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Composition and structural studies of glass fertilizer

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Abstract. Glass fertilizers are new type of advanced and controlled released fertilizer and made of glass matrixes with macro elements most useful for plants and also incorporated with microelements which are important to the growth and development of corps or plants. This study the glasses sample was prepared, which may be used as slow release fertilizer for different type of plant. All of samples were analyzed by using X-ray fluorescence (XRF), X-ray diffraction (XRD) and Fourier Transform Infrared (FTIR). The results of the experiments reported here demonstrate that is possible to adjust the release of phosphate from the fertilizer to phosphate demand of the plant.

1. Introduction

Plants like all other living things need “food” for their growth, development and process of photosynthesis. In addition, there are a lot of more chemical elements that plants cannot live without, and plants typically absorb these elements from their roots. Plants require only light, water, and about 16 elements to support all their biochemical needs. These 16 elements are called essential nutrients. Three of the essential nutrients carbon (C), hydrogen (H), and oxygen (O) are taken up from atmosphere carbon dioxide and water. The other 13 nutrients are taken up from the soil and referred to as primary nutrients, secondary nutrients, and micronutrients [1-4]. The primary nutrients: nitrogen (N), phosphorus (P), and potassium (K) are commonly found in blended fertilizers. Primary nutrients are used in large amounts by crops, and therefore, are applied at higher rates than secondary nutrients and micronutrients [5]. The secondary nutrients: calcium (Ca), magnesium (Mg), and sulphur (S) are required in smaller amounts than the primary nutrients. The major source for supplementing the soil with calcium and magnesium is dolomitic lime (aglime), although these nutrients are also available from a variety of fertilizer sources. Sulphur is available in fertilizers such as potassium and magnesium sulphate, gypsum (calcium sulphate), and elemental sulphur [6]. Micronutrients: iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), boron (B), molybdenum (Mo) and chlorine (Cl) are required in even smaller amounts than secondary nutrients. They are available in manganese, zinc and copper sulphates, oxides, oxy-sulphates and chelates, as well as in boric acid and ammonium molybdate [6].
Table 1. Essential plant nutrients [1]

| Essential nutrients | Uptake form | Function of plant |
|---------------------|-------------|-------------------|
| carbon (C)          | CO₂         |                   |
| hydrogen (H)        | H₂O         |                   |
| oxygen (O)          | O₂, H₂O     |                   |
| **Primary nutrients** |            |                   |
| nitrogen (N)        | NO₃⁻, NH₄⁺  | proteins, protoplasts, enzymes |
| phosphorus (P)      | K⁺          | ATP, ADP, basal metabolism |
| potassium (K)       | H₂PO₄⁻, HPO₄²⁻, PO₄³⁻ | water relations, energy relations, cold hardiness |
| **Secondary nutrients** |            |                   |
| calcium (Ca)        | Ca²⁺        | cell structure, cell division, cell elongation |
| magnesium (Mg)      | Mg²⁺        | chlorophyll, enzymes |
| sulphur (S)         | SO₄²⁻       | proteins, protoplasts, enzymes |
| **Micronutrients**  |             |                   |
| iron (Fe)           | Fe²⁺        | chlorophyll synthesis, metabolism, enzyme activation |
| manganese (Mn)      | Mn²⁺        | hill reaction-photosystem II, enzyme activation |
| zinc (Zn)           | Zn²⁺        | protein breakdown, enzyme activation |
| copper (Cu)         | Cu²⁺        | enzyme activation |
| boron (B)           | H₃BO₃, H₂BO₃⁻, HB O₄²⁻ | sugar translocation, cell development, growth regulators |
| molybdenum (Mo)     | MoO₄³⁻      | nitrogen fixation, nitrogen use |
| chlorine (Cl)       | Cl⁻         | photosynthesis |

