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Comissão 3.2 - Corretivos e fertilizantes

PHYTOAVAILABILITY OF COPPER IN INDUSTRIAL BY-PRODUCTS AND MINERAL FERTILIZERS

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ABSTRACT

Alternative copper (Cu) sources could be used in fertilizer production, although the bioavailability of copper in these materials is unknown. The objective of this study was to evaluate the extractants neutral ammonium citrate (NAC), 2 % citric acid, 1 % acetic acid, 10 % HCl, 10 % H₂SO₄, buffer solution pH 6.0, DTPA, EDTA, water, and hot water in the quantification of available Cu content in several sources, relating them to the relative agronomic efficiency (RAE) of wheat grown in a clayey Latossolo Vermelho eutrófico (Oxisol) and Neossolo Quartzarênico (Typic Quartzipsamment). Copper was applied at the rate of 1.5 mg kg⁻¹ as scrap slag, brass slag, Cu ore, granulated copper, and copper sulfate. The extractants 10 % HCl, 10 % H₂SO₄, and NAC extracted higher Cu concentrations. The RAE values of brass slag and Cu ore were similar to or higher than those of Cu sulfate and granulated Cu. Solubility in the 2nd NAC extractant, officially required for mineral fertilizers with Cu, was lower than 60 % for the scrap slag, Cu ore, and granulated copper sources. This fact indicates that adoption of the NAC extractant may be ineffective for industrial by-products, although no extractant was more efficient in predicting Cu availability for wheat fertilized with the Cu sources tested.

Keywords: extractants, industrial waste, micronutrients, *Triticum aestivum*, X-ray diffraction.

RESUMO: FITODISPONIBILIDADE DE COBRE EM MATERIAIS SECUNDÁRIOS E FERTILIZANTES MINERAIS

Fontes alternativas de cobre (Cu) podem ser opção na produção de fertilizantes, porém a fitodisponibilidade do cobre nesses materiais é desconhecida. O objetivo deste trabalho foi avaliar os extratores citrato neutro de amônio (CNA), ácido cítrico 2 %, ácido acético 1 %, HCl 10 %, H₂SO₄ 10 %, solução tampão pH 6,0, DTPA, EDTA, água e água quente na quantificação do teor de Cu disponível em diversas fontes, confrontando com índices de eficiência agrônômica (IEA) para o trigo cultivado em Latossolo Vermelho eutrófico de textura argilosa e em Neossolo Quartzarênico. A dose de Cu aplicada foi 1,5 mg kg⁻¹ como escória de sucata, escória de latão, minério de Cu, cobre granulado e sulfato de cobre. Os extratores HCl 10 %, H₂SO₄ 10 % e CNA extraíram os maiores teores de Cu. A escória de latão e o minério de Cu apresentaram valores de IEA semelhantes ou superiores ao sulfato e cobre granulado. A solubilidade no extrator CNA, exigida oficialmente para fertilizantes minerais contendo Cu, foi inferior a 60 % para as fontes escória de sucata, minério de Cu e Cu granulado. Esse fato indica que a adoção do extrator CNA pode não ser eficiente para materiais secundários, porém nenhum dos extratores evidenciou melhor desempenho na previsão da disponibilidade do Cu para o trigo adubado com as fontes de Cu avaliadas.

Palavras-chave: difratometria de raios-X, extrator, micronutrientes, resíduos industriais, Triticum aestivum.

INTRODUCTION

In agriculture in the United States and some countries in Europe, industrial by-products have been used for decades as nutrient sources and as a cheap way of recycling materials (Tóth et al., 2013). In Brazil, this practice has been discussed by the fertilizer production sector and the Ministério da Agricultura, Pecuária e Abastecimento [Ministry of Agriculture] (MAPA) and the Ministério do Meio Ambiente [Ministry of the Environment] (MMA). The commercial sector has an interest in regulating these materials to enable their use in fertilizer production. The level of contaminants contained in these secondary sources/by-products is the main concern of the MMA, whereas their agronomic efficiency is also being questioned by the MAPA.

In Brazil, industrial by-products, called secondary materials, in addition to containing considerable amounts of micronutrients such as copper (Cu) and zinc (Zn), are cheaper than the traditional sources authorized by MAPA (Brasil, 2007a). The industrial by-products containing Cu available on the market are brass slag, a by-product generated in the production of brass and bronze alloys, and scrap slag, a by-product derived from melting scrap metal. In these materials, Cu is present predominantly in the form of oxides (Gomide, 2009). Copper ore is raw material approved of for production of mineral fertilizers (Brasil, 2007a). For fertilizer use, there must be prior processing of this source and the Cu ore should contain at least 8 % of Cu extracted in HCl (Brasil, 2007a).

Government Decree 8059 (July 26, 2013, Brasil, 2013) requires previous authorization from MAPA for the use of secondary materials for fertilizer production. Obtaining this license requires a

description of the waste-generating process, the chemical and physical characterization, and an environmental impact assessment of its use, issued by the competent environmental agency. When secondary material is sold to farmers for direct soil application, in addition to the previous conditions, a technical examination and evaluation by an official research institution must attest to its efficiency in agriculture. However, little is known about the bioavailability of micronutrients contained in these materials and their agronomic efficiency.

