obtained for this R=1 and more than 80% with R=1.5 hence Na_2CO_3 has been demonstrated to be better solvent for carbon mineralization. Similar conversions were obtained in [20] but with CaCl_2 instead of MgCl_2 . Employing air pollution control residues at R=1.2 resulted in 65.1% efficiency whereas as previously commented 78.28% was obtained in our study.

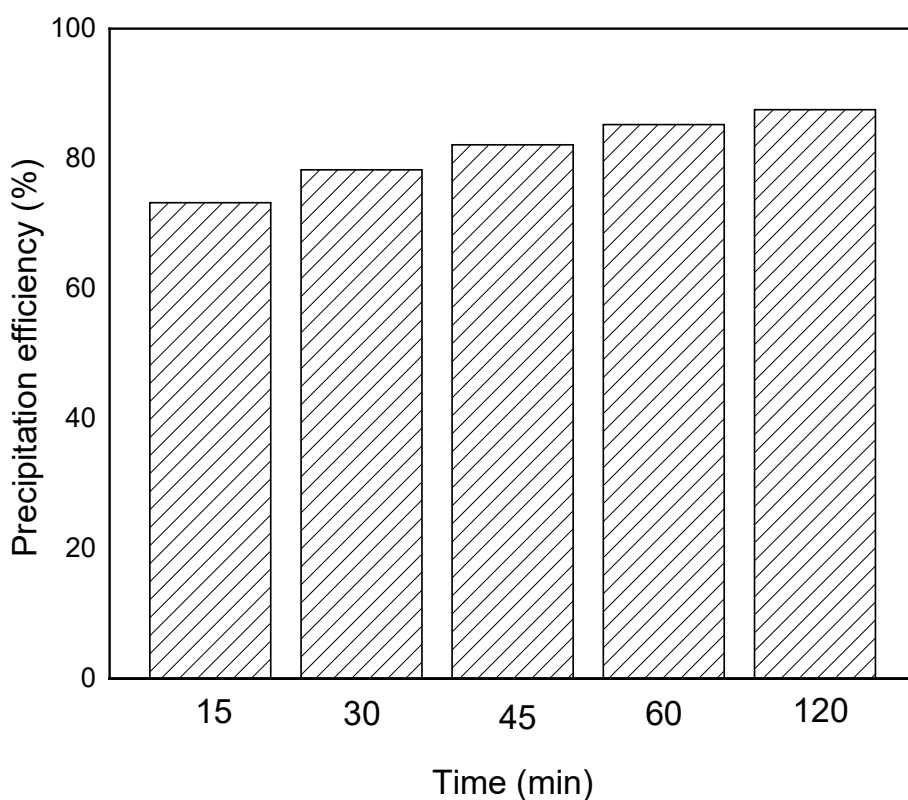
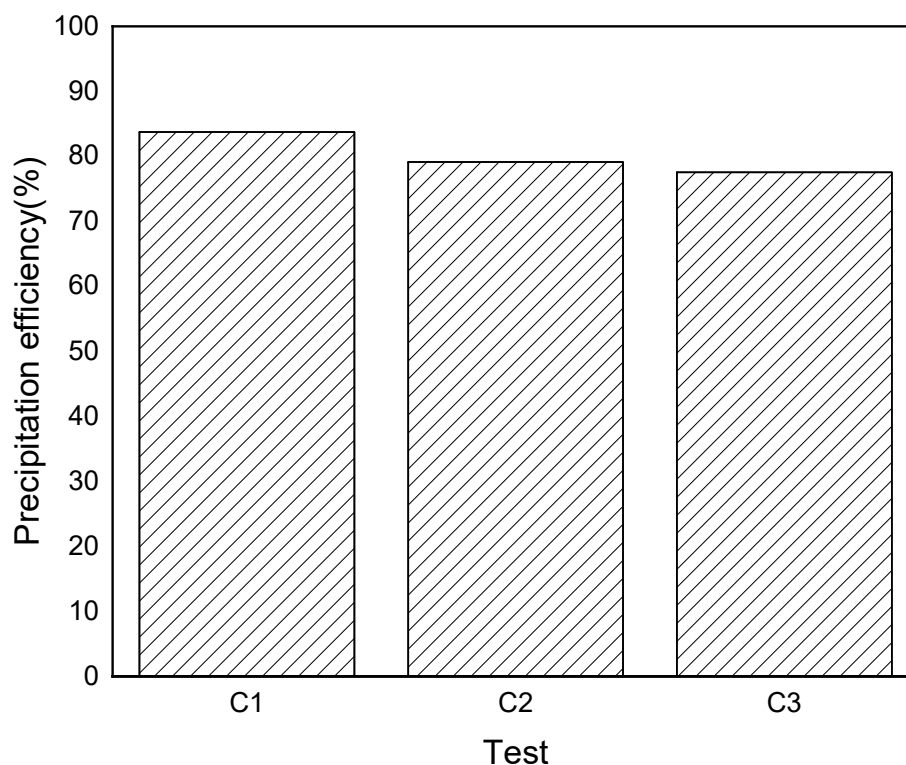


