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Application of Rice Stubble Synthesized Zeolite for Greenhouse Gas Reduction

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Abstract

This investigation aims to study the value of synthesized zeolite in reducing greenhouse gasses (GHGs) emitted by rice stubble. The experiment was divided into 2 parts. Part I comprised a study of the efficiency of GHGs reduction by synthesized zeolite and part II involved application of synthesized zeolite to reduce the cumulative GHGs emissions over 110 days from paddy rice cultivation in Khlong 4, Pathum Thani province. The experiments comprised 2 treatments: untreated control (I), and rice stubble with addition of synthesized zeolite (II). The study measured changes in the emissions of CH_4 and CO_2. , conducted 3 days per week for 1.30 hours during the cultivation period.

The results showed that rice stubble synthesized zeolite could reduce GHGs CH_4 and CO_2 under irrigated conditions. In the experiment, synthesized zeolite had an efficiency of 8.91% and 24.5% in reducing CH_4 and CO_2, respectively. Footprint analysis showed that both gases were continuously emitted throughout cultivation. In Cumulative emissions from the control treatment were 42.57 g CH_4/m^2 crop and 86.40 g CO_2/m^2 crop. Zeolite addition reduced emission levels to 30.71 g CH_4/m^2.crop and 57.77 g CO_2/m^2.crop. The reduction efficiencies CH_4 and CO_2 were 27.87% and 33.14%, respectively. It can be concluded that the rice stubble synthesized zeolite was capable of reducing GHGs significantly and that the efficiency was rate-dependent. It was clear that the GHGs emission reduction rate of synthesized zeolite was 0.148 g CH_4/m^2.g zeolite and 0.358 g CO_2/m^2 g zeolite.

Keywords: Greenhouse gases; Rice cultivation; Reduction emission; Rice stubble; Synthesized zeolite

Introduction

Rice cultivation under irrigated conditions is a major emitter of greenhouse gases (GHG), with use of nitrogenous fertilizers as a major factor. The most important greenhouse gases emitted are methane (CH_4), nitrous oxide (N_2O), and carbon dioxide (CO_2), Though N_2O emissions are relatively small compared to CH_4 or CO_2, it is considered a serious GHG with an emission factor of 310x compared with CO_2, whilst CH_4 has an emission factor of 21x [1]. Normally, CH_4 and CO_2 emission occur throughout the period of rice cultivation, whilst N_2O emission tends to peak when using excess nitrogen fertilizer [2].

The rice cultivation cycle can be divided into 3 phrases: Phase I tiller growth (60 days); Phase II reproductive growth (25-30 days); and Phase III grain filling (25-30 days) as shown in Figure 1 [3].

Generally, CH_4 emissions occur in soils containing decomposing organic matter such as rice straw and organic fertilizer [5]; methanogenesis is mediated by bacteria under anaerobic condition [6]. Whilst CH_4 is emitted throughout the duration of cultivation, the greatest amounts are emitted during the reproductive phases or when the field is flooded [7]. Gas formed in the soil diffuses into rice roots, translocated into the leaves and released into the atmosphere via the stomata. This mode of release represents 90-95% of total emissions, whilst gas bubbing up from water surface accounts for as little as 2-8% of the total [8]. CH_4 emissions peaked during the reproductive phase at 48 g CH_4/m^2 crop, or 8.3 kg CO_{2e}/kg rice [9].

Zeolite is commonly used as a soil ameliorant in rice, cereals, vegetables and fruit crops [10]. It highly porous structure and high cation exchange capacity allows it to absorb large amounts of water, cations and small nutrient molecules necessary for plant growth [11]. In many countries, zeolite is used as a slow release fertilizer, especially for nitrogen, ammonium and potassium fertilizers [12]. The high buffering capacity of zeolite can also help to stabilize soil pH [10].

