MANSOURA JOURNAL OF CHEMISTRY
Official Journal of Faculty of Science, Mansoura University, Egypt
E-mail: scimag@mans.edu.eg ISSN: 2974-4938

Synthesis, Characterization and Application of Gypsum Slow Release Fertilizers

H. S. Ali (1), **O. A. El-Gammal** (2), **Khaled S. Abou-El-Sherbini** (3), **N. I. Talha** (1) **and M. E. El-Seedy** (4)

(1) Soils, water and environment research institute, Egypt.

(2) Department of chemistry, Faculty of Science, Mansoura University, P.O.Box 70, Mansoura- Egypt.

(3) Department of Inorganic Chemistry, National Research Centre, Dokki, Giza 12622, Egypt.

(4) Soils Dept., Faculty of Agriculture, Mansoura University, Egypt.

*** Corresponding author e-mail**: hebasalah111187@gmail.com; Tel.no.: 00201063766532

Received:29/5/2024
Accepted: 10/7/2024

Abstract: A substantial number of nutrients were lost and fertilizer usage was low when fertilizers were applied excessively, which significantly reduces crop output. The negative impacts of excessive fertilizer used in agricultural activities can be lessened by establishing improved fertilizer usage methods. We created Gypsum Slow Release Fertilizer (GSRF) for this investigation. A few of the primary ingredients utilized in the synthesis of the NPK delayed release fertilizer were urea, potassium sulfate (K_2SO_4), and single super phosphate (SSP) in order to meet the requirements for nitrogen (N), phosphorus (P), and potassium (K). In addition to those ingredients, gypsum was added to the fertilizer to improve its qualities. To find out how quickly N, P, and K were released cumulatively, column leaching studies were carried out.

keywords: Gypsum, Cumulative release rate, Slow release and Fertilizer.

1.Introduction

The population of the globe is predicted to rise during the coming years, approaching 9 billion by 2050, necessitating a matching rise in crop productivity and food supply [1]. In order to fulfill the global population's demand for food, NPK fertilizers have received a lot of attention [2]. These fertilizers greatly advance modern agriculture and contribute to food security. It is commonly recognized that the majority of commercial fertilizers have low plant nutrient uptake efficiency [3-5]. However, due to quick losses to the environment, only 40%–70% of the nitrogen and 80%–90% of the phosphorus found in conventional fertilizer are absorbed by crops [6]. Potassium fertilizer is lost by leaching and surface runoff; phosphate fertilizer is lost through ineffective transformation and surface runoff; and nitrogen fertilizer is lost through denitrification, volatilization, and leaching [6-9]. The nutrients in slow-release fertilizers are applied to the plant in a way that either delays their uptake and use by the plant or prolongs their availability for a much longer period of time than a "rapidly available nutrient fertilizer," such as potassium chloride, ammonium phosphate, ammonium nitrate, or urea [10, 11]. Slow-release fertilizers have various advantages over standard fertilizers, including a decreased rate of fertilizer loss, a more sustainable source of nutrients, less frequent application requirements, and a reduced risk of overdosing [12, 13]. With just one application, slow-release fertilizers can provide crops with the nutrients they need for the whole season, saving money on spreading and lowering the need for the human work that topdressing operations require during the short growing season [14-16]. In contrast, the composition of gypsum ($CaSO_4.2H_2O$) is 20.9% combined water (H_2O), 32.6% calcium oxide (CaO), and 46.5% sulfur trioxide (SO_3) [17, 18]. Compared to commercial fertilizers, gypsum lowers ammonia volatilization, and when used consistently, gypsum fertilizers can provide the soil with calcium and sulfur, which are essential for plant nutrition [19]. By encouraging improved aggregation, raising water infiltration, and lowering loss of soluble phosphorus (P), it can enhance physical and chemical qualities. Furthermore, because gypsum creates a hard substance, using it as a nutrition transporter may induce a sluggish and extended release of nutrients. All of these traits suggest that a fertilizer based on gypsum could lessen leaching, boost nutrient bioavailability, and ultimately increase biomass production and crop development [20-22]. This study produced gypsum slow release fertilizer (GSRF) by combining gypsum as a base ingredient with commercial fertilizers. With gypsum serving as a nutrient carrier, the particular goals were to: (1) create an N-P-K slow-release fertilizer; and (2) compare the physicochemical characteristics and nutrient release behavior of the GSRF to a typical chemical fertilizer.

