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Research Article

Reaction and Leaching Potentials of Magnesium Rich Synthetic Gypsum in Acidic Ultisol and Oxisol

***Ibrahim Wasiu Arolu[1], Fatai Ayanda Arolu[2], Kazeem Kolapo Olalekan[3] and Oladosu Yusuff[4]**

[1]Department of Soil Science, Faculty of Agriculture, Kaduna State University, P.M.B., Kaduna 2339, Nigeria
[2]Department of Soil Science, Faculty of Agriculture, Universiti Putra Malaysia (UPM), UPM, Serdang 43400, Malaysia
[3]Department of Agronomy, Osun State University, Osogbo, Osun State, Nigeria
[4]Institute of Tropical Agriculture and Food Security, Universiti Putra Malaysia (UPM), UPM, Serdang 43400, Malaysia
****Corresponding Author's email*: wasiu.ibrahim@kasu.edu.ng**

ABSTRACT

Ultisols and Oxisols, the common soil in Malaysia, have low levels of cations such as K, Ca, and Mg, required for crop productivity. Thus, the management of input plays an important role in crop production in these soils. An incubation study was conducted to assess the effect of MRSG on the chemical properties of Ultisol and Oxisol in Malaysia. The incubation experiment is a factorial experiment consisting of 2 soil types, 3 treatments, and five rates, including control (0, 1, 2, 4 and 8) and laid out as a completely randomized design (CRD). The amount of nutrients released from treatments into the soil solution and on the soil exchange sites was fitted into different functions using a Python programming script. The pattern of nutrient release from MRSG was similar in the two studied soils, and the amounts of nutrients released increased with the duration of the experiment. The models were efficient in describing nutrient release kinetics for all samples. The models showed good performance (R^2 value in the range 0.9 to 0.99) in most samples tested, except for the kieserite treatments. The model indicates that MRSG has a disintegration behaviour similar to GML and can be used to achieve a similar result in acid soil amelioration and soil nutrient enhancement; thus, MRSG can be a potential substitute for lime (GML) on acid soils.

Keywords: Acid Soils; Fertility; Incubation study; Modelling; Soil nutrient

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INTRODUCTION

Acid soils, which are mainly Ultisols and Oxisols, are extensively distributed in the tropical and subtropical parts of the world, where intense chemical weathering and leaching is the dominant soil conditions (Fageria and Baligar, 2008). The clay fraction of these highly weathered soils contains variable-charged minerals such as kaolinite, goethite, and gibbsite. Soil acidity is a major constraint to crop production as aluminium (Al) and manganese (Mn) accumulate to toxic levels and nutrients in the soil (Ca, Mg, K, and P) become unavailable; thus, impairing crop growth on these soils (Shamshuddin *et al.,* 2018).

Historically, lime and gypsum have been used to correct soil acidity. Liming has been proven to be an effective method of alleviating soil acidity constraints such as impaired plant root development resulting from Al in soil solution (Kochian *et al.,* 2015; Kopittke *et al.,* 2015). The use of lime can increase the pH of the soil as the charges present on the surface of the soil clay minerals are variable-charged and affected by lime application (Fageria and Baliga, 2008). Limitations such as low solubility and lime retention in the topsoil have made lime ineffective in ameliorating subsoil acidity. The presence of variable charged minerals in acid soils increases cation retention on the addition of lime, resulting in an increase in pH of the topsoil. However, the cations in the soils are confined to the negatively charged soil surfaces; hence, the effect of the liming material is confined to the zone of incorporation (Ren-yong *et al.,* 2019). This makes liming ineffective when deeply rooted crops such as cocoa are planted on acid soils where aluminium toxicity greatly affects their growth (Shamshuddin and Ismail, 1995).

Many industrial by-products (coal fly ash, alkaline slag, red mud, and phosphogypsum) containing calcium and sulfate can act as alternative amendments (Li *et al.,* 2010; Li et *al.,* 2015). One of such industrial by-products is magnesium-rich synthetic gypsum (MRSG), which has practical benefits in solving the global problem of soil acidity constraint and associated infertility. MRSG has a gypsum content of 75%, as well as calcium sulfate and calcium carbonate. This by-product was reported to be highly effective in correcting soil acidity in field and glasshouse trials when its efficacy as a magnesium fertilizer was tested (Ayanda *et al.,* 2020). However, its potential to correct soil acidity needs to be evaluated to understand its mode of action. Thus, the amelioration effect of MRSG on soil acidity and fertility in an Ultisol and Oxisol, and its behaviour in the soil, was studied through an incubation experiment and with GML and kieserite (both conventional Mg-fertilizers) included for comparison. The study was carried out to determine the effectiveness of the MRGS in ameliorating the soil acidity, its effectiveness against GML and kieserite on the soil nutrient and its solubility in acid soil.

MATERIALS AND METHODS

Characterization of MRSG

MRSG used in the study was characterized for nutrients using standard procedures as detailed by Ayanda et al. (2021).

Site description and soil sampling

The soils used for the incubation experiment were collected from Universiti Putra Malaysia (UPM) Farm, Puchong (02.5858 N, 101.3847 E) and RISDA plantation in Kg Awah, Pahang, Malaysia (03.27362 N, 102.58044 E). The temperature in the sites ranges between 25 and 35 °C, while the relative humidity exists between 80 and 90%. Based on the Köppen-Geiger system, the area's climate is classified as Af, i.e., tropical rainforest climate. The sampling sites for this study were selected according to their soil pH and mineralogical characteristics, which are important in soil-crop productivity and sustainability.

Soil physicochemical analysis

The soil pH analysis was conducted using a soil pH meter at the soil-to-water ratio of 1:2.5. Electrical conductivity (EC) was determined at a soil-to-water ratio of 1:5. Basic exchangeable cations were extracted using 100 mL of 1 M ammonium acetate buffered at pH 7. The concentration of Ca and Mg in the solutions was determined by a Perkin Elmer Model AAS 3110 atomic absorption spectrophotometer (AAS). Exchangeable Al was extracted using 1 M KCl, and the Al in the extract was measured by Perkin Elmer Optima 8300, Norwalk, CT, USA, inductively coupled plasma-optical emission spectrometer 45 (ICP-OES).