Naturally, those plants will die and decompose back into the soil, helping to return all of that much needed nutrients. In farming and gardening, the plants are removed from their location, to be consumed. This means that all of that matter has now exited the soil permanently. Over years of use, soils become less nutritious. To mend this, we add inputs back into the soil. Often times, this is in the form of a fertilizer. Fertilizer is simply a material added to soils or directly to plant tissues that contains nutrients essential to the growth and health of the plant. Usually, this means N, P, and K. These basic elements are usually in the form of chemical compounds that can be converted by the plant to access the needed elements (Table 1) [1]. Use of fertilizer in agriculture is very benefit to the plants, but at the same time it may be very dangerous for the environment. It may cause soil deterioration, greenhouse gas emissions, and water contamination. Slow-releasing fertilizers have long been recognized as the best solution to the various environmental problems caused by traditional water-soluble fertilizers [7,8]. With slow-release fertilizers, dosage requirements are lowered, fertilizer use efficiency is improved and environmental pollution problems are practically eliminated. Glass fertilizers are a new type of advanced and controlled released fertilizer and made of glass matrixes with macro elements (K, P, Mg, S, Ca). There are most useful for the plants and can be incorporated with microelements (B, Fe, Mo, Cu, Zn, Mn) which are important to the growth and development of corps or plants [1,8,9].

The use of glass fertilizers offers a lot of advantages as a result of:

- Low or controlled solubility it avoid underground water pollution; the soil pH can be regulated by the pH of the glass matrix
- None release acid anions(Cl⁻, SO₄²⁻) which are harmful for plants so there is no risk of soil burning when they are incorrectly dosed
In a single type of fertilizer it can be embedded into almost all useful elements for plants.

The controlled rate of solubility in water can be adjusted easily by changing the composition of glass matrix.

The objective of this paper is to present the structural glass fertilizer samples. The structure of the samples has been studied through XRD, XRF and FTIR spectra.

2. Experiment

2.1 Glass preparation

Glass fertilizers were prepared by melt and pouring in the water. The compositions of the samples are listed in Table 2. About 20 g of the batch composition is completely ground using an agate mortar, homogeneously mixed and placed into a porcelain crucible before being melted in a high-temperature furnace. The glass melt become homogenous and then pouring it in water. Finally, remove the samples from the water and dry it as shown in Figure 1.

| Glass codes | Glass composition (mol%) |
|-------------|--------------------------|
| F1          | P₂O₅ 18.24 Na₂O - S 11 K₂O 40.83 CaO 11.51 MnO 0.38 Fe₂O₃ 0.86 CuO 0.01 BaO 0.30 WO₃ 0.39 |
| F2          | P₂O₅ 58 Na₂O - S 10 K₂O 20 CaO 10 MnO 0.5 Fe₂O₃ 0.5 CuO - BaO 1 WO₃ - |
| F3          | P₂O₅ 65 Na₂O 25 S - K₂O - CaO 10 MnO - Fe₂O₃ - CuO - BaO - WO₃ - |
| F4          | P₂O₅ 45 Na₂O 15 S 13 K₂O 15 CaO 10 MnO 0.5 Fe₂O₃ 0.5 CuO - BaO 1 WO₃ - |
| F5          | P₂O₅ 50 Na₂O 10 S 12 K₂O 15 CaO 10 MnO 0.5 Fe₂O₃ 0.5 CuO 0.3 BaO 1 WO₃ 0.4 |

Figure 1. Glass fertilizer samples (a) F1, (b) F2, (c) F3, (d) F4 and (e) F5.
2.2 Characterization
The X-ray diffraction (XRD) measurements of five samples were carried out using a Shimadzu XRD 6100 diffractometer. The X-ray fluorescence (XRF) measurements of five samples were carried out. The element determinations were performed by X-Ray Fluorescence Spectrometer Minipal-4, Panalytical. For Fourier Transform Infrared spectrometry (FTIR) measurements were made to identify the fundamental stretching vibrations. The spectra were obtained using a Fourier transform infrared spectrometer model IRAffinity, manufactured by Shimadzu, with a resolution in the wavenumber range 500–5000 cm$^{-1}$ after 45 scans, using the transmittance mode.

3. Results and discussion

3.1 XRD analysis
The structure and crystalline of glass fertilizer samples were studies. XRD pattern of the samples were recorded in the range of $10^\circ \leq \theta \leq 80^\circ$. As shown in Figure 2 for F1, the $2\theta$ angles peaks of 23.7°, 30.3°, 32.5°, 37.7°, 39.6° and 45.0° were observed in potassium calcium phosphate. For the samples of F2, F3, F4 and F5, the diffraction pattern of the samples does not exhibit any detectable peak. This pattern indicates that glass fertilizer samples are amorphous in nature and have non-crystalline structure.