2. Materials and methods

2.1. Materials

Gypsum came from the Egyptian Industrial House Company. Commercial fertilizers include potassium sulfate from Sesoda Corporation (Taiwan), single super phosphate from Egyptian Financial and Industrial Company (Egypt), and urea from Alexandria Fertilizers Company (Egypt). Sodium hydroxide El-Nasr Pharmaceutical Chemicals Company (Egypt), boric acid ADWIC (Egypt), and sulfuric acid supplied by Merck (USA).

2.2. Instruments

2.2.1. Fourier transform infrared spectra (FTIR)

The FTIR spectra of a sample of 2-3 mg diluted with 300 mg KBr as a tablet pressed at 10 ton/cm2 to create a transparent disk were obtained using the JASCO FT/IR-6800 spectrometer, in the range 4000-400 cm^{-1}. It is often required to dry the sample because there must be no moisture present.

2.2.2. Raman spectroscopy

The BWS465-532S i-Raman Plus spectrometer, which runs at a wavelength of 65 to 4200 cm^{-1} (B&W Tek, Inc, Plainsboro Township, NJ, USA), was used to perform the Raman study.

2.2.3. Flame atomic absorption spectrometry (FAAS)

Sens AA double-beam atomic absorption spectrometer (GBC Scientific Equipment USA LLC, Hampshire, IL) with Na and K hollow-cathode lamps as radiation sources and a deuterium background corrector was used to perform flame atomic absorption spectrometry (FAAS) measurements.

2.3. Methods

2.3. Synthesis of GSRF

An N-P-K nutrition solution was created by dissolving a certain amount of commercial NPK fertilizers in distilled water. The gypsum and the N-P-K nutrition solution were mixed together. This led to the production of the slow release fertilizers (GSRFs).

2.3. 1. Analysis of metal concentration

A conical flask containing 5 milliliters of H_2SO_4 was used to digest 0.25 grams of the GSRF sample, which had been collected and ground in a Wiley stainless steel mill. The sample is broken down using an electric heater until dense white vapors emerge, at which point the approximately 5-milliliter solution turns clear. Allow the sample to cool before quantitatively transferring it into a 50 ml volumetric flask and diluting it with distilled water. Use distilled water to note the volume makeup. Filter paper is used throughout the filtering process.

2.3.2. Determination of nutrient release patterns

These studies were conducted in order to verify the release of nutrients from the GSRF. The samples were combined with tap water to monitor the leaching of the different nutrient patterns. For ten days, each experiment was conducted inside a glass column. One gram of BSRF was put to the glass containing the five grams of sand soil after 120 milliliters of distilled water had been added. Thirty milliliters of water were removed from the glass column after 3, 7, 14, and 21 days. It was tagged and characterized in order to monitor the nutritional leakage, respectively. Potassium ions in the water samples were assessed using a flame photometer, while the quantities of phosphate and nitrate ions were determined using a U-V visible spectrophotometer.

I. Determination of Nitrogen

Add four drops of the indicator and 10 milliliters of H_3BO_3 4% to the Erlenmeyer flask. Place the flask so that the surface of the boric acid is below the lower tip of the glass receiver tube. Add ten milliliters of 40% NaOH to the solution sample. Running the condenser's cooling water and begin heating the boiler water to a boil. The released Nitrogen ($mg.L^{-1}$) was calculated by Eq.1 :