In addition, zeolite is useful for organic and inorganic adsorption especially gas separation or gas purification due to its ability to adsorb or separate different gases by their differing molecular size. The zeolite structure can be adjusted to specifically adsorb different gases [13]; zeolites such as NaA, Nax, and NaY can reduce methane, ethane and propane. CH_4 adsorption is the highest efficiency and 4A zeolite is the most used for adsorption [14]. Natural zeolite, synthesized zeolite or reed straw can also adsorb GHGs emissions from stored duck manure [15].

In agriculture, zeolite is used to reduce GHGs, especially nitrogen-related compounds [16]. Research on the GHG reduction by dolomite and/or zeolite in peat land for rice production in Jakenan, Indonesia found that dolomite and zeolite could reduce emissions by approximately 27.3% and 21.4%, respectively [17]. In addition, the use of zeolite 4A to reduce GHGs emission from rice cultivation was studied in Pathum Thani province, Thailand.

Rangsit, in Pathum Thani Province, was selected for the study due to its suitability for rice cultivation. In this area, three rice crops per year rice can be grown, leading to high levels of GHGs emission. The rice variety, Patumthani rice (RD-41), is the most cultivated variety in Pathum Thani Province.

This study aimed to reduce GHGs emission using rice stubble synthesized zeolite in the rice field. The study measured the reduction efficiency of synthesized zeolite in reducing CH_4 and CO_2 in normal and irrigated systems, using the rice variety RD-41 in rice fields located at Khlong 4, Pathum Thani Province, Thailand.

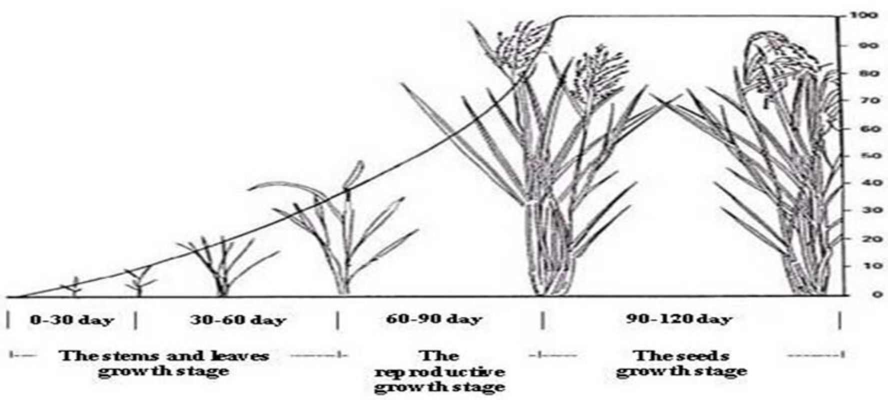

Figure 1 The rice cultivation cycle [3]

Materials and methods

1) Synthesis of zeolite from rice stubble

The experiment was conducted with zeolite synthesized from rice stubble via a hydrothermal process via 3M NaOH activated time in 2, 4 and 6 hrs. The rice stubble was first burned to rice stubble ash (RSA). Pretreatment of the RSA consisted of mechanical, thermal and acid treatment at 60^oC for 1.5 hrs. The mass ratio between the powdered RSA and acid solution (HCl) was 1:1. The solid phase was then separated from the solution by vacuum filtration, rinsed with deionized water until the pH of the filtrate reached 6-7. After thermal treatment was at 700^oC for 1 hr, the material was cooled in a desiccator over dry silica gel. The RSA was then mixed with NaOH in a weight ratio of 1:1.2, then heated at 550^oC for 1 hr. Then, the fused mixture was cooled and 3M NaOH was added for each run. Finally, the suspension was submitted to a further hydrothermal treatment in a stainless steel reactor at 105 ±5^oC for different periods of time (1 to 6 hrs). The solid products were filtered off, washed and dried at 105^oC for 24 hrs. The rice stubble synthesized zeolite was then characterized to determine the calcium exchange capacity and identified by X-ray diffracttion (XRD).