Incubation study

A factorial experiment consisting of 2 soil types, 3 treatments and five rates, including control (0, 1, 2, 4 and 8) was laid out in a completely randomized design (CRD). The study comprised two soil orders, viz. Ultisol and Oxisol, belonging to the Bungor and Segamat series. The rates of 0, 1, 2, 4, and 8t ha^{-1} of MRSG, GML and kieserite, respectively, amounting to 0, 1.92, 3.86, 5.79, 7.72 and 9.65 g, which was added into 500g of soil (≤ 2 mm size). The rates of treatments used for this study were based on earlier incubation studies on amending acid soils with basalt and gypsum, respectively (Shamshuddin and Ismail, 1995; Anda et al., 2015). The soil and each of MRSG, GML, or Kieserite was thoroughly and mixed on a plastic tray before transfer into the pot. Soil moisture content was adjusted to 80% water holding capacity using deionized water and the plastic was covered to prevent moisture loss. The soils were incubated for six months in a dark spot to prevent the growth of mould. Sub-samples were collected every 30 days for the duration of the experiment. During the sampling period, about 70 g of soil was collected, air-dried, ground and used for soil analyses. The release of nutrients from the dissolution of the materials into soil solution was evaluated every 30 days by sampling the soil solution. The period of soil solution sampling corresponds to the soil sampling time, where the soil solution was first sampled, followed by soil sampling. The soil solution was collected with the aid of a rhizon soil moisture sampler (Rhizosphere Research Products, Wageningen, Netherlands). The sampler is made of a hydrophilic, porous polymer, and a connector used to attach a vacuum syringe (20 mL) to extract soil solution. The sampler was fitted with an internal steel wire, giving the sampler adequate rigidity for insertion into the soil. Upon extracting 20 mL soil solution aliquot from the treatment at each sampling time, 20 mL of distilled water was added to the soil surface to make up for the extracted soil solution and maintain field capacity moisture content. The extracted aliquot was used for pH measurement using a pH meter (Model Metrohm 827, Riverview, FL, USA). The Ca, Mg and Al in the solution were determined using the ICP-OES. The collected soil samples were analyzed using the soil chemical analyses described earlier. Cations released from the materials were measured in exchangeable forms.

Modeling Nutrient release using Python programming script

Modelling was performed to provide an enhanced understanding of the process of nutrient release from incubated materials into soil solution and the soil exchange site. The amount of nutrients released into the soil solution and present on the soil exchange site due to the application of treatments at various rates was fitted into different models using the curve fit function (curve fit) in Python programming. The function that best fit the data points was selected, and the considered functions are:

Data Analysis

All the data collected were subjected to statistical analyses using SAS version 9.4 (SAS Institute, Inc., 2013). Analysis of variance (ANOVA) was performed to study the effect of the treatment on all measured soil parameters, while means comparison at a significant level was determined at $p \leq 0.05$ using Tukey's studentized range (HSD) to determine difference between mean values of MRSG rates and of incubation periods for a given soil property. The relationship between soil properties and treatment at different rates and the incubation period was modelled using Python script modelling software.

RESULTS AND DISCUSSION

The physical and chemical properties of the soils were determined, and some properties of the soils used are presented in Table 1. The soil collected from UPM Farm and RISDA plantation were identified as Bungor and Segamat Series, respectively, using the criteria established by the Department of Agriculture, Malaysia (DOA, 2018). According to Soil Taxonomy (USDA, 2018), the Bungor soil belonged to the clayey, kaolinitic, isohyperthermic family of Typic Paleudults, while the Segamat soil was identified as clayey, oxidic, isohyperthermic family of Haplic Acrothox. According to USDA classification (USDA, 2018), the two soils are classified as Ultisols and Oxisols. The physicochemical properties of the two studied soils indicate the predominance of clay in the Ultisol and Oxisol (59.23–70.27%), very low CEC (8.46 and $\text{cmol}_c\ \text{kg}^{-1}$) and cation content, whereas there is a high amount of aluminum saturation in the studied soil (Table 1). Mineralogical constituent of the clay fractions, the abundance of highly weathered clay minerals, especially kaolinite (75–84%) alongside gibbsite, goethite, and hematite.

Table 1: The physico-chemical properties of the soils used in the glasshouse study

Soil properties	Ultisol	Oxisol
Sand (%)	31.06	17.37
Silt (%)	9.65	12.36
Clay (%)	59.23	70.27
Textural class	Clayey	Clayey
pH (water)	4.25±0.01	3.86±0.01
EC (dSm^{-1})	0.05±0.01	0.06±0.01
Av. P (mg kg^{-1})	3.53±0.04	1.29±0.02
Total N (%)	0.18±0.01	0.09±0.01
Total C (%)	1.12±0.02	1.07+0.03
Exch. Ca (cmol_c kg-^{1})	0.56±0.02	0.43+0.03
Exch. Mg (cmol_c kg-^{1})	0.15±0.01	0.18±0.01
Exch. K (cmol_c kg-^{1})	0.14±0.02	0.09±0.01
Exch. Al (cmol_c kg-^{1})	1.53±0.03	2.69±0.04
CEC	8.64±0.21	7.42±0.19
Cu (mg kg^{-1})	42.50±0.16	67.50±0.34
Fe (mg kg^{-1})	2251.63±5.33	7524.50±11.34
Mn (mg kg^{-1})	96.50±0.75	185.70±1.08
Zn (mg kg^{-1})	35.70±0.19	74.45±0.26
Note: Av. P = available	phosphorus,	N = Nitrogen, C = Carbon, CEC = Cation

Note: Av. P = available phosphorus, N = Nitrogen, C = Carbon, CEC = Cation Exchange Capacity, Exc. K = exchangeable potassium, Exc. Ca = exchangeable calcium, Exc. Mg = exchangeable magnesium, Exc. Na = exchangeable sodium, Exc. Al = exchangeable aluminium.

In the variable charged Oxisol belonging to the Segamat series, there was a high proportion of hematite. This observation was supported by the reddish colouration of the soil, which confirmed the abundance of hematite in the soil. The chemical and mineralogical properties reflect the soil's status as having experienced extensive weathering and leaching, thereby resulting in the low productivity of these soils. For the incubation experiment, the bulk samples of the topsoil (0–15 cm) from the two soils were taken to represent soils existing under field conditions that have undergone severe leaching and erosion.