For mineral fertilizer with Cu, the minimum solubility requirement is 60 % of total Cu by concentrated HCl in the extractant neutral ammonium citrate+water 1:1 (Brasil, 2007a). This extractant was selected based on studies that showed its good performance in predicting Cu availability to rice plants (Vale and Alcarde, 1999, 2003; Bastos et al., 2007a). However, for secondary materials and ores containing Cu, the law requires only a declaration of the levels determined in HCl (Brasil, 2007b). In other words, the bioavailability of Cu contained in these sources is unknown, as well as their behavior in the soil, since no chemical extractants were tested for this determination. Furthermore, little is known about the chemical composition of Cu compounds in these industrial by-products.

The purpose of this study was to chemically characterize the Cu minerals contained in industrial by-products, ore, and mineral fertilizers; evaluate the capacity of the extractants NAC+water 1:1, 2 % citric acid, 1 % acetic acid, 10 % HCl, 10 % H₂SO₄, buffer solution at pH 6.0, 50 mmol L⁻¹ DTPA, 5 mmol L⁻¹ EDTA, water, and hot water in quantifying available Cu; and compare the results of agronomic efficiency of these sources in wheat plants cultivated in pots and grown in a greenhouse.

MATERIAL AND METHODS

Mineralogical characterization of Cu sources and Cu contents extracted

In this part of the study, we used samples of industrial by-products, Cu ore, granulated fertilizer, and material that are marketable as raw material and fertilizer (Cu sulfate). The chemical characterization of these sources is shown in table 1. The samples were quartered, ground and sieved through an ABNT standard 20 mesh (0.84 mm) (Brasil, 2007b).

Mineralogical characterization was performed by X-ray diffraction using a Shimadzu XRD-6000 device with an iron tube and graphite monochromator. Measurements were programmed at a speed of 2°/min in the range 5-70° (2 θ). The resulting X-ray diffractograms were interpreted using Jade software.

Three replications were used to determine the total and soluble Cu contents in the extractants, and in each battery of tests, one blank control. The extractants tested for their ability to extract Cu from sources were neutral ammonium citrate+water 1:1 and 2 % citric acid, both methods according to Brasil (2007b); 10 % H₂SO₄ (Bastos et al., 2007b); 10 % HCl (Souza et al., 2013); 1 % acetic acid (Gallo, 1954); 0.24 mol L⁻¹ buffer solution Bis (hydroxymethyl) - 2,2,2'-nitrilotriethanol (C₈H₁₉NO₅) pH 6.0 (FDACS, 2013); 50 mmol L⁻¹ diethylenetriaminepentaacetic acid (DTPA) (modified from Vale and Alcarde, 1999); 5 mmol L⁻¹ ethylenediaminetetraacetic acid (EDTA); water, as described by Vale and Alcarde (1999); and hot water (AOAC, 1997). The total Cu content was assessed by 37 % heat-concentrated HCl (hot plate), the official method of MAPA (Brasil, 2007b). Analytical quantification was performed using the technique of inductively coupled plasma with optical emission spectrometry (ICP-OES). The details of the methods were described by Souza et al. (2013).

The Cu content quantified through the extractants in the sources was subjected to analysis of variance and the means were compared by the Scott-Knott test at 95 % probability. The variation factors considered were the extractants (10).

Availability of copper to wheat plants and efficiency of extractants

The assessment of Cu availability from the sources and the performance of extractants were evaluated from the results of a greenhouse experiment with wheat plants.

Samples were taken from the surface layer (0-20 cm) of a clayey Latossolo Vermelho eutrófico [Oxisol] (LV) (390 g kg⁻¹ clay, 196 g kg⁻¹ silt, and 414 g kg⁻¹ sand), and a Neossolo Quartzarênico [Typic Quartzipsamment] (RQ) (49 g kg⁻¹ clay, 25 g kg⁻¹ silt, and 926 g kg⁻¹ sand). The Cu concentrations determined in DTPA pH 7.3 were 0.4 mg dm⁻³ (LV) and 0.2 mg dm⁻³ (RQ), considered as medium and low, respectively, according to the interpretation ranges proposed by Raij et al. (1996). The complete description of the chemical characteristics of the soils is described in table 2.

The soil samples were air-dried, sieved (2 mm), and limed to increase base saturation to 70 % by the application of calcium carbonate+magnesium carbonate, both pure for analysis (PA), at a Ca:Mg ratio of 3:1. The pots with 3 kg of soil were incubated for 20 days, and soil moisture maintained at around 60 % of the total pore volume (TPV).

The experiment was set up in a completely randomized 2 × 6 factorial design (two soils × six treatments - five Cu sources + control without Cu application), with four replications. The Cu sources were as described in the previous section, applied in powder form (ABNT 20, mesh 0.84 mm) at rates of 1.5 mg kg⁻¹ Cu (based on the total content), and blended with the soil together with other fertilizers for base fertilization. After mixing, the samples of

Table 1. Characterization of Cu sources evaluated for mineralogical composition and soluble contents in several extractants

Cu source	Cu content ⁽¹⁾	Type	Contaminant ⁽²⁾				Form
			Cd	Cr	Ni	Pb	
	dag kg ⁻¹		mg kg ⁻¹				
Scrap slag	35	IB ⁽³⁾	18	154	316	2,128	Powder
Brass slag	17	IB ⁽³⁾	8	43	450	14,113	Powder
Cu ore	17	RM ⁽⁴⁾	20	30	366	3,268	Powder
Granulated Cu	11	F ⁽⁵⁾	36	148	308	999	Granulated ⁽⁷⁾
Cu sulfate ⁽⁸⁾	31	F-RM ⁽⁶⁾	4	3	12	15	Powder

⁽¹⁾ Content present in the sample in the HCl method (official MAPA method, Brasil, 2007b); ⁽²⁾ Content present in the sample in USEPA 3051a method (official MAPA method, Brasil, 2006); ⁽³⁾ IB: industrial by-products with potential for use as raw material in fertilizer production. ⁽⁴⁾ RM: raw material for the production of fertilizer. ⁽⁵⁾ F: fertilizer registered and available on the market; ⁽⁶⁾ F-RM: material which can be marketed as raw material and as fertilizer; ⁽⁷⁾ Fertilizer that, in its processing, produces a granulating reaction with sulfuric acid; ⁽⁸⁾ Sample subjected to drying in a desiccator.

