

Agronomic potential of two different glass-based materials as novel inorganic slow-release iron fertilizers

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Abstract

BACKGROUND: Large amounts of chemical fertilizers are still currently used to compensate the soil nutrients scarcity in order to increase and sustain crop yield with consequent rising of environmental pollution and health problems. To mitigate these environmental risks, fertilizers with slow-release behaviours have been developed. The aim of this study was to assess the agronomic potential of two different glass-based materials (by-products from the ceramic sector) as inorganic slow-release iron (Fe) fertilizers.

RESULTS: The X-ray powder diffraction confirmed the presence of amorphous structure and the richness in Fe of the investigated materials. The solubility analysis highlighted the slow Fe release from the glassy network and that the maximum of the Fe release was at alkaline pH suggesting their potential use as slow-release Fe fertilizers, especially in calcareous soils. The pot and leaching experiments demonstrated that although the glass-based materials increased the amount of soil available Fe, we did not observe Fe leaching and plant toxicity. This fact would suggest their reliability to increase soil fertility without negative effects on the environment.

CONCLUSION: The use of glass-based materials, specifically by-products from the ceramic sectors, as inorganic slow-release Fe fertilizers can be sustained. The tests performed at three different pH conditions testified the slow-release behaviour of the tested materials and underlined that the Fe release increases at alkaline environment. Therefore, the present study pointed out the glass-based materials by products from the ceramic sector as novel slow-release and environmental-friendly fertilizers in agriculture.

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Keywords: ceramic frits; slow-release fertilizers; amorphous structure; leaching; pot experiment

INTRODUCTION

Plants growth is strictly connected to mineral nutrition and water availability. Until today, to increase and sustain an optimal crop yield, large amounts of diverse fertilizers have been applied to the soil which has given rise to environmental pollution and health problems.¹⁻³ Therefore, in a view of rising resource scarcity and environmental preservation, the development of environmentally-friendly fertilizers is necessary. To mitigate these environmental risks, fertilizers with slow-release behaviours have been developed.⁴ Slow-release fertilizers (SRFs) are a class of water-insoluble/partially soluble materials ideally capable to release nutritive elements on plant's requirements^{5,6}; additionally, any excess of nutrients persists in the soil for the next plant's need. Their application has a considerable ecological effect due to the fact that plants and animals do not assimilate the toxic

concentration, whereas the utilization of chemical fertilizers could cause soil and water pollution.⁷ Among the SRFs,⁸ several glass-based materials have been successfully investigated as environmentally-friendly fertilizers.^{9,10} Indeed, concerning their

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chemical and structural features, the glass-based materials can include into their structure a wide range of nutrients, such as silicon (Si), phosphorus (P), magnesium (Mg), calcium (Ca), potassium (K), iron (Fe) and other metals, which coexist together in an oxide glass structure.^{11–13}

It is known that the glass solubility in water is low but it can be enhanced by changing both the chemical composition and the granularity of the final product, to such an extent that the glassy network could act as a carrier of nutrient elements over time in relation to the conditions of the soils (pH, humidity, temperature) in which the glass is dispersed.

On the basis of these considerations, the chemical and structural features of glass-based materials make them interesting SRFs as a possible substitute of the chemical fertilizers whose consumption is still increasing¹⁴; furthermore, interesting agronomic products can be obtained by including specific nutrients in the glassy network. For example, a glass-containing Fe could be useful for treating Fe chlorosis diseases. Focusing on Fe, it is the third-most limiting element for plant growth due to the low solubility in soils with high pH, high electrical conductivity and presence of free carbonates.¹⁵ Currently, the common Fe fertilizers used in agriculture include chelated-Fe fertilizer, inorganic-Fe fertilizer and organic-Fe fertilizer. The chelated-Fe fertilizers are the most expensive, effective and commonly used.¹⁶ Whereas, the soluble inorganic-Fe fertilizers and the organic-Fe fertilizers weakly increase the Fe availability because the former does little to improve the available Fe content in alkaline calcareous soils, and the latter is readily adsorbed onto soil particles.¹⁷

The aim of this study was to assess the agronomic potential of two different glass-based materials, (by-products from the ceramic sector) as inorganic slow-release Fe fertilizers. In fact, the selected materials comprised, among the modifier oxides, iron(II) oxide (FeO); furthermore, they were heavy metal-free.