Figure 4. Evolution of precipitation efficiency in time. Test carried out at R=1.2 and T=50°C.

Again the influence of the reaction time is quite remarkable on precipitation efficiency comparing to the effect of temperature variation. As shown in Figure 4 a noticeable improvement was obtained from 15 minutes (73.23%) to 60 min (85.23%). Even if this means a reactor size four times bigger, a possible enhancement of 12% would be a reason of optimization regarding a potential industrial application. Furthermore, in a potential industrial process other configurations could be tested, such as continuous stirred tank reactor (CSTR), to obtain a higher reaction time which could minimize the investment costs of the reactor. Additionally, the results obtained at 30 min (78.28%) could be an optimum trade-off between precipitation efficiency and reactor size. In comparison with previous studies there are remarkable differences regarding reaction time. Probably these discrepancies are originated by the different precipitator agent employed in each study. Baciocchi and co-workers reported ca. 90% efficiency of the carbonation reaction in terms of KOH regeneration for 1 hour-experiment [37]. On the other hand, 50% of conversion was obtained with steel slag as precipitator at 30 minutes [38]. Thus, our innovative system has proved to be in line with Baciocchi's work and almost 30% better in terms of precipitation capacity than the work by Morone et al.

So far to avoid crossed-interactions between two parameters which could hide the effect of each individual parameter, we decided to change one parameter at time in this work. As shown in Figures 2-4, we obtained a positive tendency for each analyzed parameter. From these results in principle no interactions in terms of worsen precipitation efficiencies among the key parameters is expected when two parameters are simultaneously manipulated. Nevertheless we have performed an extra experiment varying simultaneously 2 parameters for sake of deeper understanding of the crossed-parameter's influence on the novel process studied, as shown in Figure 5. As can be seen, the positive variation of molar ratio and time result in a higher impact on the overall precipitation efficiency than increasing temperature in the range study, which further confirms our previous results.



*Figure 5. Crossed-parameter's influence. Tests carried out at the following conditions:
 C1: $T=30^{\circ}\text{C}$, $R=1.5$ and $t=45$ min; C2: $T=60^{\circ}\text{C}$, $R=1$ and $t=60$ min; C3: $T=70^{\circ}\text{C}$, $R=1$
 and $t=45$ min.*

3.2 Physicochemical Characterization Results

The purity and the quality of the resulting precipitate determines its market opportunities and could be a plus for the proposed strategy. The white powder obtained as precipitated samples was characterized by means of Raman, XRD and SEM in order to determine its physicochemical properties. Firstly, Raman was adopted to ascertain whether a carbonate phase was presented in our samples. Figure 5 represents selected Raman spectra for our experiments indicating undoubtedly the formation of the carbonate phase. Indeed, the presence of a strong band at 1100 cm^{-1} characteristic of carbonates confirms this statement [41]. Thus, the presence of this band means that the predominant

compound presents in our sample is MgCO_3 . Furthermore, another characteristics weaker bands are presented at around 480 and 740 cm^{-1} [42,43]. Hence these results confirmed that the mineralization reactions entirely met our hypothesis. Nevertheless, due to the multiple existing carbonate phases as well as particle shapes and morphologies, the use of standalone Raman does not allow to confirm the crystal structure and purity of the resulting solid.