Table 2. Soil chemical properties after liming in an experiment with Cu sources on wheat

Determination	LV ⁽¹⁾	RQ ⁽²⁾
pH(CaCl ₂)	5.3	5.4
OM (g dm ⁻³) ⁽³⁾	49	18
P (mg dm ⁻³) ⁽⁴⁾	7	5
K (mmol _c dm ⁻³) ⁽⁴⁾	1.2	0.5
Ca (mmol _c dm ⁻³) ⁽⁴⁾	44	12
Mg (mmol _c dm ⁻³) ⁽⁴⁾	17	4
Al (mmol _c dm ⁻³) ⁽⁵⁾	0	0
H+Al (mmol _c dm ⁻³) ⁽⁶⁾	38	13
SB (mmol _c dm ⁻³)	62	16
CTC (mmol _c dm ⁻³)	100	30
V (%)	62	55
S (mg dm ⁻³) ⁽⁷⁾	10	11
B (mg dm ⁻³) ⁽⁸⁾	0.4	0.2
Cu (mg dm ⁻³) ⁽⁹⁾	0.4	0.2
Fe (mg dm ⁻³) ⁽⁹⁾	48	26
Mn (mg dm ⁻³) ⁽⁹⁾	4.3	1.2
Zn (mg dm ⁻³) ⁽⁹⁾	1	0.7
Cd (mg dm ⁻³) ⁽⁹⁾	<0.01	<0.01
Cr (mg dm ⁻³) ⁽⁹⁾	<0.01	<0.01
Ni (mg dm ⁻³) ⁽⁹⁾	0.03	<0.01
Pb (mg dm ⁻³) ⁽⁹⁾	1.2	0.3

⁽¹⁾ LV: Latossolo Vermelho eutrófico; ⁽²⁾ RQ: Neossolo Quartzarênico; ⁽³⁾ Colorimetric method - sulfuric acid and potassium dichromate; ⁽⁴⁾ Ion exchange resin extractant; ⁽⁵⁾ KCl extractant; ⁽⁶⁾ SMP buffer solution; ⁽⁷⁾ Calcium phosphate extractant; ⁽⁸⁾ Hot water extractant; ⁽⁹⁾ DTPA extractant pH 7.3 and ICP-OES reading. The analyses were performed according to Raij et al. (2001).

soil+fertilizer were left to stand for 3 days before sowing the wheat, and moisture was adjusted to 60 % TPV.

Basic compound fertilizer was applied for the soil P, K, and Ca equivalent at the rates of 232, 190, and 203 mg kg⁻¹ in the form of CaHPO₄ and K₂HPO₄, as well as application of other nutrients in aqueous solution to the soil, corresponding to 38 N, 43 S, 0.5 B, and 5 Zn mg kg⁻¹ through the sources (NH₄)₂SO₄, H₃BO₃, and ZnSO₄·H₂O. The RQ was also treated with 3 mg kg⁻¹ of Mn (MnSO₄·H₂O) due to the low available content in the soil (1.2 mg dm⁻³ through the extractant DTPA at pH 7.3). All sources were pure for analysis (PA) and in powder form.

Sixty wheat seeds of cultivar IAC 24 were sown in pots with 3 kg soil, and a week later thinned to 15 healthy and uniform wheat plants per pot. Moisture was maintained at around 70 % TPV by adding distilled water, defined by periodic weighing of the pots. During the assay, N was applied through an aqueous solution of Ca(NO₃)₂·4H₂O, in six applications of 50 mg kg⁻¹ N each, totaling

300 mg kg⁻¹ N and 430 mg kg⁻¹ Ca applied at 9, 16, 23, 30, 37, and 44 days after emergence (DAE).

The wheat shoots were cut at 53 DAE, washed in distilled water, dried at 65 °C to constant weight (the dry weight was quantified), and ground in a Willey mill. The roots were separated from the soil by sieving, washed in tap water, immersed for 90 min in a 0.02 mmol L⁻¹ disodium EDTA solution (Gabos, 2008), dried at 65 °C, and ground. The levels of macro- and micronutrients were assessed by digestion with concentrated HNO₃ and H₂O₂ in a microwave oven (Abreu et al., 1997), and determined by ICP - OES.

The Cu recovered from the sources by the wheat plants was calculated using the relative agronomic efficiency index (RAE) of the sources in relation to copper sulfate:

$$RAE (\%) = \frac{A_{\text{source}} - A_{\text{control}}}{A_{\text{standard source}} - A_{\text{control}}} \times 100$$

where A_{source} is Cu accumulation (mg/pot) in shoots of plants grown in pots containing industrial by-products/fertilizers; A_{control} is Cu accumulation (mg/pot) in shoots of plants grown in pots without addition of industrial by-products/fertilizers; and A_{standard source} is Cu accumulation (mg/pot) in shoots of plants grown in pots containing copper sulfate.