The selected glass-based materials were synthesized recycling the waste products of the ceramic sector by mixing them with other mineral components for a percentage of 30% avoiding their disposal in landfills.

MATERIALS AND METHODS

Characterization of the glass-based materials

Two different ceramic frits (hereafter: CF1 and CF2; frit refers to ceramic composition that has been fused, quenched, and granulated), as by-products from the ceramic sector, were selected and used without further purification (patented WO2018114671 – Plant protection product in the form of a frit). Their chemical composition as claimed by SICER s.p.a., the ceramic company which kindly provided the selected frits, is reported in Table 1.

Before use, CF1 and CF2 were finely ground and the particles size of the resulting powders was determined by dynamic light

scattering (DLS) measurements (Nicom 380 ZLS (PSS, CA), equipped with a HeNe laser source at 632.8 nm). The structural features of CF1 and CF2 were determined by X-ray powder diffraction (XRPD) analysis (D8 Advance equipped with LynxEye detector, Bruker, Karlsruhe, Germany) and the quantification of the mineral phases (QPA) was performed using the Rietveld method.

By means of gravimetric assay, the solubility of CF1 and CF2 was evaluated in citrate buffer at three different pH values which mimic the pH of acid (pH 5.70), neutral (pH 7.00) and alkaline (pH 8.30) soils (solutions prepared as reported in Gaudiano and Guadiano¹⁸). Specifically, 0.20 ± 0.01 g of each CF were shaken in 20 mL of citrate buffer at the selected pH value at room temperature (25 °C) for 1, 3, 5, 7, 14 and 28 days; at the predetermined time, the samples were centrifuged and supernatants analysed by inductively coupled plasma optical emission spectrometry (ICP-OES, 5100 Agilent Technologies, Santa Clara, CA, USA; see Table S1 of Supporting Information for instrumental details) to determine solubilized Fe; the residue solids were rinsed three times with distilled water to remove any trace of citrate buffer, and weight losses were determined after drying in an oven at 90 °C for 24 h. Each measurement was performed in three replicates. The collected data were expressed as percentage of solid weight loss (% weight loss), calculated as reported in Eqn (1):

$$\% \text{weight loss} = \frac{\text{weight}_{\text{initial}} - \text{weight}_{\text{residue}}}{\text{weight}_{\text{initial}}} \times 100 \quad (1)$$

where $\text{weight}_{\text{initial}}$ represents the weight (in grams) of CF1 or CF2 before being shaken in citrate buffer; $\text{weight}_{\text{residue}}$ represents weight (in grams) of CF1 or CF2 after being shaken in citrate buffer and successively rinsed in water and dried at 90 °C.

Glasshouse and leaching experiments

The soil used for the glasshouse experiment and Fe leaching was collected from 0 to 20 cm soil layer in a wheat field. The soil was air-dried at room temperature, ground, and passed through a 4 mm sieve.

The soil had a silty clay texture (120 g kg⁻¹ sand, 460 g kg⁻¹ silt and 420 g kg⁻¹ clay), 14.0 g kg⁻¹ of total organic carbon (C), 0.8 g kg⁻¹ of total nitrogen (N), 300 g kg⁻¹ of calcium carbonate (CaCO₃), a pH of 8.25, 266 mg kg⁻¹ of available K, 53 mg kg⁻¹ of available P and a cation exchange capacity of 17.52 cmol(+) kg⁻¹.

Each CF was mixed with soil at a rate of 10, 20 and 40 g kg⁻¹ by weight and 2 L pots (diameter: 15 cm, height: 14 cm) were filled with the soil–CF mixtures. For the glasshouse experiment, the pots were planted with kiwi (*Actinidiadelicosa* A. Chev. cultivar Hayward clone 8), courgette (*Cucurbita pepo* L. cultivar Colosseo) and melon (*Cucumismelo* L. cultivar cantalupensis). The pots planted with kiwi were incubated for 90 days, while those with melon were incubated for 21 days. During the incubation the plants were irrigated with distilled water without the addition of

Table 1. Ceramic frit 1 (CF1) and ceramic frit 2 (CF2) chemical composition, as claimed by SICER s.p.a. company

Material	Chemical composition (weight %)					
	SiO ₂	P ₂ O ₅	MgO	CaO	K ₂ O	FeO
CF1	30	8	3	5	13	41
CF2	25	10	4	6	15	40

Silicon dioxide (SiO₂), phosphorus pentoxide (P₂O₅), magnesium oxide (MgO), calcium oxide (CaO), potassium oxide (K₂O) and iron(II) oxide (FeO).

any fertilizer. Each treatment, including the control, was performed in four replicates. At the end of the experiment, the plant leaves were collected and dried in a forced-draft oven at 60 °C for 48 h and finely ground. The soils were air-dried and sieved through a 2 mm sieve.