Chemical characterization of treatments

The result of the physicochemical characterization of MRSG has been discussed by Ayanda et al. (2021). The elemental composition of GML and MRSG is presented in Table 2 below

Table 2: Chemical composition of GML and kieserite

Soil properties	MRSG	GML	Kieserite
pH	9.17±0.02	8.41±0.02	8.44±0.03
EC (dS m^{-1})	7.12±0.01	0.06±0.1	0.06±0.01
Ca (%)	17.2±0.32	19.8±0.32	2.29±0.03
Mg (%)	5±0.01	9.12±0.12	15.78±0.43

Model development

In this experiment, the best-performing model was selected for a test run of each experimental treatment group. The selected models are the parabolic diffusion, elovich, power, and polynomial equations. This selection is similar to those used in a study on potassium release in acid soils by Darunsontaya *et al.* (2010), but for an additional polynomial equation. The use of the polynomial model helped improve performance, especially at points where the other three earlier models (i.e. parabolic diffusion, power, and elovich) showed low R^2 values. The experimental results of the different treatment groups (a particular treatment applied together) fitted into the different model equations, and the models that had the best R^2 were selected. Where the earlier three models, namely parabolic, elovich, and power, showed poor performance, the polynomial model was incorporated to boost the R^2 reading. For the polynomial equation, only order 2 was used for this study to avoid overfitting of the model. Fitting of the experimental data in the models was conducted using Python programming scripts and codes. Python's machine-learning curve fit module was used for this purpose. The development of handwritten codes was necessitated by the fact that the use of programming codes provides a script for future reference.

The models showed good performance (R^2 value in the range 0.9 to 1.0) in most samples tested, except for the kieserite treatments. The use of polynomial equations helps to improve the model performance of the kieserite treatment, but still, in most cases, less than R^2 value of 0.7 was recorded. The Parabolic diffusion model and Power function showed a better stable performance than the Elovich model. At points where the experimental values are high, Elovich tends to underperform. The Polynomial provided a buffer at points where these three other models underperformed, considering its ability to capture non-linear or curved patterns in the behaviour of nutrient release or dynamics in the soil due to treatment effects. From trial observation, the Parabolic diffusion and Elovich models are suitable for modeling in soils treated using the MRSG and GML treatments, which is similar to an experiment on modeling potassium release in acid soils reported by Darunsontaya *et al.* (2010). These models also showed good behaviour in some selected kieserite treatment samples but will not be recommended for this purpose. The parabolic diffusion and the polynomial model are the recommended models with the capacity to capture variations in soil behaviour.

Effect of treatment on soil pH

MRSG incubation for a six-month duration extensively increased soil pH from 4.82 to 6.58 in the Ultisol and from 4.51 to 5.93 for the Oxisol. The pH values recorded increased with the rates of MRSG applied in the two soils and the length of incubation time. In all cases, a significant increase was recorded in soil pH values with increasing MRSG rate at all incubation periods (Table 3).

Table 3: ANOVA for Soil Properties at Each Month of Incubation

		At 1-month				**At 2-month**				**At 3-month**			
Source	**DF**	**Soil pH**	**Exch Al**	**Exch Ca**	**Exch Mg**	**Soil pH**	**Exch Al**	**Exch Ca**	**Exch Mg**	**Soil pH**	**Exch Al**	**Exch Ca**	**Exch Mg**
Soil (S)	1	4.47**	20.46**	0.50**	3.76**	3.04**	17.73**	0.49**	3.33**	2.55**	16.94**	0.66**	2.55**
Trt (T)	2	3.83**	2.89**	0.19**	3.88**	5.04**	3.45**	0.35**	3.38**	6.28**	4.92**	0.56**	2.57**
Rate (R)	4	2.58**	1.75**	0.14**	2.54**	2.93**	1.92**	0.21**	2.91**	3.34**	2.43**	0.28**	3.32**
SxT	2	0.03**	0.40**	0.08**	1.74**	0.02**	0.58**	0.13**	1.01**	0.03**	0.70**	0.14**	0.55**
SxR	4	0.03**	0.06**	0.01**	0.67**	0.02**	0.12**	0.01**	0.61**	0.02**	0.11**	0.01**	0.53**
TxR	8	0.32**	0.21**	0.05**	0.74**	0.39**	0.22*8	0.06**	0.70**	0.45**	0.30**	0.07**	0.61**
SxTxR	8	0.01**	0.01ns	0.02**	0.31**	0.02**	0.02ns	0.02**	0.22**	0.02**	0.03**	0.03**	0.14**
Error	60	0.01	0.02	0.08	0.11	0.02	0.02	0	0.02	0.02	0.02**	0.08	0.03

		At 4-month				**At 5-month**				**At 6-month**			
Source	**DF**	**Soil pH**	**Exch Al**	**Exch Ca**	**Exch Mg**	**Soil pH**	**Exch Al**	**Exch Ca**	**Exch Mg**	**Soil pH**	**Exch Al**	**Exch Ca**	**Exch Mg**
Soil (S)	1	2.78**	14.43**	0.98**	1.99**	3.29**	13.12**	1.00**	1.62**	3.44**	11.39**	1.12**	1.20**
Trt (T)	2	6.91**	6.29**	0.86**	1.99**	8.62**	7.86**	1.15**	1.46**	10.61**	10.84**	1.82**	1.09**
Rate (R)	4	4.08**	2.79**	0.40**	3.62**	4.97**	3.31**	0.51**	3.94**	5.59**	4.26**	0.68**	4.51**
SxT	2	0.01**	0.84**	0.16**	0.25**	0.02**	0.93**	0.18**	0.10**	0.01**	1.31**	0.21**	0.04
SxR	4	0.01**	0.20**	0.03**	0.49**	0.02**	0.20*8	0.02**	0.42**	0.03**	0.27**	0.03**	0.43
TxR	8	0.48**	0.37**	0.09**	0.57**	0.61**	0.46**	0.11**	0.49**	0.81**	0.62**	0.17**	0.49
SxTxR	8	0.01**	0.03**	0.02**	0.09**	0.01**	0.03*	0.03**	0.06**	0.07**	0.05**	0.05**	0.07
Error	60	0.00	0.02	0.01	0.00	0.00	0.02	0.00	0.04	0.00	0.02	0.00	0.00

As the incubation period increased, the magnitude of soil pH values showed relatively constant trends for MRSG increase, demonstrating that the residual effect of these rates in maintaining soil pH could occur over six months or longer. Further increase in incubation rates to 4 and 8 t ha^{-1}, pH values still continuously increased with time until the end of the experiment. For example, the pH values of Bungor soil treated with MRSG 8 t ha^{-1} increased from 5.87 to 5.96 by month 3 and continuously increased to 6.53 by month 6.