Statistical analysis was based on analysis of variance and then comparison of means by the Scott-Knott test at 95 % probability. The extractants were evaluated by means of statistical correlations between the calculated amount of potentially available Cu (mg/pot), considering the content extracted by each extractant, *versus* Cu accumulation (mg/pot) in wheat shoots and the relative agronomic efficiency (RAE) of the sources.

RESULTS AND DISCUSSION

Mineralogical characterization of Cu sources and extracted Cu contents

The mineral composition of scrap slag (Table 3) indicated the presence of Cu in the form of oxides (Cu₂O cuprite, and CuO tenorite) and metallic Cu in the crystalline phase. These minerals are typical of the scrap melting process, e.g., of silicon as a fluxing agent in the form of quartz (SiO₂).

The brass slag sample contained Cu exclusively as oxide (Cu₂O), and Zn as oxide (ZnO) and bonded to silicon (Zn₂SiO₄) (Table 3). The Fe found in oxide form as magnetite [Fe²⁺(Fe³⁺)₂O₄] may have resulted from the addition of other materials to the melting process for production of brass and bronze alloys (Gomide, 2009).

Table 3. Mineralogical composition of copper sources by X-ray diffraction

Source	Mineral	Chemical formula
Scrap slag	Cuprite (Cu oxide)	Cu_2O
	Tenorite (Cu oxide)	CuO
	Quartz	SiO_2
	Metallic Cu	Cu
Brass slag	Cuprite (Cu oxide)	Cu_2O
	Willemite	Zn_2SiO_4
	Zincite (Zn oxide)	ZnO
	Magnetite (Fe oxide)	$\text{Fe}^{2+}(\text{Fe}^{3+})_2\text{O}_4$
	Quartz	SiO_2
Cu ore	Quartz	SiO_2
	Phlogopite - 2M1	$\text{KMg}_3\text{AlSi}_3\text{O}_{10}\text{OHF}$
	Ramsbeckite	$\text{Cu}_{15}(\text{SO}_4)_4(\text{OH})_{22} \cdot 6\text{H}_2\text{O}$
	Fe and Zn oxide	ZnFe_2O_4
	Calcite (Ca carbonate)	CaCO_3
	Cuprite (Cu oxide)	Cu_2O
	Chalcopryrite (Cu and Fe sulphide)	CuFeS_2
	Chalcopryrite (Cu and Fe sulphide)	CuFeS_2
	Anhydrite (Ca sulfate)	CaSO_4
	Azurite (Cu carbonate hydroxide)	$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$
Granulated Cu	As sulphide	AsS
	Gypsum (crude gypsum)	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
	Quartz	SiO_2
	Urusovite (As, Al and Cu oxide)	$\text{CuAlO}(\text{AsO}_4)$
	Malachite (Cu carbonate hydroxide)	$\text{Cu}_2\text{CO}_3(\text{OH})_2$
Cu sulfate	Hydrated copper sulfate	$\text{CuSO}_4(\text{H}_2\text{O})_5$

In the sample of Cu ore, Cu appeared in the form of sulfide (chalcopryrite - CuFeS_2), oxide (cuprite - Cu_2O), and connected to the sulfate mineral ramsbeckite - $\text{Cu}_{15}(\text{SO}_4)_4(\text{OH})_{22} \cdot 6\text{H}_2\text{O}$ (Table 3). Chalcopryrite is an ore containing sulfide, commonly used by the fertilizer industry and authorized by MAPA (Brasil, 2007a) as a Cu source, provided it is treated in an ore roasting process consisting of oxygen injection at high temperatures with the aim of transforming Cu from sulfide into oxide form, whose solubilization in the soil is facilitated with the release of Cu to the soil solution. Furthermore, the use of chalcopryrite is allowed only for the production of complex mineral fertilizer, in a chemical reaction, usually with sulfuric acid, for partial solubilization of the micronutrients. The Cu and Zn found in the form of oxides (Cu_2O and ZnFe_2O_4) evidence the possible blend with another source of Cu. In this case, the source was most likely brass slag since this industrial by-product contains Zn and Cu in the form of oxides, in addition to quartz, which is required to produce brass and bronze alloys.

The mineralogical composition of granulated Cu (Table 3) shows the use of ores as raw material in the production of this fertilizer since the occurrence of azurite is closely associated with malachite deposits. Chalcopryrite ore was not expected to be found in the commercial product since its presence may indicate that the ore roasting process was not applied at all or may not have been performed adequately. Ore roasting should transform the Cu from the sulfide to the oxide form, as required by law (Brazil, 2007a). The presence of calcium sulfate in the minerals anhydrite (CaSO_4) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), in addition to quartz (SiO_2), are due to the addition of these materials for completion of the formula. Arsenic sulfide (AsS) was detected and may be a result of the reaction of sulfuric acid with arsenic-containing urusovite for being a granulated product.

As expected in the sample of copper sulfate, Cu was linked to sulfate in the synthetic mineral hydrated copper sulfate ($\text{CuSO}_4(\text{H}_2\text{O})_5$) as a result of industrial production.

Analysis through X-ray diffraction helped identify the major chemical forms of minerals in

the samples and deepen understanding of the chemical behavior of these sources of Cu in the soil. This analysis may become an interesting tool in the description of industrial by-products and the adoption of them represents an advance in the quality control of these sources.