$$Nppm = \frac{Vt \times N \times 14 \times 1000}{Vs \times Wt} \qquad (1)$$

Vt is the volume of H_2SO_4 consumed in titration

N is the H_2SO_4 normality

V_e is the volume of Potassium sulphate used in the extraction

V_s is the sample volume used in titration

Wt is the sample weight

II. Determination of phosphorus

Reagent A: Dissolve 12 g of ammonium molybdate in 250 ml of distilled water. In 100 ml of distilled water dissolve 0.2908 g of antimony potassium tartrate. Add both of the dissolved reagents to 1000 ml of 5 N H_2SO_4 (148 ml, 90% H_2SO_4 liter), mix thoroughly and make to 2,000 ml. Store in pyrex glass bottle in a dark and cool compartment. Reagent B: Dissolve 1.056 g of ascorbic acid in 200 ml of reagent A and mix. This reagent should be prepared as required as it does not keep for more than 24 hours. Pipette aliquots containing 5ml of the sample into 25-ml volumetric flasks. Add distilled water to make the volume to 20 ml, and then add 4 ml of reagent B. Make to volume with distilled H_2O and mix. Report the intensity of the color on the spectrophotometer at a wavelength of 880 nanometers after at least 10 minutes of adding ascorbic solution. After adding distilled water to get the level to 20 milliliters, add 4 milliliters of reagent B. Add distilled water to make to volume and stir. Following the addition of ascorbic solution for at least ten minutes, record the intensity of color at a wavelength of 880 nanometers on the spectrophotometer. The released Phosphorus ($mg.L^{-1}$) was calculated by Eq. 2 :

$$P(ppm) = \frac{Reading \times factor \times A \times B}{G \times C} \qquad (2)$$

A Volume of volumetric flask in which the color is formed

B Volume of sample

C Volume of the sample taken for estimation

G Sample weight

III. Determination of Potassium

When potassium ions are atomized from solution, led to a burner, and exited to spectrum emission in a flame, their quantity can be measured quantitatively. An element may be quantitatively determined by measuring the amount of light it produces, since the intensity of light emitted by each element is essentially determined by the concentration of its atoms in the flame at any given time. Ammonium acetate, around 1 N, is Reagent A. Potassium chloride, 0.02 N is Reagent B. Potassium chloride, or Reagent C, is 0.02 N in 1 N Ammonium Acetate for potassium measurement. The D Reagent is 0.05 N lithium Chloride. A series of standard KCl solutions with the same lithium chloride content were made using reagents B and D. Using reagents C and D and dilution with A, a comparable series of standard KCl solutions was made. KCl concentrations of 0, 0.2, 0.4, 0.6, 0.8, 1, 2, 3, and 4 meq/L were advised. Pipetting into a volumetric flask, an aliquot of the solution to be examined (less than 0.2 meq. of K) was obtained. The concentration of lithium chloride in the 50 ml solution was precisely equal to the concentration in the standard KCl solutions after reagent D was added and diluted. Using the suitable calibration curve and the flame photometer set to 589 and 766.5 nm, respectively, the amounts of sodium and potassium were ascertained.

3. Results and Discussion

3.1. Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra of the GSRF (Gypsum Slow Release Fertilizer) sample are displayed in figure 1. Broad peaks that show up at 3339 and 3450 cm^{-1} are associated with the urea's OH and NH_2 groups stretching vibration. At 1461 cm^{-1}, the v (C–N) frequency band was detected. Furthermore, urea's C=O absorption band showed up as two distinct peaks at 1627 and 1678 cm^{-1} [23, 24]. In addition, the vibrations of OH stretching, P=O stretching, P–OH stretching, and HO–P–OH bending are indicated by the peaks that emerge at 2850 cm^{-1}, 1466 cm^{-1}, 1141 cm^{-1}, and 1098 cm^{-1}, respectively. Furthermore, in a single super phosphate, the absorption peak corresponding to PO_4 vibration was seen at 553 cm^{-1} [25]. The SO_4 groups are thought to be bent asymmetrically in the band seen at 620 cm^{-1}[26].