The increase in soil pH can be mainly attributed to the acid-neutralizing capacity of MRSG. MRSG, like most industrial residues, has specific characteristics that ameliorate soil acidity conditions owing to its alkaline nature and high acid-neutralizing capacity. The high content of $CaSO_4.2H_2O$ results in a high pH of the material, thus giving it a high capacity to ameliorate soil acidity. This is consistent with the previous study by Li *et al.* (2015), where phosphogypsum, an industrial by-product, showed the presence of gypsum, which gave the material a high acid-neutralizing property.

In addition to this, other processes were believed to have accounted for the change in pH in the two studied acid soils incubated with MRSG. Apart from releasing cations such as Ca2+, Mg2+, MRSG also contains anions such as SO_4^{2-}. Specific adsorption of this anion in the two soils will induce the release of hydroxyl ions from iron (Fe) and Al oxides/hydroxides due to ligand exchange between OH^- and the SO_4^{2-} (Shamshuddin and Ismail, 1995). Alternatively, soil pH increase due to incubation with MRSG may be attributed to the hydroxyl ions released by Mg and Ca hydroxides as well as the reaction of calcite, a liming agent, contained in MRSG.

The increase in soil pH in GML treatment was due to the addition of calcium carbonate in GML to the soils, which neutralizes pH. The increase in soil pH resulting from GML incorporation can be attributed to hydroxyl ion production upon its dissolution and subsequent hydrolysis. This is represented by the equation below.

1. $Mg(CO_3)_2+H_2O \longrightarrow Ca^{2+}+Mg^{2+}+2CO_3^{2-}$
   $CO_3^{2-}+H_2O \longrightarrow HCO_3^-+OH^-$

This hydroxyl ion reacts with Al in the soil solution to precipitate Al as aluminium hydroxide, which may eventually crystallize into inert gibbsite. The changes in soil chemical characteristics following soil application of GML [$CaMg(CO_3)_2$] can be explained using the equation (Fageria and Baligar, 2008).

2. $CaMg(CO_3)_x+2H^+ \Leftrightarrow 2HCO_3^-+Ca^{2+}+Mg^{2+}$
3. $2HCO_3^-+2H^+ \Leftrightarrow 2CO_2+2H2O$
4. $CaMg(CO_3)2+4H^+ \Leftrightarrow Ca^{2+}+Mg^{2+}+2CO_2+2H_2O$

The above equation indicates that lime neutralization of acidic media occurs in two steps. Initially, calcium and magnesium react with hydrogen ions on the exchange site, where Ca^{2+} and Mg^{2+} substitute H on the exchange sites (negatively charged particles of clay or organic matter) to form HCO_3^- (Fageria and Baligar, 2008). In the second step, HCO_3^- reacts with H^+ to form CO_2 and H_2O to increase pH. These reactions are mostly affected by soil moisture, temperature, and properties of the treatment e.g., GML. Goh *et al.* (1998) reported a quadratic increase in soil pH due to GML application. This observation was also supported by Suswanto *et al.* (2007), who reported an increase in soil pH upon the addition of GML, and this was attributed to a corresponding decrease in the exchangeable soil aluminium. According to the researcher, applying 4 t ha^{-1} GML increased soil pH from 4.27 to 4.93.

A slight increase in soil pH was recorded in kieserite treatment; the increase in soil pH due to incubation with kieserite in the Ultisol was somewhat erratic and fitted with the polynomial model 0.35-0.82. Most studies report that kieserite does not affect soil pH (Goh *et al.,* 1998; Cristancho, 2010); however, this was contrary to the result obtained in this study. The slight increase in soil pH due to kieserite treatment can be attributed to the specific adsorption of SO_4^{2-} ions on the surface of oxides.