Regarding the use of extractants for the quantification of soluble and potentially phytoavailable Cu, the Cu concentrations extracted by the NAC+water extractant (1:1) (parameter considered only in the analysis of Cu-containing fertilizers) were less than 60 % in relation to the content of HCl in the sources of scrap slag, Cu ore, and granulated Cu fertilizer (Table 4). Brass slag showed high solubility (82 %) in the NAC extractant (Table 4), whose X-ray diffraction revealed the presence of Cu only in oxide form (Table 3). However, the low solubility of Cu was found in the scrap slag (Table 4), in which the element appears in the form of oxide (Table 3), as well as the metallic form. According to Bastos et al. (2007a), metallic Cu in the crystalline phase is related to its difficult solubilization and could be better solubilized in stronger extractants derived from nitric acid, hydrochloric acid or their mixture. In addition to the presence of metallic Cu, the high concentration of Cu in this sample (35 dag kg⁻¹, Table 1) may have reduced the extraction capacity of NAC+water (1:1); and the presence of Zn and other minerals in Cu ore, shown by X-ray diffraction (Table 3), also decreased the solubilizing capacity of this extractant. Further studies evaluating the ratio of fertilizer:NAC+water extractant (weight:volume), which in this study was 1.0:100, or an increase in the concentration of neutral ammonium citrate, should be performed to evaluate the ability of the extractant to predict Cu soluble forms in industrial by-products.

Interestingly, the granulated Cu fertilizer did not reach the required minimum solubility (Table 4), although it is registered and authorized by MAPA for the market. This fertilizer contains Cu in the form of alloy (urusovite), carbonate (malachite and azurita) and sulfide (chalcopyrite) (Table 3), which

are chemical forms known for their lower solubility (Bastos et al., 2007a; Moura, 2010).

The extractants tested as alternatives to NAC differ statistically in extracted Cu content (Table 5). In general, greater extractive capacity was observed for 10 % HCl, followed by 10 % H₂SO₄ and NAC, whose extracted Cu concentrations (mean) did not differ from each other (Table 5). Although hydrochloric and sulfuric acids are both considered strong, sulfuric acid has an equilibrium constant for dissociation of the second hydrogen, which could explain the higher extraction with the HCl solution diluted at 10 %. However, the chelating ability and Cu extraction of NAC with 7.0 pH solution was the same as that of 10 % H₂SO₄, whose effect on the solubilization of sources was due to the acidity of the medium.

A dual action of chelation and acidification of the medium, resulting in the solubilization of the Cu sources, was attributed to the extractant 2 % CA, whose pH in solution is 2.3. Although this extractant has both acidification and chelation properties, its ability to recover Cu was 16.7 % lower than that of NAC (Table 5). The greater Cu extraction ability by NAC (Table 5) can be attributed to the greater stability of the chelate Cu-citrate, formed under neutral rather than under acidic conditions, as in the case of the extractant 2 % CA. At pH 2.3, the deprotonation of the three carboxyl groups from the molecules of citric acid, which is a condition for the release of oxygen as an electron donor group to the metal chelate, is more difficult (Alcarde and Ponchio, 1979), resulting in a complexing action of lower intensity in the 2 % CA solution than in NAC. Other authors also reported higher solubility of Cu sources in the NAC extractant compared to 2 % CA (Bastos et al., 2007a; Moura, 2010).

The extraction capacity of 1 % AA, DTPA and BS pH 6.0 was intermediate, with a Cu recovery percentage in relation to NAC of about 68, 67, and 53 %, respectively (Table 5). A low Cu recovery capacity from the sources was observed in the extractants W and HW, since almost all sources are water-insoluble (except for Cu sulfate) (Table 5).

Table 4. Mean Cu values and standard deviation, in parentheses, extracted with NAC + water (1:1) solution, and in relation to the weight and the content of HCl in industrial by-products and mineral fertilizers

Source	HCl content	NAC requirement ⁽¹⁾	NAC content ⁽²⁾	NAC % Cu ⁽³⁾
		Cu (dag kg ⁻¹)		mass/mass
Scrap slag	35 (2)	-	16 (0)	45
Brass slag	17 (0)	-	14 (0)	82
Cu ore	17 (0)	-	8 (1)	48
Granulated Cu fertilizer	11 (0)	7	4 (0)	31
Cu sulfate ⁽⁴⁾	31 (1)	19	33 (1)	107

⁽¹⁾ The MAPA requires 60 % solubility in the NAC extractant in relation to the Cu content of concentrated HCl only in fertilizers containing Cu; ⁽²⁾ Soluble content in the NAC + water 1:1 extractant (NAC); ⁽³⁾ % Cu (mass/mass) in the NAC + water (1:1) extractant (NAC) compared to the content of concentrated HCl considered as 100 %; ⁽⁴⁾ Sample dried in a desiccator.