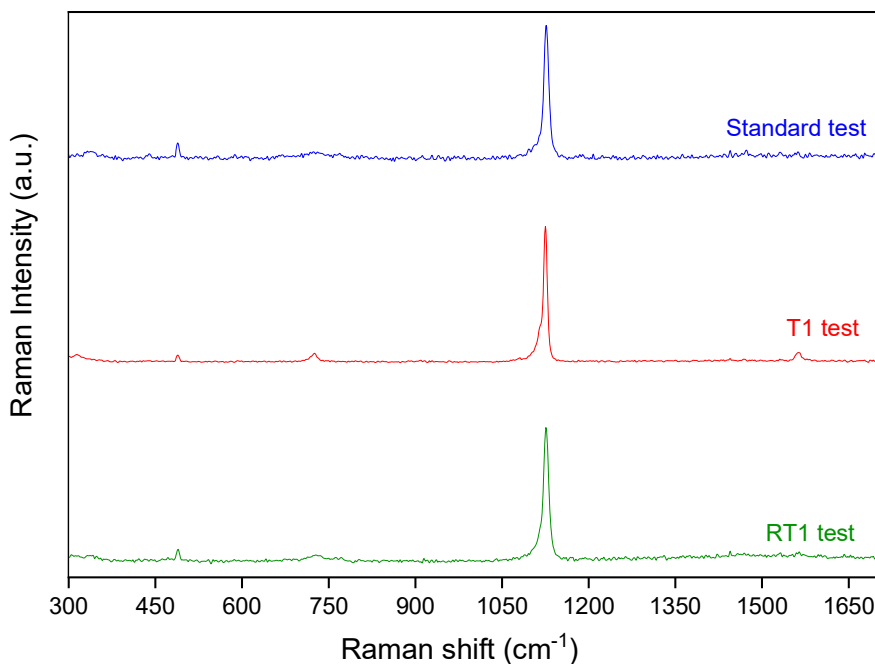


Figure 6. Raman spectra of the samples obtained in different tests.

For this purpose XRD and SEM were conducted in our study. Once confirmed that the solid samples obtained are MgCO_3 , it is important to investigate the crystal polymorphs in which the precipitation has resulted to assess their commercial value. MgCO_3 can be obtained in multiple crystal polymorphs form such as for example Magnesite, Barringtonite, Nesquehonite, Dypingite, and Hydromagnesite. Hydromagnesite, typically known as Hydrated Magnesium Carbonate (HMC), can be split in two main categories

according to the number of water molecules attached in their empirical formula - Light Hydrated Magnesium Carbonate (LHMC) with 4H₂O molecules and Heavy Hydrated Magnesium Carbonated (HHMC) which contains 5H₂O molecules [44]. Figure 6 shows the XRD patterns of the MgCO₃ samples obtained during the standard test. According to previous studies, this XRD pattern agrees fairly well with that of the HHMC samples. As can be seen, there are some peaks characteristics of Dypingite (e.g. 15, 31 or 33 2θdegrees) as well as diffractions attributed to Nesqueonite (e.g. 22 or 52 2θdegrees) and some of them which appear in both diffractograms Dypingite-Nesqueonite (D-N in Figure 6) of these species [44–47]. As previously documented, these products present a variety of commercial applications and can be used as inorganic filling agents [48], filler pigment in paper [49], or to produce cement and basic refractory bricks [50] reinforcing the commercial viability of the biogas upgrading strategy coupled with added value by-product generation proposed in this work.