2) Adsorption testing

10 g of zeolite as placed in a 30 ml plastic bottle with 2 holes for gas inlet and the outlet. 10 ml of the standard gas of 50% CH_4 and 30% CO_2 (balanced with N_2) was sucked into a 10 ml syringe and compressed into the bottle. The outlet gas was vented to another syringe and collected in a gas vacuum tubes for analysis by gas chromatography (GC) using a Shimadzu 2014 model. In this study, Helium (He) was used as the carrier gas. Injector termperature, the thermal conductivity detector (TCD) temperatures, and Unibeads C (column temperature) were set to 150^oC, 230^oC, and 130^o C, respectively.

3) Chamber Collector

The chamber collector comprised a 50x50 cm acrylic box pressed into the soil to a depth of 10 cm, leaving 50 cm. protruding above the soil surface as shown in Figure 2 (a) and (b). The collector gas tube is on the top as shown in Figure 2 (c). The chamber contained two fans for air circulation.

4) Field experiment: GHGs emission estimation

The experiment was conducted in 2 treatments: (I) untreated control, and (II) addition of 80 g of rice stubble synthesized zeolite. The rice field was located at Khlong 4, Pathum Thani Province, Thailand (Latitude: 14^{o}8'38.44" N, Longitude: 100^{o}41'9.37" E). The soil type is classified as Rangsit soil, which is very fine, mixed, semiactive, acid, isohyperthermic Sulfuric Endoaquepts. The properties of Rangsit soil in this research are shown in Table 1. The rice variety used was Pathum Thani rice (RD41) with a seed rate of 25 kg/rai. GHG emissions were sampled in triplicate from 11.00-12.00 at 30-minute intervals until 13:30 h throughout the 110-day cultivation period [19, 20, 21], from April-July 2014. The gas samples were collected in gas vacuum tubes and analyzed by gas chromatography. The chromatogram of CH_4 and CO_2 is shown at 3.370 mins and 5.843 mins respectively.

Methodology

The experiment was divided into 2 parts: part I comprised a study of the efficiency of GHGs reduction by synthesized zeolite and part II involved application of synthesized zeolite to reduce the cumulative GHGs emissions from paddy rice cultivation The GHGs emissions analysis was conducted on every 3 days (Monday, Wednesday and Friday) per week for 1:30 hrs collecting gas during the rice plantation period to collect raw data for analysis GHGs emission of rice cultivation [19-21]. The CH_4 flux and CO_2 flux were observed to evaluate each gas emission per crop. The reduction emission of each gas was demonstrated in the form of reduction efficiency and reduction emission rate.

1) Synthesis zeolite from rice stubble

X-Ray Diffraction (XRD) patterns of rice stubble zeolite synthesized by the hydrothermal pro cess (Figure 3) indicate similarity with that of 4A zeolite. The result found that the optimum conditions obtained for synthesis of zeolite was 2 hours activiation time. The cation exchange capacity (CEC) of the synthesized zeolite ranged from 644-700 mg $CaCO_3$/g zeolite, which is close to that of zeolite 4A (738-797 mg $CaCO_3$/g zeolite).