Table 5. Copper extracted by the extractants and percentage in relation to the extractant neutral ammonium citrate + water (1:1) (NAC) from industrial by-products and mineral fertilizers

Source	NAC ⁽¹⁾	H ₂ SO ₄ ⁽²⁾	HCl ⁽³⁾	AA ⁽⁴⁾	CA ⁽⁵⁾	DTPA ⁽⁶⁾	EDTA ⁽⁷⁾	BS ⁽⁸⁾	W ⁽⁹⁾	HW ⁽¹⁰⁾
Cu (dag kg ⁻¹)										
SS ⁽¹¹⁾	15.68 c	21.32 b	32.71 a	7.85 d	8.52 d	5.70 e	0.97 g	3.10 f	0.02 g	0.03 g
NAC ⁽¹²⁾	100.0	136.0	208.6	50.1	54.3	36.4	6.2	19.8	0.1	0.2
BS ⁽¹³⁾	13.81 b	14.04 b	17.26 a	6.66 d	9.10 c	4.02 e	1.01 f	1.37 f	0.10 g	0.06 g
NAC ⁽¹²⁾	100.0	101.7	125.0	48.3	65.9	29.1	7.3	9.9	0.7	0.4
CO ⁽¹⁴⁾	8.02 b	13.63 a	14.34 a	4.18 c	7.78 b	4.37 c	1.86 d	4.64 c	0.01 e	0.02 e
NAC ⁽¹²⁾	100.0	170.0	178.8	52.1	97.1	54.4	23.1	57.8	0.1	0.3
GC ⁽¹⁵⁾	3.50 b	5.76 a	6.75 a	3.29 b	4.12 b	4.20 b	2.85 b	3.10 b	2.20 c	1.59 c
NAC ⁽¹²⁾	100.0	164.7	193.0	93.9	117.6	120.0	81.4	88.7	62.9	45.4
CS ⁽¹⁶⁾	33.21 a	21.08 f	33.24 a	31.17 b	27.17 d	30.83 b	23.39 e	29.43 c	19.57 g	20.85 f
NAC ⁽¹²⁾	100.0	63.5	100.1	93.9	81.8	92.8	70.4	88.6	58.9	62.8
Mean	14.8 B	15.2 B	20.9 A	10.6 D	11.3 C	9.8 E	6.0 G	8.3 F	4.4 H	4.5 H
NAC ⁽¹²⁾	100.0	127.2	161.1	67.6	83.3	66.5	37.7	53.0	24.6	21.8

⁽¹⁾ NAC: neutral ammonium citrate + water (1:1); ⁽²⁾ H₂SO₄: 10 % (v/v) H₂SO₄; ⁽³⁾ HCl: 10 % (v/v) HCl; ⁽⁴⁾ AA: 1 % (v/v) acetic acid; ⁽⁵⁾ CA: citric acid 2 % (m/m); ⁽⁶⁾ DTPA: 50 mmol L⁻¹ DTPA; ⁽⁷⁾ EDTA: 5 mmol L⁻¹ EDTA; ⁽⁸⁾ BS: buffer solution pH 6.0; ⁽⁹⁾ W: water; ⁽¹⁰⁾ HW: hot water; ⁽¹¹⁾ SS: scrap slag; ⁽¹²⁾ NAC: % of Cu soluble (m/m) in the NAC extractant (= 100 %); ⁽¹³⁾ BS: brass slag; ⁽¹⁴⁾ CO: Cu ore; ⁽¹⁵⁾ GC: granulated copper fertilizer; ⁽¹⁶⁾ CS: copper sulfate, sample dried in a desiccator. Mean values followed by the same letter in a row did not differ from each other by the Scott-Knott test at 95 % probability.

The Cu-extraction capacity by the chelating agent EDTA was considered low, and the levels were lower than those obtained with DTPA, regardless of the material (Table 5). The stability constant with the metal micronutrients of EDTA is greater than that of DTPA and, therefore, the opposite would be expected, namely, higher Cu extraction by EDTA. However, the concentration of DTPA solution (50 mmol L⁻¹) was 10 times higher than that of EDTA, which must have enhanced the chelating action of DTPA. A study by Vale and Alcarde (1999) evaluating the solubility of some micronutrients, including Cu, in 30 samples of commercial fertilizers using EDTA and DTPA as extractants, both at a concentration of 5 mmol L⁻¹, in addition to the extractants of water, 2 % CA and NAC, showed low solubilization of the metals in EDTA and DTPA. The authors reported that the highest concentrations could have better results in evaluation of the solubility of micronutrient fertilizers. Another aspect is that high Cu concentrations in the sources could exceed the chelating ability of the complexing agent, as reported by Norvell (1984) in regard to high Cu concentrations in the soil exceeding the chelating ability of DTPA, as must have been the case with EDTA in this study.

The weak organic acids 2 % CA and 1 % AA had a similar behavior pattern in extraction from the different sources. Copper extracted with 2 % CA was statistically equal to or higher than almost all materials, except for Cu sulfate, whose Cu content recovered by 1 % AA was higher (Table 5).

An analysis of the effect of the extractant for each Cu source showed that from the materials with a solubility lower than 60 % in NAC in relation to the Cu content in concentrated HCl, i.e., scrap slag, Cu ore, and granulated Cu fertilizer (Table 4), higher Cu levels were extracted by 10 % HCl (Table 5). For scrap slag and Cu ore, the levels recovered in 10 % H₂SO₄ were also high (Table 5). The Cu recovery rate from the above sources by these acid extractants, expressed in values relative to NAC, ranged from 136 to 209 % (Table 5).