For the Fe leaching, the experiment was conducted without plants and the bottom of the pots were covered with a Whatman 42 filter paper to prevent soil loss. Before starting the Fe leaching experiment, distilled water was added from the top in order to have a homogeneously moistened soil at field capacity of 36.7% w/w. During the leaching period, an amount of 100 mL distilled water was applied from the top of each pot at 2, 3, 5, 8, 12, 19 and 26 days after the soil homogenization at water holding capacity.

Plant leaves, soil, ceramic frits and leachate analysis

About the analysis of total Fe in plant leaves, 0.25 ± 0.01 g of each finely ground sample, with additions of 8 mL of concentrated nitric acid (HNO₃) (65% v/v; Carlo Erba, Milan, Italy) and 2 mL of hydrogen peroxide (H₂O₂) (30% v/v, Carlo Erba), was microwave digested (ETHOS One high-performance microwave digestion system; Milestone Inc., Sorisole, Bergamo, Italy). The digested solutions were filtered using a 0.45 µm filter and diluted to 20 mL with distilled water.

Soil available Fe was extracted with 0.005 mol L⁻¹ DTPA [diethylenetriaminepentaacetic acid +0.1 mol L⁻¹ triethanol amine +0.01 mol L⁻¹ calcium chloride (CaCl₂)] at 1:2 soils to extract ratio, shaken for 2 h and filtered by Whatman 42 filter paper. The same procedure has been performed on the CFs to extract the potential

available Fe. We used DTPA extraction also for the CFs because it is a suitable method for neutral and near-alkaline soils which mimics the Fe mobilization strategies used by plant roots.^{19,20}

Iron concentration in soil and CF extracts, plant filtrates and in soil leachates, was recorded by atomic absorption with a Shimadzu AA-6800 spectrophotometer (Tokyo, Japan; see Table S2). The chemical analysis of total Fe in plants were validated by including plant reference material (Standard Reference Material 1573a Tomato Leaves; mean recovery rate 96%).

Statistical analysis

The results were expressed as means and standard errors. Statistical analysis was performed using R software 4.0.5. Two-way analysis of variance (ANOVA) was performed to assess the effect of CFs and their doses on Fe content in soil DTPA-extracts and in plant leaves. Tukey's *post hoc* test (*P* < 0.05) was used for comparison among treatment means.

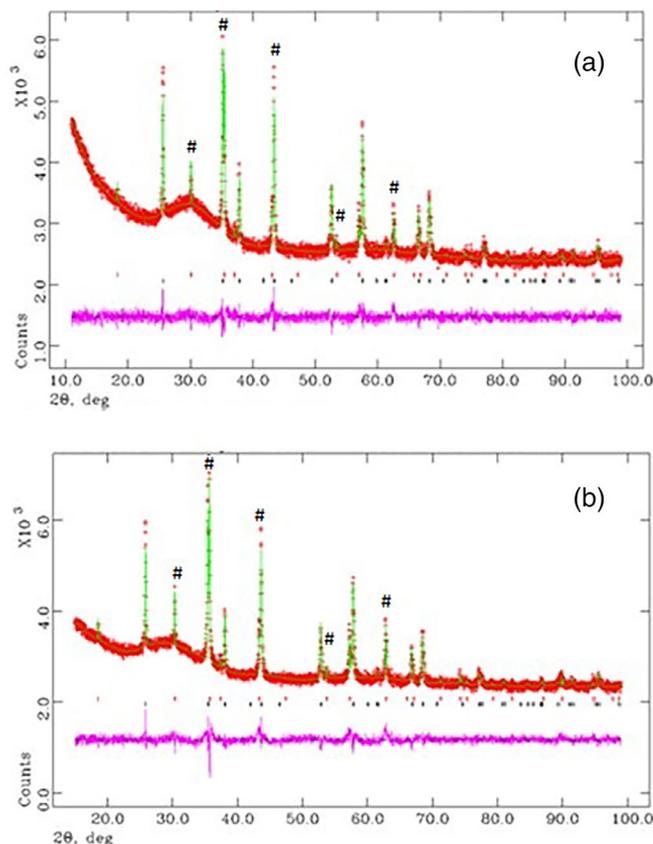


Figure 1. X-ray powder diffraction Rietveld refined patterns of ceramic frit 1 (CF1) (a) and CF2 (b). # indicates the peaks of magnetite (Fe₂O₃).