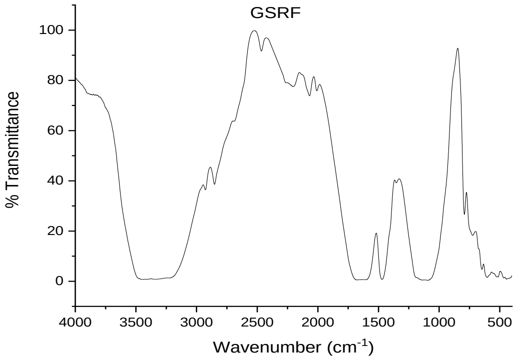


Figure 1: FTIR Spectra of GSSRF (Gypsum slow-release fertilizer)

3.2. Raman Spectroscopy

Figure 2 shows raman spectra of Urea, Single super Phosphate, Potassium sulfate and Gypsum slow-release fertilizer. 545.25, 1007.05, 1174.56, 1467.33, 1538.11, 1574.90, and 1643.40 cm^{-1} peaks are the distinctive peaks of urea [27, 28]. The distinctive peaks of a single superphosphate fertilizer are situated in the 600–1200 cm^{-1} range [29]. For Raman spectra of solid potassium sulfate, the wavenumber range 980.76 cm^{-1} clearly displays the strongest Raman peak. 450.21 cm^{-1} is where the v_2 mode occurs. The range of the triplet v_3 mode is 1107.07-1143.50 cm^{-1}. The 618.26 cm^{-1} is where the v_4 mode is located [30]. Figure 3 shows Raman microscope images of Urea and GSRF.

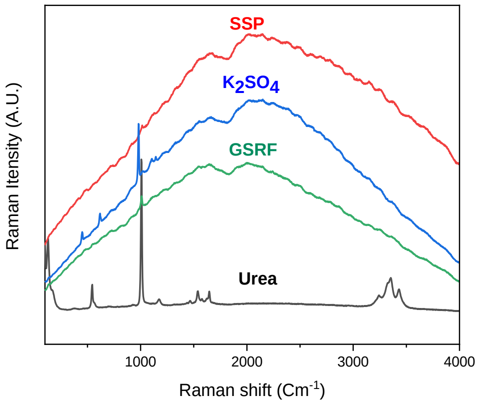


Figure 2: Raman spectra of Urea, SSP (Single super Phosphate), K_2SO_4 (Potassium sulfate) and GSRF (Gypsum slow-release fertilizer).

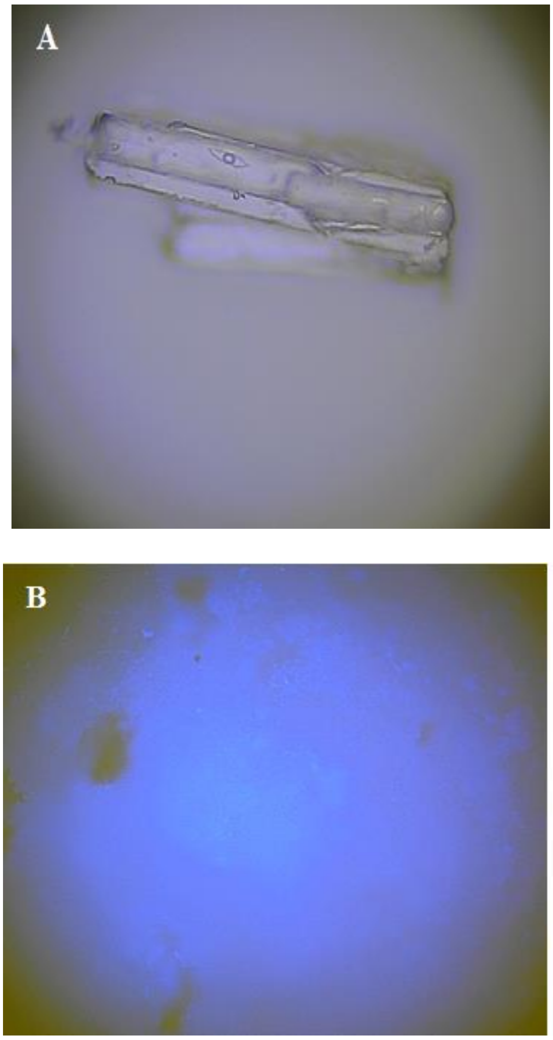


Figure 3: Raman microscope images of (A) Urea and (B) GSRF.