The solubility of granulated Cu fertilizer was low in most extractants (Table 5) and its use would be disapproved because it showed solubility in NAC extractant lower than 60 % and did not meet legal requirements (Brasil, 2007a) (Table 4). An explanation for the lower solubility of this source may be the Cu found in the forms of sulfide (chalcopyrite) and carbonate (azurite and malachite) and that connected to Al in oxide form (urusovite). Solubility was higher in the diluted strong acid extractants 10 % HCl and 10 % H₂SO₄ (Table 5), with extractions of 61 and 52 %, respectively, compared to Cu content in concentrated HCl (Table 4). Of all the materials tested, with the exception of Cu sulfate, which is water-soluble, the granulated Cu fertilizer was the source with the highest water-soluble Cu extracted by water and hot water (Table 3), suggesting that granulation with sulfuric acid resulted in partial solubilization of the Cu contents.

From Cu sulfate, 20 to 33 % Cu was recovered by all extractants (Table 3), which was expected since this is the only water-soluble source tested. The

recovery percentage of Cu in relation to the NAC extractant ranged from 59 % in hot water to 100 % in 10 % HCl (Table 3), indicating that sulfate-linked Cu is easily solubilized by various extractants.

Information about the chemical form Cu assumes in the different sources, particularly in industrial by-products with potential to be used as raw material in fertilizer production, and understanding the solubility of these materials in various extractants are important for the establishment of parameters that result in better quality control of these inputs. However, beyond that, it is essential to understand the behavior pattern of Cu and its actual bioavailability in the soil-plant system, with a view to optimizing the agronomic efficiency of these potential sources.

Copper availability to wheat plants and efficiency of extractants

More Cu was accumulated in wheat shoots in sandy soil (RQ) than in clay soil (LV) (Table 6). This fact may be related to soil texture since in the experiment with the use of pots, daily irrigation promotes soil compaction, which may result in less root growth and nutrient uptake compared with plants grown in sandy soil texture. For both soils, Cu accumulation in the shoots was lower in the control treatment (Table 6). The highest amount of Cu was accumulated in plants grown in LV when treated with Cu ore, while in RQ, this source also resulted in the highest Cu uptake, along with the scrap slag and Cu sulfate sources, which did not differ from each other statistically (Table 6).

The relative agronomic efficiency (RAE) of the sources for Cu accumulated in wheat shoots was higher for the Cu ore source than the Cu sulfate soluble source (Table 6), showing that

poorly water-soluble materials, but with chemical composition of Cu in the sulfide (chalcopyrite) and oxide forms (cuprite) and as Cu connected to sulfate in the mineral ramsbeckite (Table 3) can be solubilized in the rhizosphere and made available to plants. Possibly, the higher Cu availability in this source was due to its presence in oxide and sulfate rather than sulfide forms (Table 3), and this may also be related to the slow solubilization of this source in the soil.

Bastos et al. (2007a) stated that the availability of Cu to wheat plants by the application of some mineral sources to the soil resulted in lower uptake of the element when the source was chalcopyrite ore, followed by industrial copper oxide 40 %. The other Cu sources evaluated in this study were Cu sulfate, cupric oxide mixture+ground Cu metal, ground Cu metal, and cupric oxide. The authors attributed this low Cu supply capacity to plants to the slow solubilization of chalcopyrite ore in the soil, resulting in lower phytoavailability of the element. Studies with the aim of assessing the availability of this source of Cu in crops with a perennial cycle should be performed since in these crops, slow solubilization could favor plant development.

High agronomic efficiency was also observed for brass slag (Table 6), with a predominance of Cu in the form of cupric oxide (mineral cuprite) (Table 3) in both soils. Lower agronomic efficiency was observed only in LV for granulated Cu fertilizer (Table 6) and the scrap slag industrial by-product, whose X-ray analyses revealed the predominance of Cu in carbonate (malachite and azurite ore) and sulfide forms (chalcopyrite ore), and in formation of alloys with Al (mineral urusovite) (Table 3) for granulated Cu fertilizer, and in oxide form (mineral cuprite and tenorite) and metallic Cu in the scrap slag (Table 3).

Table 6. Copper accumulation in wheat shoots and relative agronomic efficiency (RAE) of the Cu sources in comparison with Cu sulfate (100 %)

Cu source	Cu in shoot			RAE ⁽³⁾		
	RQ ⁽¹⁾	LV ⁽²⁾	Mean	RQ ⁽¹⁾	LV ⁽²⁾	Mean
	mg/pot			%		
Control	0.06 Ac	0.06 Ac	0.06 c			
Scrap slag	0.14 Aa	0.08 Bc	0.11 b	93	39	66
Brass slag	0.12 Ab	0.10 Bb	0.11 b	73	90	82
Cu ore	0.15 Aa	0.15 Aa	0.15 a	114	237	175
Granulated Cu	0.13 Ab	0.09 Bc	0.11 b	79	56	67
Cu sulfate	0.14 Aa	0.10 Bb	0.12 b	100	100	100
Mean	0.12 A	0.10 B				

⁽¹⁾ RQ: Neossolo Quartzarênico (Typic Quartzipsamment); ⁽²⁾ LV: Latossolo Vermelho eutrófico (Oxisol) Mean values followed by the same capital letter in a row did not differ from each other by the F test of Anova for the soil type factor. Mean values followed by the same lower case letter in a column did not differ from each other by the Scott-Knott test at 95 % probability for the Cu sources factor; ⁽³⁾ RAE: relative agronomic efficiency.

These low RAEs may be associated with the effects of compaction and smaller roots developed in LV since in the sandy soil (RQ), this effect was not observed. The analysis of X-ray diffraction only qualifies the main minerals present in the samples, so it is not possible to infer the contribution of each chemical matrix in the sources, which would help explain the results of solubility and availability of copper to plants.