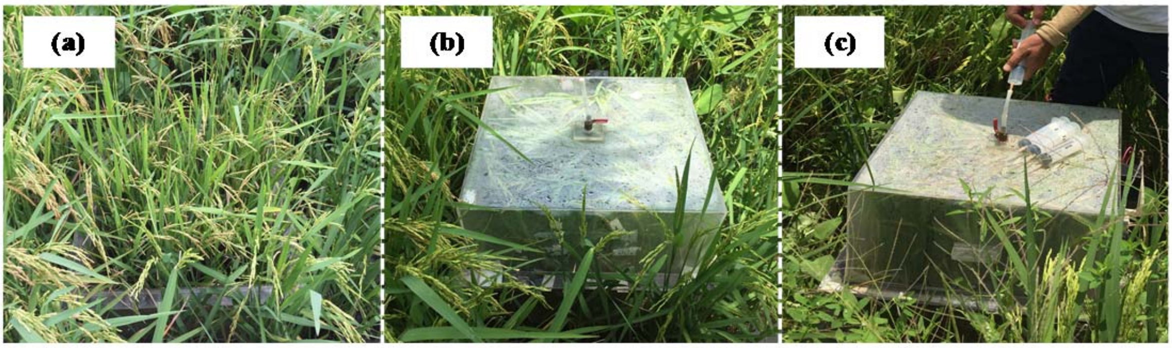

Figure 2 (a) rice plantation in rice field; (b) collecting gas in the chamber; and (c) gas sampling

Table 1 Properties of Rangsit soil

Parameter	Unit	Value
pH		6.72-6.93
EC	dS/m	0.20-0.32
OM	%	1.84-2.24
Available P	mg/kg	4.17-12.11
Exchangeable K	mg/kg	213.17-386.70
Exchangeable Ca	mg/kg	3,126.92-3,678.10
Exchangeable Mg	mg/kg	278.91-317.44
CEC	Cmole/kg	18.82-22.72

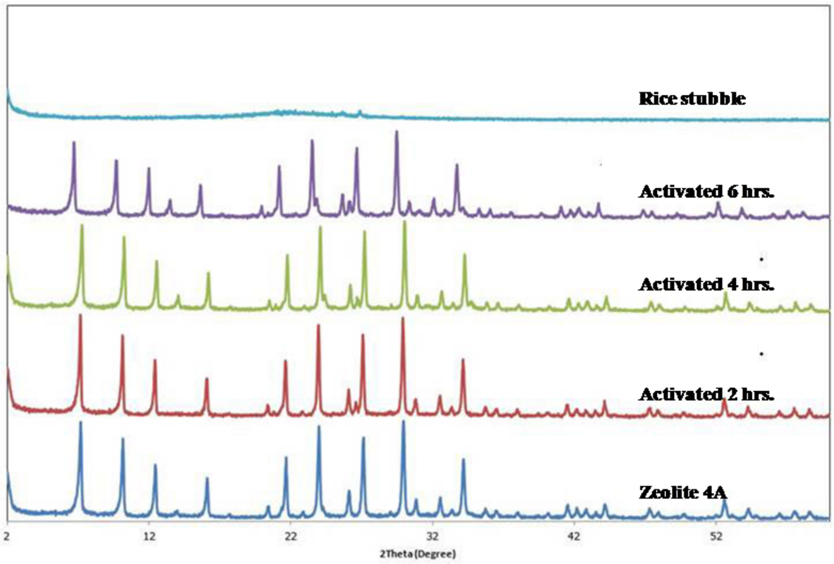

Figure 3 The XRD pattern of rice stubble synthesized zeolite and zeolite 4A

2) CH_4 and CO_2 adsorption testing

The results are shown in Table 2 and Figure 4. From the experiments, CH_4 and CO_2 gas are adsorbed by the rice stubble synthesized zeolite; however, the adsorption mechanisms for the two gases differ. For CH_4, zeolite can be readily adsorbed in the pore matrix- a physical mechanism. In contrast, CO_2 gas is not only physically adsorbed in the pores, but also reacts with cations in the zeolite (a physical and chemical mechanism) [22, 23]. Therefore reduction efficiency was higher for CO_2 than for CH_4.

It appears that synthesized zeolite impregnated with alkaline earth cations (group II) such as Ca for chemical adsorption between Ca and CO_2 so the CO_2 reduction efficiency increased more than CH_4. For CH_4 gas, the efficiency depended on the porosity of the zeolite. The amounts of CH_4 and CO_2 adsorbed increased with rate of zeolite applied. Adsorption of both of CH_4 and CO_2 was temporary; zeolite will begin to release both gases to the atmosphere when the pressure of each gas is high [22, 23]. In normal or dry condition, synthesized zeolite can reduce CH_4 and CO_2 by 12.46% and 29.68%, respectively. On the other hand, CH_4 and CO_2 reduction efficiency in irrigated or flooded conditions were 8.94% and 24.25%, respectively. Reduction efficiency was reduced under flooded conditions (especially for CH_4) due to competition between water and CH_4 and CO_2 for adsorption sites within the pore matrix [22, 23].