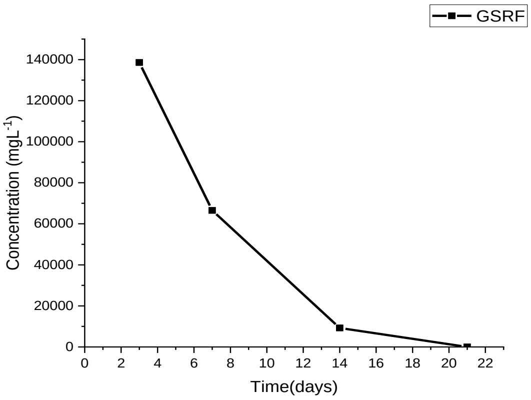
3.3. Evaluation of metal concentrations from commercial and Slow-release fertilizers

The applied extraction agents H_2SO4 and $HClO_4$ measured the leached metal ion values from GSRF (gypsum slow-release fertilizers) and found that the values for nitrogen, potassium, and phosphorus were 220528, 11328, and 63570 mg L^{-1}, respectively.

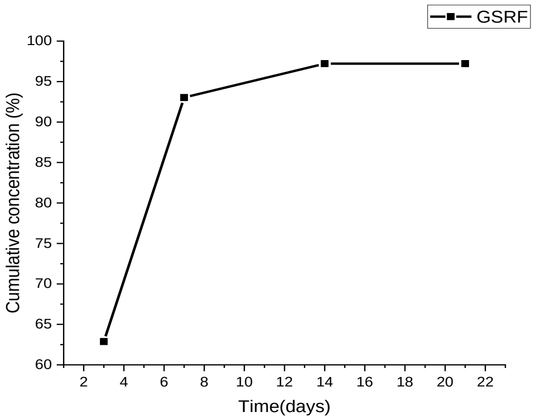
3.4. Slow-release studies

The cumulative nitrogen release rate of gypsum slow release fertilizer is displayed in Figure 4. On the seventh day, the cumulative nitrogen release rate of GSRF was around 93.03%, and on the fourteenth day, it exceeded 97.22%. After seven days, the GSRF's cumulative rate of P releases is 71.99 percent. Fertilizer P release patterns showed an overall downward trend over time. Since the cumulative rate releases for the GSRF were 95.02% of the monitoring time, the full release of P was not measurable at the conclusion of the experiment. For a period of fifteen days, the cumulative rate of K release from GSRF was reported to be 98.49%. K release for GSRF indicated a general decrease over time.