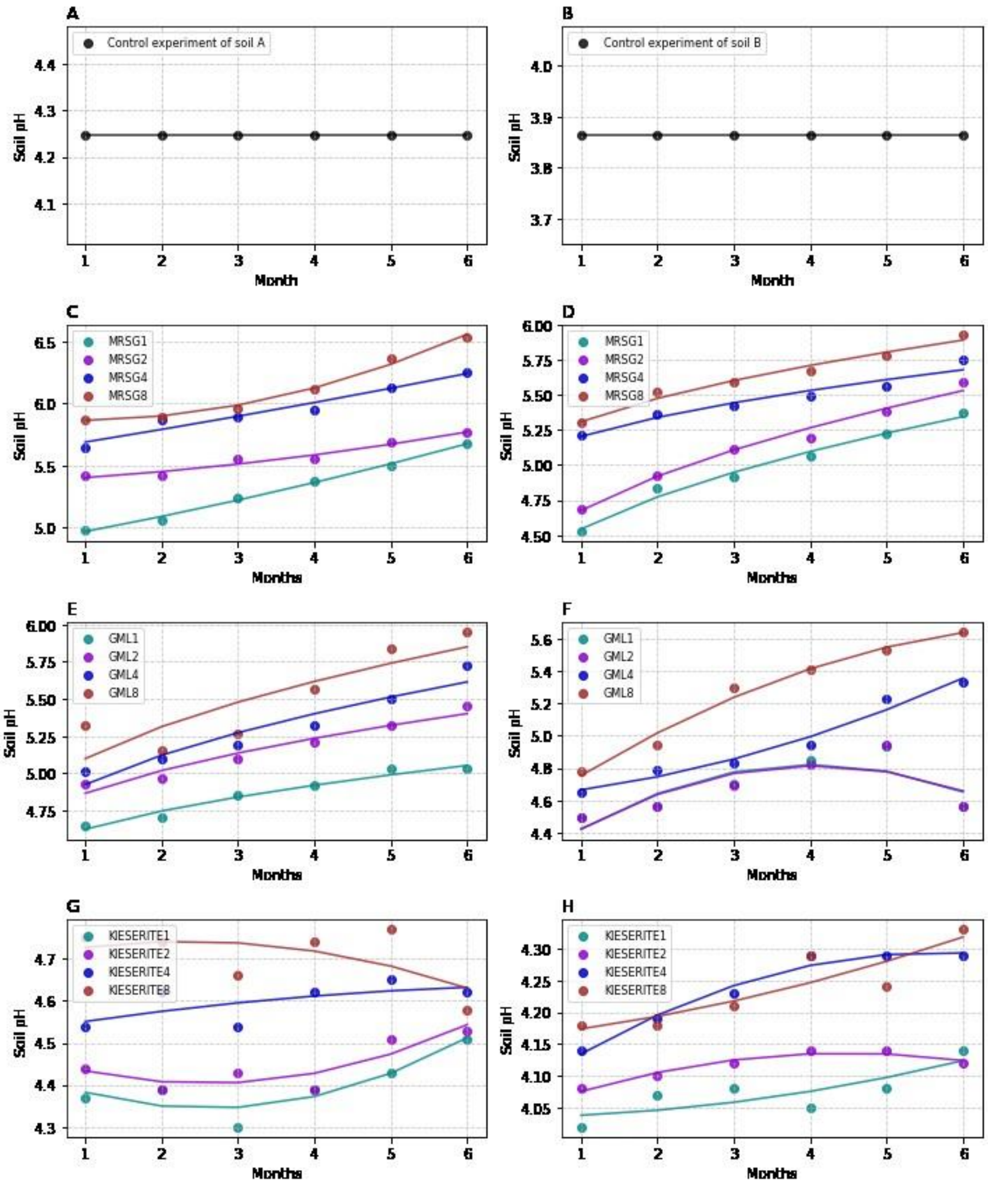

Figure 1: Data fitted to different models describing trends of treatment effect on soil pH in the studied Ultisol and Oxisol. A- Control in Bungor B Control in Segamat C-MRSG at different rates in Bungor D-MRSG at different rates in Segamat E- GML at different rates in Bungor F-GML at different rates in Segamat G- Kieserite at different rates in Bungor, Kieserite at different rates in Segamat

Effect of treatment on soil exchangeable Al

The result of ANOVA shows that a significant difference ($p \leq 0.05$) was recorded in exchangeable Al among soils, treatments, and rates, and their respective interactions except for the interaction between soil x treatment x rate were not significant ($p > 0.05$) in the first two months of soil incubation. In all treatments, across the length of incubation period, the best response in amelioration of exchangeable Al was recorded in Bungor Series soil compared to Segamat series. MRSG incubation significantly ($p \leq 0.05$) decreased exchangeable Al for Bungor and Segamat with increasing period of incubation compared to control and other treatments (Figure 2). The incubation of Ultisol and Oxisol with MRSG treatment showed a decreasing trend of soil aluminium with increasing rate and length of the incubation time. In order to reveal the dynamic of MRSG incubation in the two studied soil over a certain period in this experiment, the trend of exchangeable Al was plotted against time. As indicated in Figure 2, the exchangeable Al was well fitted to the parabolic diffusion model represented by K=a+bt1/2.

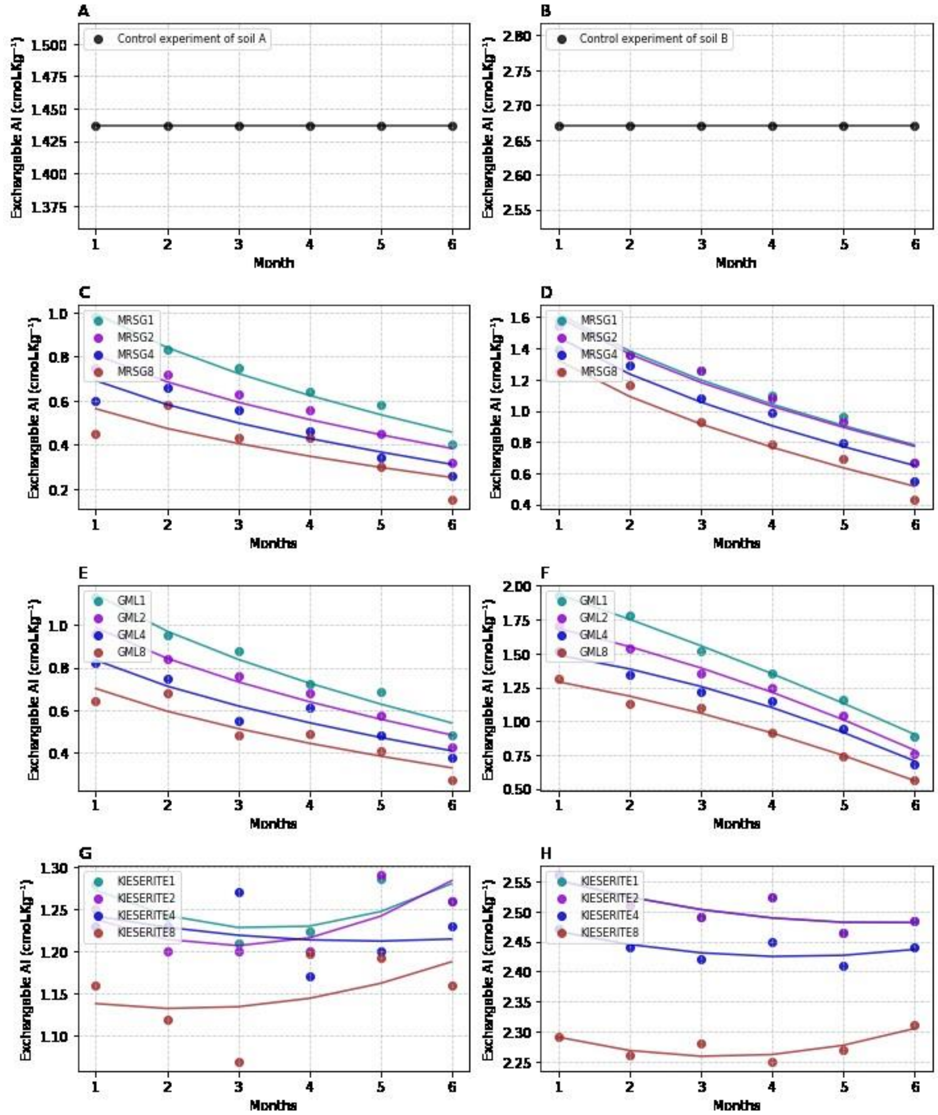

Figure 2: Data fitted to different models describing trends of treatment effect on exchangeable Al in the studied Ultisol and Oxisol. A- Control in Bungor B Control in Segamat C-MRSG at different rates in Bungor D-MRSG at different rates in Segamat E- GML at different rates in Bungor F-GML at different rates in Segamat G- Kieserite at different rates in Bungor, Kieserite at different rates in Segamat

The dynamics or trends of exchangeable soil Al at all rates of MRSG treatment were similar in the two studied soils. Exchangeable Al was significantly ($p \leq 0.05$) reduced from 0.98 to 0.40 cmolc kg−1 at MRSG rate of 1 t ha^{-1} in Bungor soil, and the same trend of pH increase was recorded in the Segamat soil. As MRSG rate was increased to 8t ha^{-1}, exchangeable Al continuously decreased, indicating that higher application rates of MRSG influence the reduction of aluminium at the soil exchange site. From the result obtained, it appears MRSG rate at 1t ha^{-1} was sufficient to achieve a low value (approximately 0.40 cmolc kg^{-1}) of exchangeable aluminium at the end of the incubation study.