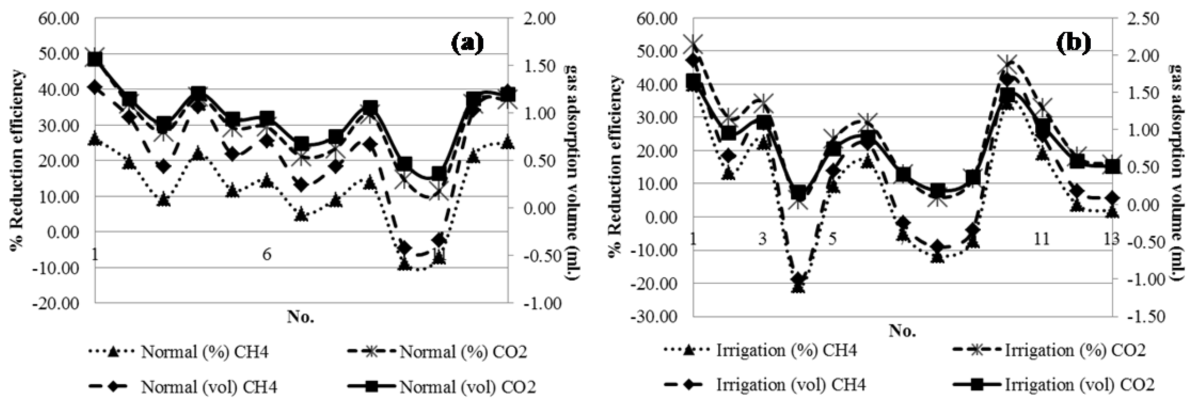

Figure 4 The reduction efficiency and gas adsorption volume in (a) normal and (b) irrigatated conditions using synthesized zeolite

Table 2 Reduction efficiency of rice stubble synthesized zeolite under normal and irrigated conditions

	Volume gas adsorption (ml)				Reduction efficiency (%)			
	Normal		Irrigated		Normal		Irrigated	
	CH_4	CO_2	CH_4	CO_2	CH_4	CO_2	CH_4	CO_2
1	1.27	1.57	1.93	1.66	26.18	48.94	39.90	51.85
2	0.95	1.15	0.65	0.96	19.70	35.98	13.32	29.82
3	0.44	0.89	1.09	1.10	9.13	27.93	22.43	34.19
4	1.07	1.21	-1.01	0.17	22.00	37.77	-20.75	5.17
5	0.57	0.94	0.45	0.75	11.74	29.25	9.20	23.36
6	0.70	0.94	0.81	0.90	14.48	29.45	16.76	28.23
7	0.25	0.68	-0.25	0.41	5.11	21.16	-5.15	12.70
8	0.44	0.75	-0.57	0.19	9.00	23.39	-11.71	5.87
9	0.67	1.05	-0.34	0.36	13.79	32.87	-7.07	11.38
10	-0.42	0.47	1.67	1.47	-8.74	14.53	34.43	45.96
11	-0.34	0.36	0.92	1.05	-7.07	11.38	19.06	32.90
12	1.03	1.15	0.17	0.58	21.25	35.98	3.60	18.01
13	1.23	1.19	0.09	0.51	25.35	37.20	1.77	15.81
Minimum	-0.42	0.36	-1.01	0.17	-8.74	11.38	-20.75	5.17
Maximum	1.27	1.57	1.93	1.66	26.18	48.94	39.90	51.85
Total gas adsorption volume (ml)					7.84	12.36	5.61	10.10
Total gas volume (ml)					62.97	41.66	62.97	41.66
Total reduction efficiency (%)					12.46	29.68	8.91	24.25