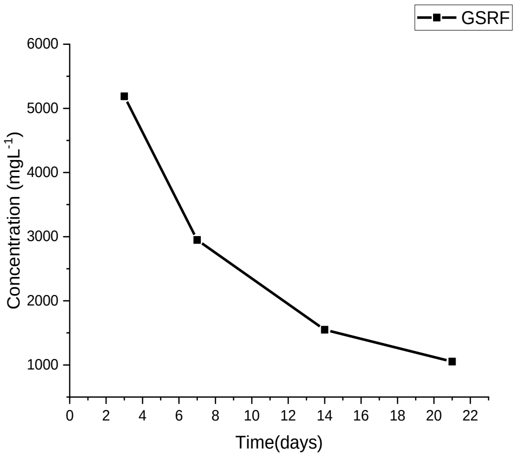
(a) Nitrogen



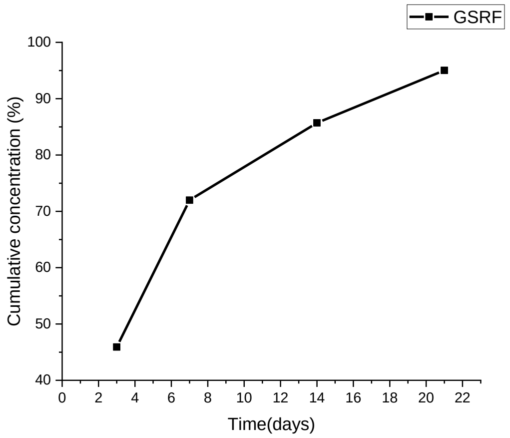
(b) Nitrogen



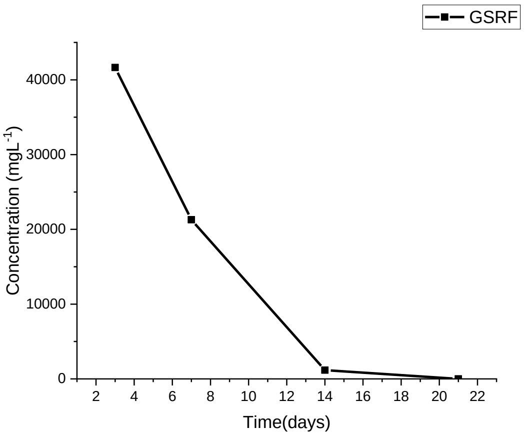
(c) Phosphate



(d) Phosphate



(e) Potassium



(f) Potassium

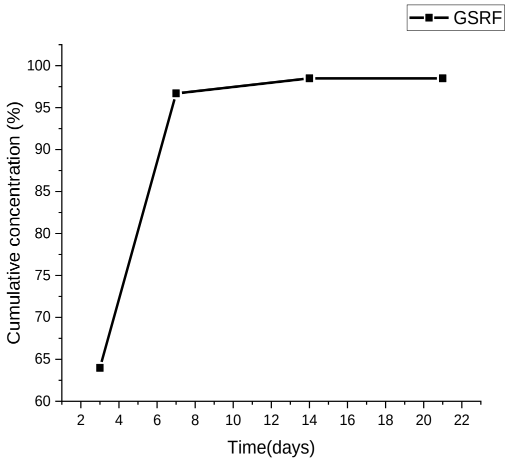


Figure 4: Instantaneous (a, c and e) and cumulative (b, d and f) concentration of Nitrogen, phosphate and potassium released from GSRF (Gybsum slow-release fertilizer) during a 21-day period of sequential leaching.

Conclusion

The nutrient release patterns of a slow-release fertilizer based on gypsum were compared to those of traditional chemical fertilizers. Gypsum was an efficient nutrient carrier for the manufacture of a N–P–K fertilizer, as demonstrated by FTIR and Raman spectroscopy. The slower release of nutrients in the gypsum-based slow release fertilizer suggested that it would be better than traditional chemical fertilizers. Increased crop nutrient use efficiency is implied by the gradual release characteristic, which also suggests decreased nutrient leaching.

4. References

1. Tripathi, A.D., et al (2019)., Estimates for world population and global food availability for global health, in The role of functional food security in global health., Elsevier. p. 3-24.
2. Ciceri, D. and A. Allanore, (2019) .Local fertilizers to achieve food self-sufficiency in Africa. Science of the total environment, **648**: p. 669-680.
3. Sofyane, A., et al., (2021) Slow-release fertilizers based on starch acetate/glycerol/polyvinyl alcohol biocomposites for sustained nutrient release. Materials Today: Proceedings,. **36**: p. 74-81.
4. Majeed, Z., et al., (2015) .A comprehensive review on biodegradable polymers and their blends used in controlled-release fertilizer processes. Reviews in Chemical Engineering, **31**(1): p. 69-95.
5. Davidson, D. and F.X. Gu, (2012) Materials for sustained and controlled release of nutrients and molecules to support plant growth. *Journal of agricultural and food chemistry*,. **60** (4): p. 870-876.
6. Wang, W., et al., (2021) Synthesis of a slow-release fertilizer composite derived from waste straw that improves water retention and agricultural yield. Science of the Total Environment,. **768**: p. 144978.
7. Zhang, Z., et al., (2022).Impacts of fertilization optimization on soil nitrogen cycling and wheat nitrogen utilization under water-saving irrigation. Frontiers in Plant Science, **13**: p. 878424.
8. Pal, A., et al., (2020) .Nitrogen transformation and losses in soil: A cost-effective review study for farmer. International *Journal of Chemical Studies*, **8 (3)**: p. 2623-2626.
9. Singh, U., et al., (2012) Nitrogen transformation, ammonia volatilization loss, and nitrate leaching in organically enhanced nitrogen fertilizers relative to urea. *Soil Science Society of America Journal*,. **76(5)**: p. 1842-1854.
10. Salimi, M., et al., (2023) A comprehensive review on starch: Structure, modification, and applications in slow/controlled-release fertilizers in agriculture. Carbohydrate Polymers,: p. 121326.
11. Liu, G., et al.,(2014).Controlled-Release and Slow-Release Fertilizers as Nutrient Management Tools: HS1255/HS1255, 10/2014. EDIS, **2014** (8).
12. Elhassani, C.E., et al., (2019) Urea-impregnated HAP encapsulated by lignocellulosic biomass-extruded composites: A novel slow-release fertilizer. Environmental technology & innovation,. **15**: p. 100403.
13. Sales, H.B., et al., (2024).Advances in Agricultural Technology: A Review of Slow-Release Nanofertilizers and Innovative Carriers. Communications in Soil Science and Plant Analysis, **55**(12): p. 1849-1882.
14. Sempeho, S.I., et al., (2014) Meticulous overview on the controlled release fertilizers. Advances in Chemistry,. **2014** (1): p. 363071.
15. Wesołowska, M., et al., (2021) New slow-release fertilizers-economic, legal and practical aspects: a Review. International Agrophysics,. **35** (1): p. 11-24.
16. Liu, A., et al., (2022).Single dose fertilization at reduced nitrogen rate improves nitrogen utilization without yield reduction in late-planted cotton under a wheat–cotton cropping system. Industrial Crops and Products, **176**: p. 114346.
17. Watts, D.B. and W.A. Dick, (2014).Sustainable uses of FGD gypsum