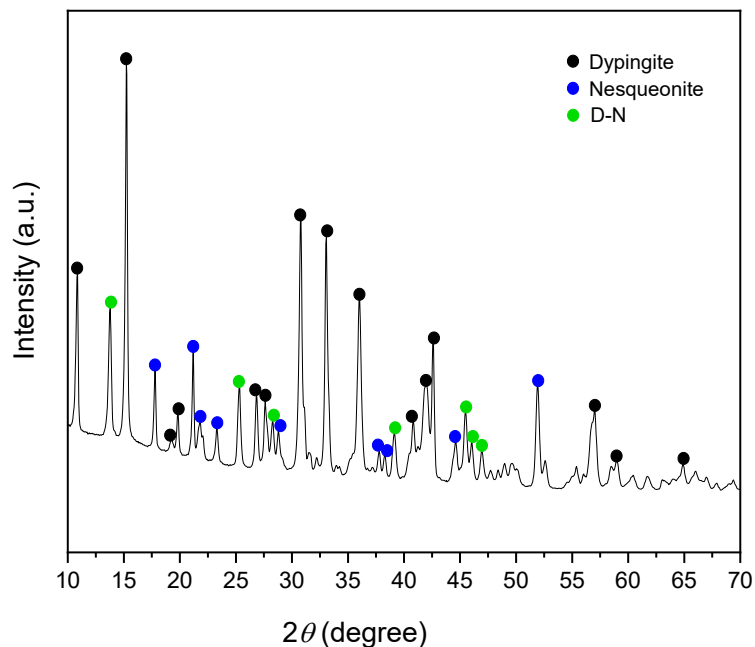
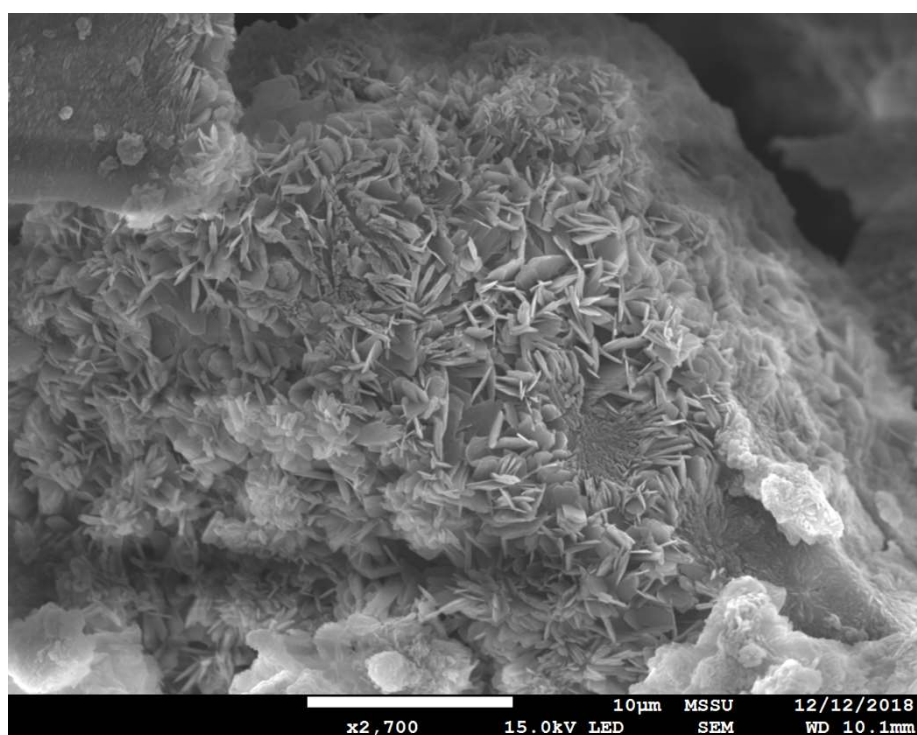


Figure 7. XRD diffractogram of MgCO₃ obtained (time=30min, T=50°C, R=1.2).

In order to examine the morphology of the solid samples to complement the results provided by XRD, SEM images were taken of the selected samples. Figure 7 shows HHMC typical morphology in which Dypingite shape alike aggregated plate crystals are recognized as in previous studied by other authors [12,44]. Nevertheless, the presence of some Nesqueonite portion can be seen in the needless shapes in some parts of the sample, confirming our previous XRD results. Thus, the products of our innovative process present different morphologies and sizes, which could make them useful in various industrial applications.