The trend of soil aluminium decrease in all rates may be attributed to the liming properties of MRSG. Aside from their liming properties and complexation, the silicate minerals in MRSG can function as adsorbents for Al^{3+} (Valle *et al.,* 2016). Aluminium species in the soil solution readily change with changes in pH and the composition of the soil solution, due to the higher charge of Al ions and relatively smaller hydrated ionic radius as well as good chelating ability with inorganic and organic ligands. Increased pH favours hydroxylation, polymerization and precipitation of Al in soil solution. Therefore, MRSG and GML may have decreased total soluble Al, since they increased soil pH. Garrido *et al.* (2003) and Illera *et al.* (2004) emphasized that the formation and retention of hydroxyl aluminium polymers are the major mechanisms in the alleviation of Al following the application of gypsum- and lime-rich by-products in acid soils.

The trend of exchangeable aluminium decrease was also recorded at all rates in GML treatment, and the trend was well described by the parabolic diffusion model, which gives a high value of R^2 in the two studied soils. The soil aluminium content decreased with increasing incubation time, suggesting that the slow reactivity of the material and that GML may go on to further lower aluminium in the soil beyond the incubation period. The addition of GML to the soil increases pH, leading to the precipitation of aluminium as inert gibbsite. Reduced soil aluminium following increased soil pH in acid soils treated with GML is due to the replacement of aluminium (Al) by calcium on the exchange site and by the subsequent precipitation of Al as $Al(OH)_3$ (Amsalu and Beyene, 2020).

In terms of kieserite treatment, the data obtained in this study made it difficult to make a conclusive statement due to the erratic values recorded at all rates in the two soils. The model for the soil aluminium trends in the two soils is best fitted using the polynomial model. Thus, the pattern of soil aluminium with the length of incubation period were mostly unpredictable. However, lower aluminium values were recorded at higher kieserite rates in the two soils. This was attributed to the increased formation of $AlSO_4$ compounds in the soils. This observation was supported by previous studies conducted by Cristancho *et al.* (2010), where kieserite reduced the aluminium content of the Batu Anum series in Malaysia. Studies on kieserite application show that kieserite treatment may result in a slight increase in soil pH, although this is usually lower than that resulting from GML treatment (Ayanda *et al.,* 2020); this explains why kieserite gave higher exchangeable Al values compared to MRSG and GML.

Effect of treatment on soil exchangeable Ca

Results of statistical analyses on exchangeable Ca in the two soils due to incubation with MRSG, GML and kieserite show a significant difference ($p \leq 0.05$) between soil, treatment, rate and their respective interaction. In MRSG treatment, the trend of exchangeable Ca in the two soils over the study duration was well described using the parabolic diffusion model represented by K=a+bt1/2 (Figure 3). This model adequately described the effect of MRSG treatment on soil exchangeable Ca compared to the other models. The dynamics or trends of exchangeable Ca increase at all rates of MRSG treatment in the two soil types were similar throughout the incubation period. The incubation of Ultisol and Oxisol with MRSG showed the trend of Ca increase with increasing rate and length of the incubation time. Soil exchangeable Ca increase due to MRSG treatments was attributed base cations in the material, with higher rates amounting to higher availability in MRSG.

This observation was supported by results from the elemental analysis of MRSG conducted by Ayanda et al (2020), which shows the predominance of calcium in MRSG. Similarly, the X-ray diffraction of MRSG shows the major crystalline component of the solid phase of MRSG is gypsum. The dissolution of this compound may result in a high Ca on the exchange site of the studied Ultisol and Oxisol. According to Li *et al.* (2015), nutrients such as Ca, Mg and K in industrial by-products are usually available in the form of carbonates and hydroxides and the concentrations of available nutrients vary with different by-products. MRSG contains abundant quantities of gypsum alongside a small amount of calcite; the dissolution of the compounds will increase the level of calcium in the soil.

For GML treatment, the trend of soil exchangeable Ca was similar to that recorded in MRSG treatment. The exchangeable Ca recorded increased with increasing GML rate in the two studied soils (Figure 3). The reaction and trend of exchangeable Ca increase related to the dissolution of this material was adequately described using the power function model of phyton script and parabolic diffusion model in the Ultisol and Oxisol.