3) Application of rice stubble synthesized zeolite in rice cultivation

The field results are shown in Table 3 and Figure 5. Footprint analysis showed that both CH_4 and CO_2 gas were continuously emitted during sowing and transplanting. This is explained by decomposition of surface soil organic matter in aerobic conditions, emitting CO_2 from the surface into the atmosphere [9]. However, at depth, soil organic matter is decomposed under anaerobic conditions, emitting CH_4 which diffuses into rice roots and is translocated through the leaf sheaths and leaves, and released into the atmosphere via stomata. CH_4 gas is also released into the atmosphere directly from the soil, bubbling up through the water surface [24]. Normally, CH_4 emissions are highest under flood irrigation because of the prevailing anaerobic soil conditions [5].

From Figure 5, the footprints of CH_4 emissions from the control and synthesized zeolite treatment indicate that CH_4 gas was continuously emitted during planting and transplanting, and the CH_4 emissions from the untreated control were slightly higher than those from the synthesized zeolite addition. CO_2 was also continuously emitted, with the untreated control emitting greater amounts than the zeolite-treated plots. Clearly, the zeolite can adsorb greater amounts of CO_2 than CH_4.

The results shown in Table 3 indicate that CH_4 emissions from the untreated control were much lower than CO_2 emissions. Cumulative CH_4 and CO_2 emissions in the untreated control were 42.57 g CH_4/m^2.crop and 86.40 g CO_2/m^2 crop, respectively. Furthermore, the flux for the two gases was 500.80 mg CH_4/m^2 hr. and 1016.52 mg CO_2/m^2.hr. In contrast, the cumulative emissions for the zeolite treatment addition were 30.71g CH_4/m^2.crop and 57.77 g CO_2/m^2.crop, with gas flux of 361.25 mg CH_4/m^2 hr. and 679.66 mg CO_2/m^2 hr.

Table 3 CH_4 and CO_2 emission rates in rice cultivation

Unit	Treatment			
	Control		With zeolite	
	CH_4	CO_2	CH_4	CO_2
g/m^2 crop	42.57	86.40	30.71	57.77
mg/m^2 hr	20.87	42.35	15.05	28.32