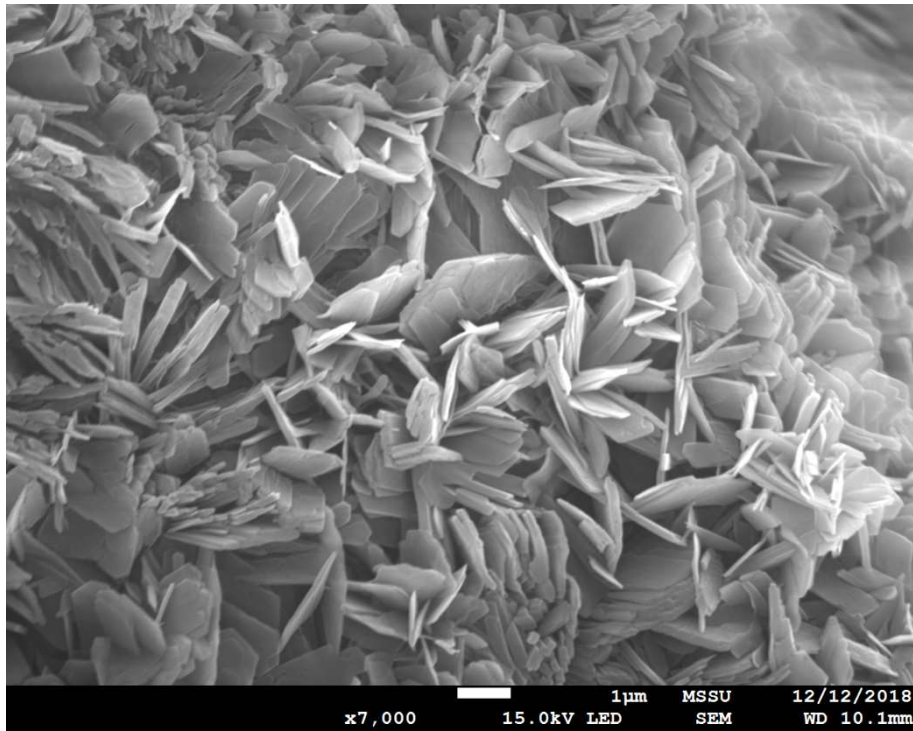


Figure 8. SEM images of the PCC obtained (time=30min, $T=50^{\circ}\text{C}$, $R=1.2$).

4. Conclusions and future remarks

This work showcases the technical feasibility of an innovative process for CO_2 mineralization in a biogas upgrading unit through the re-utilization of MgCl_2 residues opening promising opportunities in the field of renewable energy production. The influence of main precipitation parameters has been studied. The temperature variation showed that a remarkable precipitation efficiency (75%) can be obtained at room temperature which means a less energy intensive process compared to previous reports. As for the R value the optimum is around 1.2 since both the precipitation efficiency and the concentration of final NaCl solution will be acceptable. Regarding the reaction time further studies would be required for optimizing between 30 min and 60 min to confirm the final reactor capacity in a hypothetical industrial process.

The overall performance of the regeneration experiments reaches an acceptable range in term of precipitation efficiencies (69-85%). Among the studied parameters in the selected ranges for our tests, the molar ratio between $MgCl_2$ and Na_2CO_3 is the most influencing parameter, while interestingly temperature has a minor impact on the precipitation efficiencies.

The physicochemical characterization results obtained confirmed the high purity of the obtained products which is hydrated carbonate HHMC type with a mixture of Dypingite and Nesqueonite being Dypingite the dominant phase. This carbonate product could be potentially implemented in multiple commercial applications reinforcing the market opportunities of our strategy not only from the bio-methane angle but also for the by-product salability.

Overall, our work confirms the viability of the proposed route to synergize CO_2 mineralization and bio-methane production opening new avenues for research in the production of economically viable low-carbon energy vectors. Further research in these kind of novel ideas are completely necessary to improve the efficiency of renewable energy alternatives. This seminal study open scope for future works dealing with the scaling-up of the lab-unit work employed in this paper to a bench-scale system where the economy of the process could be examined more accurately. Furthermore, possible technical problems which could appears at higher levels could be studied in a bench-scale plant to further validate the concept of an advanced unit to synergize bio-gas upgrading and carbon capture – a new strategy for bio-energy generation and greenhouse gases mitigation.

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