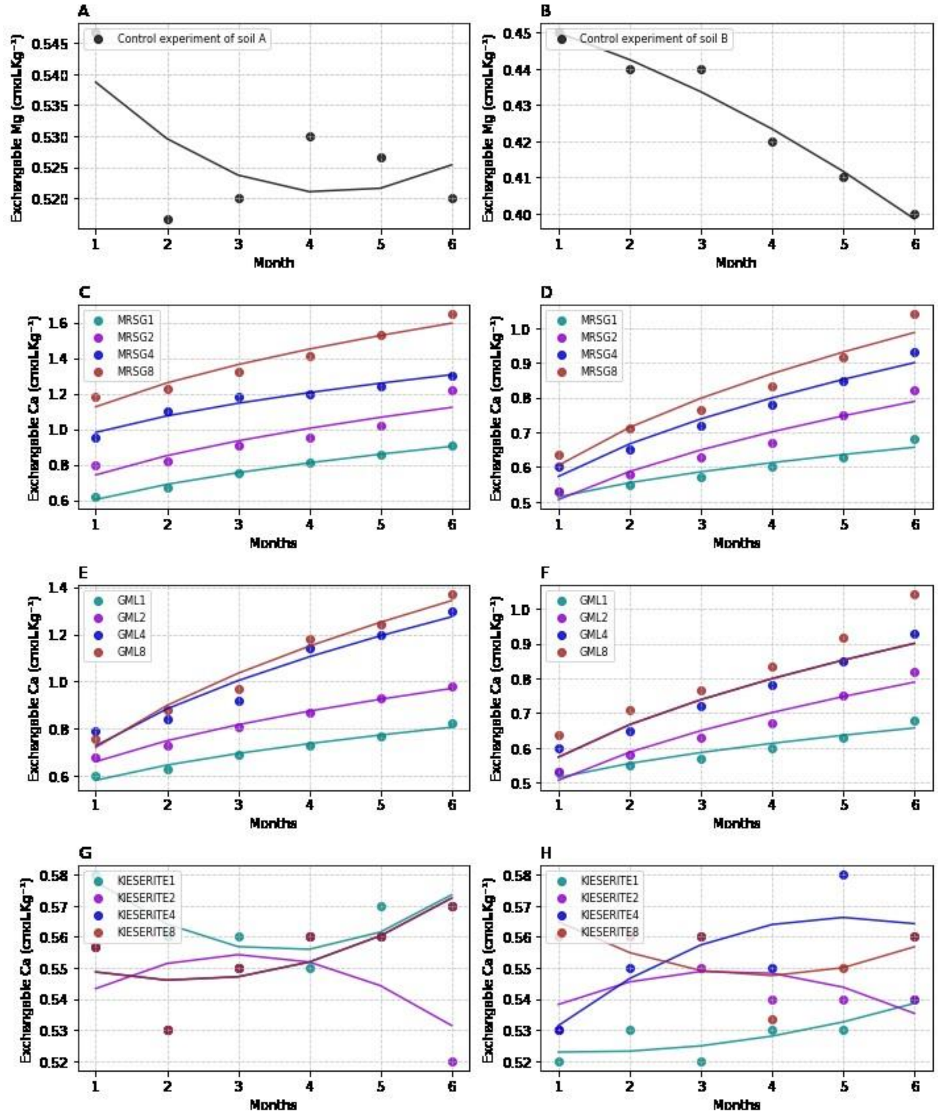

Figure 3: Trends of different treatment effects at different rates on exchangeable Ca in the studied Ultisol and Oxisol

The Ca and Mg present in GML react with H on the exchange complex, and H is replaced by Ca^{2+} and Mg^{2+} on the exchange sites (negatively charged particles of clay or organic matter), forming HCO_3^-. Various studies have reported increasing GML levels on soil exchangeable Ca (Ayanda *et al.,* 2020; Cristancho *et al.,* 2010). Liming of acid soils is mainly conducted to supply Ca and Mg to the soil in addition to neutralizing phytotoxic levels of soil Al^3 (Fageria and Baligar, 2008). The trend of exchangeable calcium in soils incubated with various rates of kieserite cannot be explained by the Parabolic, Elovich or power function. The best model for predicting exchangeable Ca in kieserite treatments in the two soils across different rates and incubation time is the polynomial function order 2. This was expected because kieserite treatment had no consistent effect on the level of exchangeable Ca in the two soils and neither was there a clear trend of increasing the rate of kieserite on the level of exchangeable Ca in the soil.

Effect of treatment on soil exchangeable Mg

The results of statistical analyses of exchangeable Mg in the two soils due to incubation with MRSG, GML and kieserite show a significant difference ($p \leq 0.05$) between soil, treatment, rate and their respective interaction. The best response was achieved in Ultisol soil compared to the Oxisol. The interaction between MRSG treatments and rates in terms of the level of soil exchangeable Mg was described by the Parabolic diffusion model (Figure 4). MRSG application at 1 t ha^{-1} raised the level of exchangeable Mg in the soil from 0.24 and 0.19 cmolc kg^{-1} of soil to 0.56 and 0.47 cmolc kg^{-1}, respectively, at the end of the experiment in the studied Ultisol and Oxisol. This increase was consistent with the application rate of MRSG and length of the incubation period, suggesting the residual effect and slow dissolution, leading to increased magnesium availability on the soil exchange site. The availability of Mg in the soil due to MRSG application was due to the content of Mg in the material. The result of elemental analysis conducted by Ayanda *et al.* (2021) indicated the presence of a high amount of Mg in MRSG.

This observation was also reported in the analysis of MRSG conducted by Golder Associates of Australia, where a high amount of $Mg(OH)_2$ (17.1%) alongside gypsum (73-74%) and other compounds was reported in the material. The FTIR analysis of MRSG shows broadbands at 3487 cm^{-1} attributed to the hydroxyl stretching modes of hydrated calcium-magnesium carbonates. Several analyses on the properties of MRSG show components such as calcium hydroxide, calcium and magnesium carbonates. The aggregates of these compounds may increase the level of exchangeable Mg in the soil upon incorporating this material into the soil. Similarly, EDX analysis of MRSG confirmed the presence of Mg in the material, and upon its dissolution, it is expected that the level of Mg in MRSG incorporated soil will be increased.

In GML treatment, exchangeable Mg content in the Ultisol was well predicted using the Parabolic diffusion model (Figure 4). In contrast, the Power function adequately predicted Mg on the exchange site of the Oxisol. The level of soil Mg was higher across all rates of MRSG compared to GML in the two soils; however, like MRSG, there was an increase in Mg level with time in the two soils.