in agricultural systems: Introduction. J*ournal of Environmental Qualit*y, **43(1)**: p. 246-252.

18. Zoca, S.M. and C. Penn, (2017) An important tool with no instruction manual: a review of gypsum use in agriculture. Advances in Agronomy,. **144**: p. 1-44.
19. Lubkowski, K., (2016) Environmental impact of fertilizer use and slow release of mineral nutrients as a response to this challenge. *Polish Journal of Chemical Technology*,. **18(1)**: p. 72-79.
20. Qu, J., et al., (2020) Biochar combined with gypsum reduces both nitrogen and carbon losses during agricultural waste composting and enhances overall compost quality by regulating microbial activities and functions. Bioresource technology,. **314**: p. 123781.
21. Tavakkoli, E., et al., (2022) Field applications of gypsum reduce pH and improve soil C in highly alkaline soils in southern Australia's dryland cropping region. Soil Use and Management,. **38** (1): p. 466-477.
22. Genedy, M., A. Ewis, and S. Genaidy, (2018) importance of gypsum, organic manure application and nitrogen, zinc fertilization for wheat crop in saline sodic soils. *Journal of Productivity and Development*,. **23** (2): p. 343-356.
23. Onija, O., et al. (2012).Preparation and characterization of urea-oxalic acid solid form. in AIP Conference Proceedings. American Institute of Physics.
24. Manivannan, M. and S. Rajendran, (2011).Investigation of inhibitive action of urea-Zn^{2+} system in the corrosion control of carbon steel in sea water. *Int. J. Eng. Sci. Technol*, **3(11)**: p. 8048-8060.
25. Laohavisuti, N., et al., (2021).Simple recycling of biowaste eggshells to various calcium phosphates for specific industries. Sci Rep 11: 15143.
26. Periasamy, A., S. Muruganand, and M. Palaniswamy, (2009) Vibrational studies of Na2SO4, K2SO4, NaHSO4 and KHSO4 crystals. *Rasayan J. Chem*,. **2(4)**: p. 981-989.
27. Khan, K.M., et al., (2015) Detection of urea adulteration in milk using near-infrared Raman spectroscopy. Food analytical methods,. **8**: p. 93-102.
28. Flores-Guerrero, J.L., et al., (2020).Novel assessment of urinary albumin excretion in type 2 diabetes patients by Raman spectroscopy. Diagnostics, **10** (3): p. 141.
29. Oliveira, E.M., et al., (2021) Simultaneous determination of phosphite and phosphate in fertilizers by Raman spectroscopy. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy,. **246**: p. 119025.
30. Qiu, J., X. Li, and X. Qi,(2019) Raman spectroscopic investigation of sulfates using mosaic grating spatial heterodyne raman spectrometer. *IEEE Photonics Journal*,. **11**(5): p. 1-12.