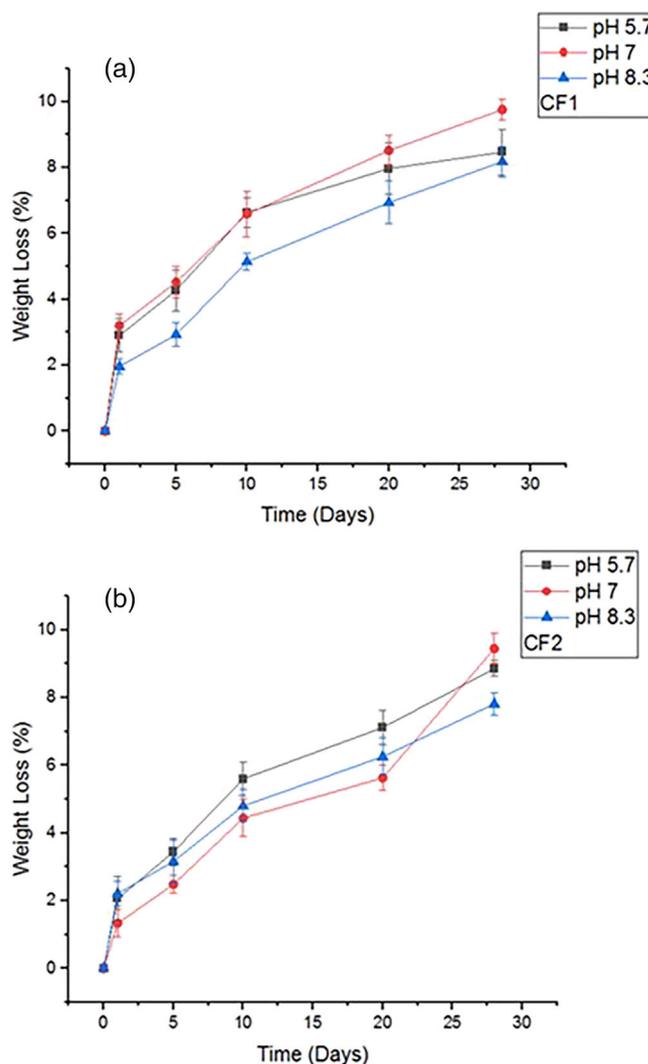


Figure 2. Weight loss profiles of ceramic frit 1 (CF1) (a) and CF2 (b) during 28-days solubility experiments in citrate buffer. Measurements were carried out at room temperature and at three different pH values which mimic the pH of soils: pH 5.7 (square), pH 7 (circle) and pH 8.3 (triangle). The collected data are reported as mean of three measurements ± standard deviation.

RESULTS AND DISCUSSIONS

The chemical composition (referred as the starting mixture of raw materials) of the selected CF1 and CF2 comprises a vitreous matrix made of silicon dioxide (SiO₂) and phosphorus pentoxide (P₂O₅) as glass forming oxides together with magnesium oxide (MgO), calcium oxide (CaO), potassium oxide (K₂O), sodium oxide (Na₂O) and FeO as network modifier oxides (Table 1). The particles size of the powders of both ceramic frits was comprised in the range 0.09–0.30 mm.