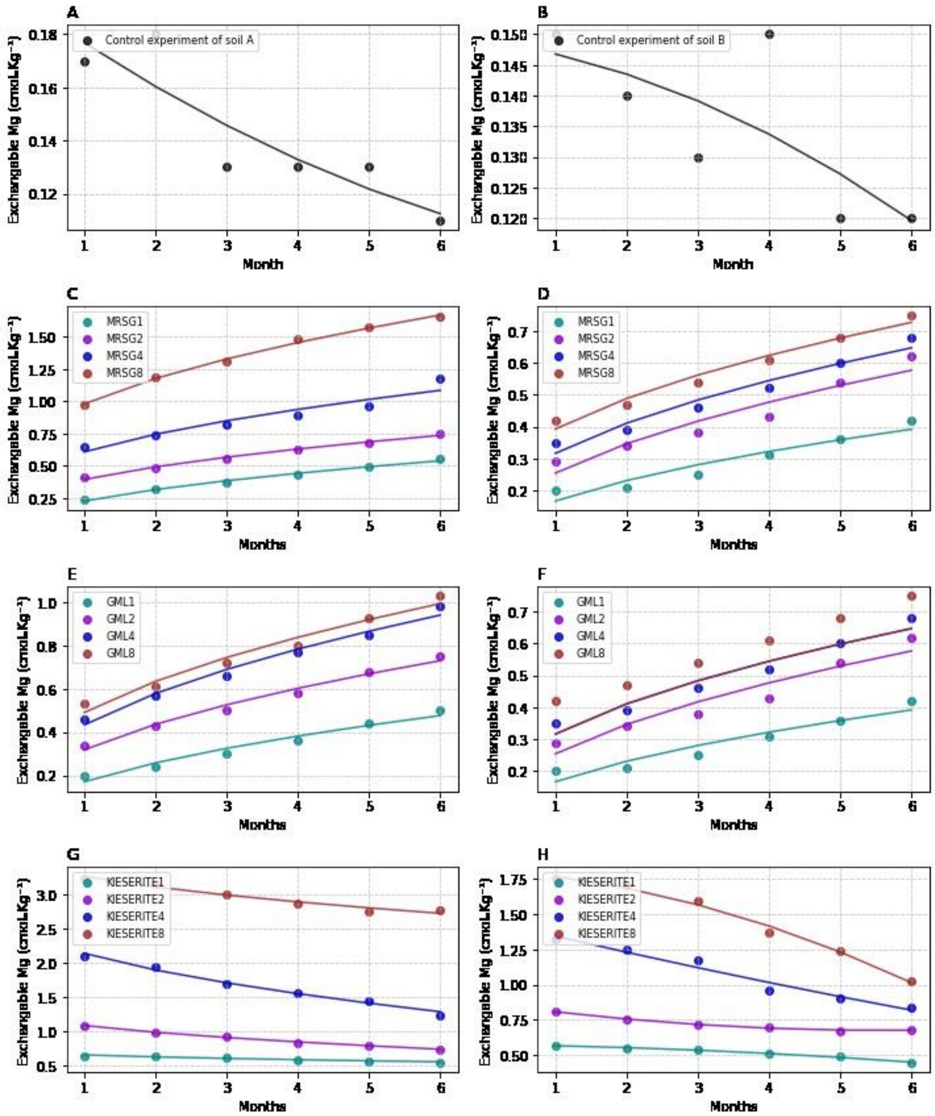

Figure 4. Data fitted to different models describing trends of treatment effect on exchangeable Mg in the studied Ultisol and Oxisol. A- Control in Bungor B Control in Segamat C-MRSG at different rates in Bungor D-MRSG at different rates in Segamat E- GML at different rates in Bungor F-GML at different rates in Segamat G- Kieserite at different rates in Bungor, Kieserite at different rates in Segamat

The explanation is that MRSG is more soluble than GML, which was confirmed in an auxiliary experiment where the solubility of MRSG, GML, and kieserite was tested in water. Besides, previous research stated that a large proportion of Mg in soil applied with GML remains in the non-exchangeable form (Cristancho *et al.,* 2010). This may have resulted from the poorer chemical reactivity of magnesium carbonate compared to calcium carbonate in soil. This also explains the increase of soil Mg with time, showing that a lengthy period is required for the Mg nutrient in GML to attain its maximum effectiveness. Goh *et al.* (1998) reported the slow reactivity of GML, making it undesirable when a rapid-acting Mg source is needed to correct Mg deficiency on acid soils. However, GML is usually desirable due to its acid-neutralizing properties, effect on soil pH, and its addition of calcium alongside Mg into the soil.

When kieserite was incubated in the two studied soils, a trend of soil exchangeable Mg recorded was well predicted by the parabolic diffusion model with a high R^2 value in the two studied soils. In the Ultisol and Oxisol, a significantly higher Mg value was recorded due to treatment, and this increased with the increasing rate of kieserite application. However, the level of MRSG sharply decreased with the length of the incubation period. This observation was related to the content of nutrients, i.e., magnesium and sulphur in kieserite, which is present in readily available (Ayanda, 2017). Similarly, the higher Mg content in kieserite and the higher solubility of kieserite tested in an auxiliary experiment indicate the fast reactivity of kieserite in water. This has also been proven in various experiments where kieserite was utilized as a source of Mg. Heming and Hollis (1995) reported a one-fold increase in the level of soil exchangeable Mg when kieserite was applied to the soil as Mg fertilizer.

According to Goh *et al.* (1998), kieserite is a rapid-acting source of magnesium with high solubility compared to dolomitic lime. Although kieserite recorded higher exchangeable Mg at one month of incubation in all kieserite treatments in the two soils (Bungor and Segamat), the trend of exchangeable Mg showed a steady decline with the length of the incubation period. This may suggest that rapid reaction in the soil following kieserite treatment may be followed by rapid loss of the nutrient through processes such as leaching and erosion. In the MRSG and GML, the exchangeable Mg increased with the length of incubation, suggesting the slow dissolution of the content of these materials into the soil. Comparing the effect of MRSG and GML in exchangeable cation levels in the two soils, MRSG increased the level of Ca and Mg better than GML. Although GML contains more Ca than MRSG, MRSG increased exchangeable Ca and Mg more in both soils. Every MRSG rate increment consistently increased Ca and Mg contents compared to GML. Generally, the trend of individual cation (Ca and Mg) increased from month 1 to month 6 in the two soils. From the models, the trend appears to be on the increase after six months, especially at higher application rates. Thus, it is supposed that there will be a longer residual effect (more than six months) of MRSG in increasing the level of cations in the highly weathered Ultisol and Oxisol.

CONCLUSION

The result of the incubation studies using highly weathered Ultisols and Oxisols affirms the effect of MRSG in ameliorating soil acidity by increasing the soil pH, which in turn alleviates aluminium and manganese toxicity while improving the nutrient content of the soil. The incubation of the soil with MRSG alongside other materials such as GML and kieserite shows close similarity in the action of MRSG and GML in the release of nutrients to improve soil chemical characteristics over time, whereas the applied kieserite showed a high initial increase in Mg content, which decreases with time. This confirms that MRSG may have a long-term residual effect comparable to GML but with more solubility compared to GML. The use of this by-product gypsum may be a valuable material in acid soil systems by reducing soil acidity constraints and providing a cost-effective Mg and Ca source.

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