Although the minimum solubility threshold of 60 % in the NAC extractant relative to total content is not required for industrial by-products, the threshold being required only for mineral fertilizers and raw materials containing Cu, the lower solubility of the granulated Cu fertilizer and industrial by-products scrap slag and Cu ore in the NAC extractant was not reflected in lower agronomic efficiency of these sources. On the contrary, the highest RAE was found in the Cu ore source. Regardless of the higher or lower solubility of Cu sources in the NAC extractant, the relative agronomic efficiency parameter in this study proved to be the most relevant in evaluating potential sources. This suggests that for Cu sources with intermediate RAE, lower agronomic efficiency may be compensated by higher rates. However, it is important to emphasize that the presence of other elements considered potentially toxic, such as arsenic, cadmium, chromium, lead, and mercury can restrict or impede the use of these Cu sources in agriculture, which was not analyzed in this study.

Another important parameter of the efficiency of fertilizers applied to the soil is the physical form (particle size). In this study, all Cu sources applied to the soil were ground and sieved through ABNT 20, which may have contributed to their solubilization in the soil. The reason is that, regardless of the chemical form in which Cu was found in the sources, in general, the values of agronomic efficiency were relatively high. Further research comparing the agronomic efficiency of Cu sources with the particle size of the materials and their chemical composition may be useful in evaluating potential sources, especially of industrial by-products that are poorly covered in the literature.

The correlations between the amount of Cu (mg/pot) potentially available according to the solubility of the different Cu sources in each extractant, and the Cu accumulated in shoots or relative agronomic efficiency (RAE) of the sources were not significant for any of the extractants in either soil (Table 7). These results show that no method was effective in evaluating Cu availability for wheat plants cultivated with the industrial by-products and mineral fertilizers studied, including the official NAC method considered by the MAPA for mineral fertilizers and raw materials containing Cu.

Table 7. Linear correlation coefficients (R) between the amount of Cu potentially available according to the solubility of the sources in each extractant and Cu accumulation in wheat plants and the relative agronomic efficiency (RAE) of the sources, in RQ (sandy) and LV (clayey) soil

Extractant Cu	Acc. Cu ⁽¹⁾		RAE (%)	
	RQ		LV	
NAC ⁽²⁾	0.00 ^{ns}	0.02 ^{ns}	0.00 ^{ns}	0.02 ^{ns}
10 % H ₂ SO ₄ ⁽³⁾	0.22 ^{ns}	0.23 ^{ns}	0.66 ^{ns}	0.66 ^{ns}
10 % HCl ⁽⁴⁾	0.14 ^{ns}	0.16 ^{ns}	0.00 ^{ns}	0.05 ^{ns}
1 % AA ⁽⁵⁾	0.14 ^{ns}	0.13 ^{ns}	0.00 ^{ns}	0.06 ^{ns}
2 % CA ⁽⁶⁾	0.17 ^{ns}	0.18 ^{ns}	0.22 ^{ns}	0.22 ^{ns}
DTPA ⁽⁷⁾	0.00 ^{ns}	0.21 ^{ns}	0.00 ^{ns}	0.02 ^{ns}
EDTA ⁽⁸⁾	0.20 ^{ns}	0.21 ^{ns}	0.00 ^{ns}	0.04 ^{ns}
BS 6.0 ⁽⁹⁾	0.37 ^{ns}	0.37 ^{ns}	0.10 ^{ns}	0.11 ^{ns}
W ⁽¹⁰⁾	0.14 ^{ns}	0.13 ^{ns}	0.14 ^{ns}	0.15 ^{ns}
HW ⁽¹¹⁾	0.17 ^{ns}	0.19 ^{ns}	0.14 ^{ns}	0.10 ^{ns}

⁽¹⁾ Acc. Cu: Cu accumulation in wheat plants; ⁽²⁾ NAC: neutral ammonium citrate + water (1:1); ⁽³⁾ 10 % (v/v) H₂SO₄; ⁽⁴⁾ 10 % (v/v) HCl; ⁽⁵⁾ 1 % AA: 1 % (v/v) acetic acid; ⁽⁶⁾ 2 % CA: 2 % (m/m) citric acid; ⁽⁷⁾ DTPA: 50 mmol L⁻¹ DTPA; ⁽⁸⁾ EDTA: 5 mmol L⁻¹ EDTA; ⁽⁹⁾ BS: buffer solution pH 6.0; ⁽¹⁰⁾ W: water; ⁽¹¹⁾ HW: hot water. RQ: Neossolo Quartzarênico (Typic Quartzipsamment). LV: Latossolo Vermelho eutrófico (Oxisol). RAE: relative agronomic efficiency of the sources calculated as a function of Cu accumulation in wheat shoots. ^{ns}: not significant at 5 %.

CONCLUSIONS

No extractant was effective in predicting Cu availability in wheat plants cultivated with industrial by-products and mineral fertilizers in this study.

The industrial by-product brass slag and the copper ore had relatively high agronomic efficiency indices, indicating the potential of these sources in Cu supply.

The lower solubility of copper (less than 60 %) in the NAC extractant in relation to the content of concentrated HCl in industrial by-products and mineral fertilizer does not result in poor agronomic efficiency of these sources. This suggests that the parameter of relative agronomic efficiency is more relevant in the evaluation of Cu sources than solubility in NAC; if the NAC extractant were adopted for industrial by-products, it could restrict the use of potential alternative copper sources.

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