The XRPD patterns of CF1 (Fig. 1(a)) and CF2 (Fig. 1(b)) confirmed the amorphous structure of glass (broad diffraction band observed in the range $20 < 2\theta$ (degree) < 35) and, more interestingly, revealed a small fraction (3% approximately) of magnetite (Fe₂O₃) as crystalline phase (JCPDS file No. 85-1436, signal #). The other detected peaks belong to the internal standard used, that is alumina. Due to the chemical and structural features described earlier, CF1 and CF2 look interesting as slow-release fertilizers, since the water solubility of glass is poor. Consequently, the release of macro (Mg, K, Ca, P) and micro (e.g. Fe) nutrients, as well as the beneficial element Si, from the vitreous matrix could occur at low rate depending on pH, temperature and granularity of the manufactured product.^{21,22} Additionally, these CFs are rich in Fe, so they could be interesting materials as slow-release Fe fertilizers for treating Fe-chlorosis diseases. As shown in Fig. 2, solubility data, expressed as percentage of weight loss, indicate that CF1 and CF2 are poorly soluble in aqueous medium (solubility values up to 10% of the initial weight within 28 days).

Accordingly, the Fe analytical determination performed on the supernatants showed that the gradual dissolution of CF1 and CF2 led to a slow Fe release from the glassy network (Fig. 3).

As shown in Fig. 3, both CF1 and CF2 gradually released Fe over time. Interestingly, the maximum of the Fe release is observed at alkaline pH, thus suggesting their potential use as Fe slow-release solids, especially in calcareous soils. This result is very interesting in view of their potential application for treating Fe-chlorosis disease in Fe-deficient calcareous soils.

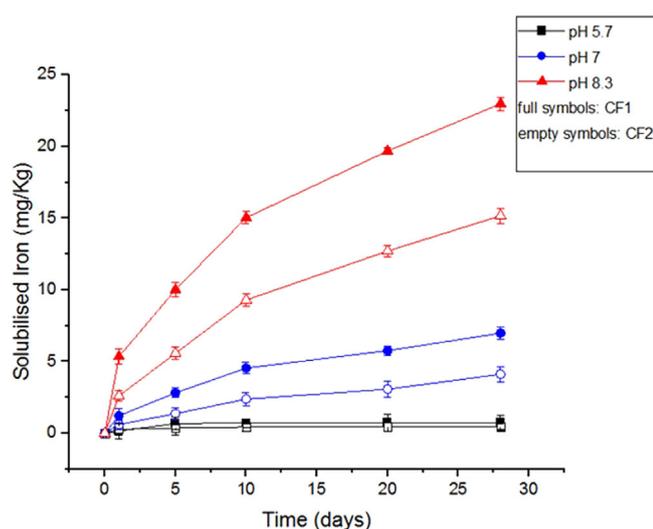


Figure 3. Iron (Fe) solubilization profile (the amount of solubilized Fe is expressed as milligrams of Fe released per kilogram of ceramic frit) at room temperature by varying pH values: pH 5.7 (square), pH 7 (circle), pH 8.3 (triangle). The collected data are reported as mean of three measurements \pm standard deviation. Full symbols refer to ceramic frit 1 (CF1), empty symbols refer to ceramic frit 2 (CF2).

The fraction of the released Fe with respect to the initial weight of the solid can be calculated by combining the weight losses of the solid matrices with the solubility data of Fe: at day 28, CF1 and CF2 released Fe up to 0.23 and 0.15% by weight at pH 8.30, respectively. It can be observed that no appreciable differences in weight losses occur at the three different pH values, while the amount of solubilized Fe is higher at alkaline pH with respect to acid or neutral pH. This fact could be attributed to different glass dissolution mechanisms, which strongly depend on glass formulation, pH value and temperature as reported in Strachan²² that verified for silicate glasses a higher dissolution rate for solution with pH value around 8 and higher.

It is known that Fe-deficiency in plants is most often a matter of availability rather than quantity; furthermore, Fe availability is strictly related to mineralogy and geochemistry of Fe in soil.²³ The obtained results showed that Fe uptake in plants did not change among the treatments, while some differences occurred for the soil available Fe (Tables 2 and 3).

As reported in Table 2, the higher available Fe content in treated soils than in the control ones suggests that both the CFs could be an important Fe source in alkaline soils. Specifically, the DTPA extractable Fe concentration in pristine CF1 was 178

Table 2. Soil available iron (Fe) content in the control and in the ceramic frit treated pots. The pots were planted with kiwi (*Actinidiadelicosa* A. Chev. cultivar Hayward clone 8), courgette (*Cucurbita pepo* L. cultivar colosseo) and melon (*Cucumis melo* L. cultivar cantalupensis)