![Figure 2. XRD patterns of glass fertilizer samples difference composition.](image)

3.2 XRF analysis
The compositions of major elements along with other elements present in all samples were measured by X-ray fluorescence (XRF) analysis as shown in Table 3. The major element concentrations of glass fertilizer samples were Na$_2$O (24.96–28.36%), P$_2$O$_5$ (29.49–74.02%), K$_2$O (10.27–24.63), CaO (26.31–6.95%), Fe$_2$O$_3$ (0.58–6.90%), BaO (1.93–2.00%). The highest concentration of Na$_2$O over 20% was found in F3 and F4 and no concentration was found in F1, F2 and F5. The concentration P$_2$O$_5$ over 20% was found all of glass fertilizer samples. The highest concentration of K$_2$O was found in F1 and lowest concentration was found in F4, F5 and F2, respectively. The highest concentration of CaO was F1 (over 20%) and lowest concentration was found in F4, F3, F2 and F5, respectively. And the lowest concentration of Fe$_2$O$_3$ and BaO were observed all of glass fertilizer samples.
Table 3. XRF composition of glass fertilizer samples difference composition

| Composition (%) | F1   | F2   | F3   | F4   | F5   |
|-----------------|------|------|------|------|------|
| Si2O            | 9.74 | -    | -    | -    | -    |
| Na2O            | -    | 24.96| 28.36| -    | -    |
| P2O5            | 29.49| 73.10| 69.31| 54.73| 74.02|
| K2O             | 24.63| 17.41| -    | 10.27| 14.04|
| CaO             | 26.31| 6.47 | 5.73 | 4.59 | 6.95 |
| MnO             | 0.63 | 0.27 | -    | 0.18 | 0.26 |
| Fe2O3           | 6.90 | 0.91 | -    | 0.58 | 0.90 |
| BaO             | 2.00 | 1.83 | -    | 1.30 | 1.93 |
| CuO             | 0.02 | -    | -    | -    | 0.26 |
| ZnO             | 0.19 | -    | -    | -    | 0.30 |
| SrO             | 0.03 | -    | -    | -    | -    |
| TiO2            | 0.06 | -    | -    | -    | -    |
| WO3             | -    | -    | -    | -    | 1.34 |
| SO3             | -    | 0.01 | -    | -    | -    |

3.3 FTIR analysis

Figure 3. FTIR spectra of glass fertilizer samples difference composition.
Figure 3 shows the FTIR spectra of glass fertilizer samples difference composition. In the IR spectra consists many bands for samples observed at ~720-2800 cm\(^{-1}\). The IR bands recorded 723, 737, 761, 869, 874 and 876 cm\(^{-1}\) are attributed to the symmetric of P-O-P group, and the peak at 991 and 958 cm\(^{-1}\) corresponds to asymmetric stretching vibration [10,12]. The peak at 1108 and 1085 cm\(^{-1}\) are assigned to PO\(_3\) while, 1253 and 1254 cm\(^{-1}\) are assigned to PO\(_2\) asymmetric stretching vibrations [11-12]. The peak at 1634, 1637, 1645 and 1647 are assigned to the mode of vibration of OH bending. The IR bands between 2121 and 2798 cm\(^{-1}\) may be due to the air moisture formed during the preparation of the samples which belongs to symmetric vibrations of O-H and H-O-H groups [12-15].

4. Conclusion
Glass fertilizers were prepared by melt and pouring in the water. The structure of the samples has been studied through XRD, XRF and FTIR spectra. For study the XRD pattern of the F1 were recorded in potassium calcium phosphate and for the samples of F2, F3, F4 and F5, the diffraction pattern of the samples does not exhibit any detectable peak. This pattern indicates that glass fertilizer samples are amorphous in nature and have non-crystalline structure. The XRF analysis shown the major element concentrations in glass fertilizer samples were Na\(_2\)O, P\(_2\)O\(_5\), K\(_2\)O, CaO, Fe\(_2\)O\(_3\) and BaO. The FTIR spectra of glass fertilizer samples difference composition shows difference the IR bands. The study of the structure of glass fertilizer. It can be used as a basis for release studies and other properties to development glass fertilizer.

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