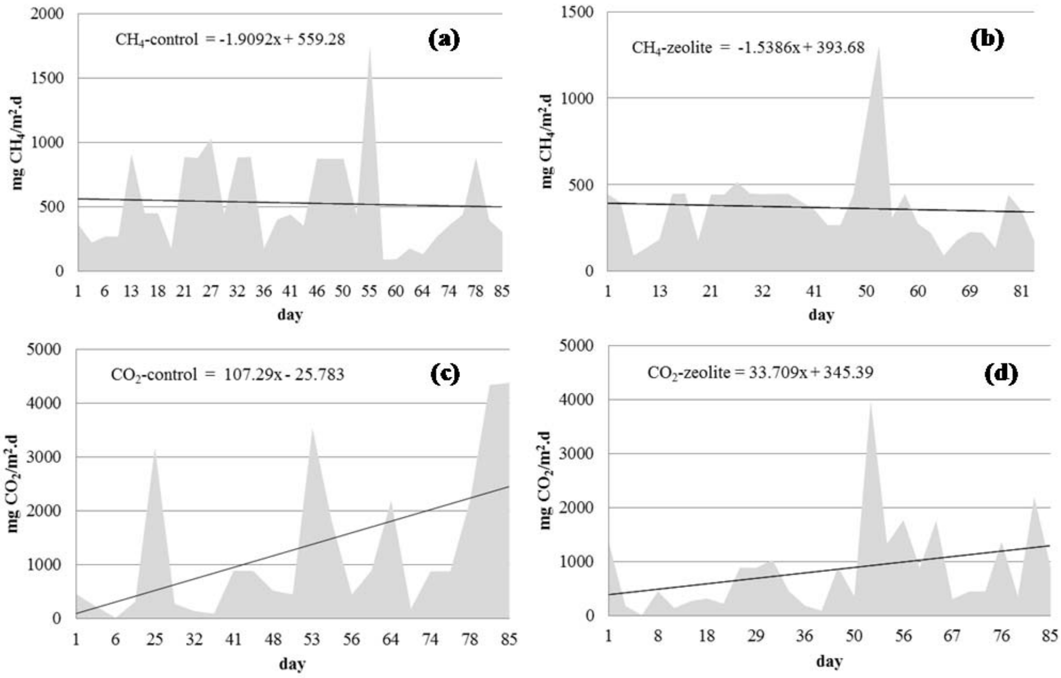

Figure 5 Emission footprints in rice cultivation for (a) CH_4 control, (b) CH_4 zeolite, (c) CO_2 control and (d) CO_2 zeolite

The results indicate that cumulative CH_4 emissions for both control and treatment were less than the cumulative CO_2 emissions. In addition, cumulative CH_4 and CO_2 emissions for the zeolite treatment were slightly less than those of the untreated control. This confirms the ability of rice stubble synthesized zeolite to reduce cumulative CH_4 and CO_2 emissions through adsorption in the pore matrix. The reduction efficiency of zeolite was 27.87% for CH_4 and 33.14% for CO_2, while the reduction emission rates were 0.148 g CH_4/g zeolite and 0.358 g CO_2/g zeolite, respectively, as shown in Table 4. The higher observed CO_2 reduction efficiency compared CH_4 is explained by high ion exchange capacity of zeolite, which allows CO_2 to bond with adsorbed cations [11]. For the same reason, the reduction emission rate of CO_2 was higher than for CH_4. However, reduction efficiency depended on pore size and structure of zeolite, and the rate of application.

Generally, zeolite is widely and successfully used as a soil ameliorant in agriculture; its highly porous structure and high CEC allows it to serve effectively as a reservoir for water and nutrients, especially N and K [10, 25]. Zeolite has therefore found favour as a fertilizer ingredient in slow release fertilizers for rice and other crops. As it increases fertilizer use efficiency through reduction of wastage by leaching, zeolite can reduce fertilizer consumption, and thus emissions, as well as maintaining optimal soil pH [12].

Table 4 CH_4 and CO_2 reduction efficiency and reduction emission rates of synthesized zeolite

Gas	Reduction emission	
	%Efficiency	Rate (g gas/g zeolite)
CH_4	27.87	0.148
CO_2	33.14	0.358

Conclusions

The findings of this experiment indicate that synthesized zeolite can reduce GHG emissions in rice, confirming earlier research showing that zeolite or reed straw and superphosphate could reduce GHG emissions from stored duck manure by up to 27% [15], and that zeolite 4A could serve as an efficient adsorbent of GHGs as well as act as a supporting slow release fertilizer. GHG emissions from rice are further reduced by the possibility of reducing rate of fertilization, and the number of applications needed. These results also indicated that GHGs emissions of single fertilization with zeolite 4A was lower than for zero fertilization and single fertilization with chemical fertilizer in Rangsit soil [18].

The study findings confirm the value of rice stubble synthesized zeolite as a GHGs adsorbent in rice cultivation because it reduced emissions of both CH_4 and CO_2 under irrigated conditions. The efficiency of CH_4 and CO_2 reduction were 8.91% and 24.25%, respectively, under irrigated or flooded conditions. The footprints of CH_4 and CO_2 indicate continuous emissions throughout the cultivation period, The reduction efficiency and emission reduction rates for CH_4 and as measured in this study confirms the utility of rice stubble synthesized zeolite in significantly reducing GHGs over the cultivation period, and that this ability was rate-dependent.

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