Amendment	Dose (%)	Kiwi (ppm)	Courgette (ppm)	Melon (ppm)
CF1	1.0	25.67 (2.81) cd	18.94 (2.67) b	21.97 (2.78) b
CF1	2.0	35.70 (1.46) ab	34.43 (3.53) ab	36.70 (1.36) a
CF1	4.0	39.23 (2.81) ab	36.66 (2.76) a	40.15 (3.78) a
CF2	1.0	31.53 (0.71) bc	31.43 (3.17) a	33.93 (2.47) a
CF2	2.0	31.75 (1.49) ac	40.01 (1.38) a	35.79 (2.12) a
CF2	4.0	41.14 (2.39) a	44.23 (4.13) a	28.76 (1.85) ab
Control		21.22 (1.54) d	11.11 (0.37) c	12.34 (0.37) c

The results are described in terms of the average of four replicates (\pm standard error) and, within each column, those sharing the same letters are not significantly different from each other (Tukey's HSD, $P < 0.05$). Ceramic frit 1 (CF1), ceramic frit 2 (CF2).

Table 3. Iron (Fe) content in plant leaves of kiwi (*Actinidia deliciosa* A. Chev. cultivar Hayward clone 8), courgette (*Cucurbita pepo* L. cultivar colosseo) and melon (*Cucumis melo* L. cultivar cantalupensis) grown in control pots and in pots amended with ceramic frits

Amendment	Dose (%)	Kiwi (ppm)	Courgette (ppm)	Melon (ppm)
CF1	1.0	86.20 (9.80) a	153.55 (42.45) a	78.92 (15.87) ab
CF1	2.0	83.20 (13.22) a	79.15 (15.78) a	86.06 (0.27) ab
CF1	4.0	68.41 (15.03) a	90.70 (15.81) a	114.99 (53.95) a
CF2	1.0	84.49 (12.34) a	113.02 (90.93) a	68.59 (10.79) ab
CF2	2.0	82.77 (16.40) a	73.40 (3.13) a	66.88 (11.40) ab
CF2	4.0	98.71 (19.07) a	101.79 (28.78) a	75.98 (12.23) ab
Control		86.64 (27.74) a	101.91 (26.68) a	51.79 (8.69) b

The results are described in terms of the average of four replicates (\pm standard error) and, within each column, those sharing the same letters are not significantly different from each other (Tukey's HSD, $P < 0.05$). Ceramic frit 1 (CF1), ceramic frit 2 (CF2).

$\pm 1 \text{ mg kg}^{-1}$ and in pristine CF2 was $155 \pm 5 \text{ mg kg}^{-1}$; the higher content of DTPA extractable Fe in CF1 than in CF2 could be attributed to the slightly higher amount of soluble Fe in CF1 (Fig. 3). More interestingly, we did not find Fe in the leachates of the CF treated soils (or the Fe amount was below the limit of detection) and this result is important in view of the CFs application as SRFs. Concerning the Fe content in plant leaves, no significant differences were observed among the different treatments (Table 3).

This result could be mainly ascribed to: (i) the available Fe content of the soil used already satisfied the Fe domain of the plants for the whole duration of the experiment, as a consequence the plants used in the experiment were not affected by Fe-chlorosis; (ii) the CF-to-soil ratio, in which the amount of CF (consequently, the Fe available fraction) was too low to contribute to a significant (and detectable) Fe uptake in plant tissues. In the future advancements of this work, these findings suggest to carry out a long-term experiment as well as the use of a CF-to-soil ratio higher than 4% by weight; furthermore, Fe hyperaccumulator plants could be useful in this type of study.

CONCLUSION

The use of glass-based materials, specifically by-products from the ceramic sectors as inorganic slow-release Fe fertilizers can be sustained. The tests performed at three different pH conditions testify it and underline that the release increases at alkaline environment. The chemistry of the glass matrix seems to influence the element release, in our case, Fe. It is also noted that the released amount of Fe is more in the first week, as verified in all of the tested pH values, specifically at alkaline conditions. Finally, our findings would indicate that the tested materials could be considered effective and novel Fe fertilizers. In fact, beside showing an effective increase of soil available Fe, the novelty of the proposed materials was the re-use of waste materials of industrial sector during the synthetization process. Moreover, the tested glass-based materials could be further improved in order to be source of other nutrients such as P, Mg and K.

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SUPPORTING INFORMATION

Supporting information may be found in the online version of this article.

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