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Recycling of solid waste rich in organic nitrogen from leather industry: Mineral nutrition of rice plants

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ABSTRACT

The leather industry produces a large quantity of solid waste (wet blue leather), which contains a high amount of chromium. After its removal from wet blue leather, a solid collagenic material is recovered, containing high nitrogen levels, which can be used as a nitrogen source in agriculture. In order to take more advantage of the collagen, it was enriched with mineral P and K in order to produce NPK formulations. The objective was also to evaluate the efficiency of such formulations as a nutrient supply for rice plants in an Oxisoil, under greenhouse conditions. The application of PK enriched-collagen formulations resulted in N contents in the vegetative parts and grains of rice plants which were equivalent or superior to those obtained with urea and commercial NPK formulations.

1. Introduction

In recent decades, a large part of the nitrogen requirement of crops has been supplied by mineral sources. The aims of agricultural N management are to provide enough N to plants to maximize growth and subsequent crop yields and also to keep it out of other ecosystems, particularly those to which added N is harmful. The ultimate source of fixed N, whether biological or industrial, is unimportant; ecosystems receiving N respond similarly because organisms cannot differentiate among different sources. However, the form in which N is delivered is vitally important: different forms of N are available at different rates to different organisms, and some forms are more easily lost through various hydrological and gaseous pathways. Nevertheless, the increased cost of these raw materials in association with the growing concern about water and environmental pollution, which is caused by the indiscriminate use of nitrogen fertilizers, has stimulated the search for alternative sources of nitrogen that can enable the total or partial substitution of mineral fertilizers [1]. The increasing urban population has also increased production of various types of waste, which, in many cases, is accumulated in the environment, without an appropriate treatment or a special recycling use. Among these wastes, the wet blue leather stands out.

The leather tanning industries do not appropriately discard their rejects in the environment due to the high cost involved in the process and the small size of most tanning businesses. These residues usually have a high chromium content (wet blue leather with about 30,000 mg Cr kg^{-1}, w/w), since chromium tanning is the most commonly used process and is used by almost 90% of all tanning companies [2]. This waste is characterized as a class 1 harmful industrial residue, according to the norm NBR 10.004 [3]. The chrome toxicity depends on its oxidation stage, and the chrome in stage VI (Cr VI) is much more toxic if compared to chrome in stage III (Cr III). Studies show that one of the factors which contributes most to the high toxicity level is the high ability of Cr VI to penetrate human cells and the fact that its reduction products are responsible for pathogenic effects such as allergic reactions, skin ulcers, perforations of the respiratory surface area and others. Furthermore, this Cr VI is highly carcinogenic [4].

There have been some studies on different types of solid and liquid leather tanning wastes which have proven to be efficient if used as fertilizers and soil agents for acidity correction according to Konrad and Castilhos [5]. Although the use of these wastes has been confirmed to be efficient, the high chromium content from both the slush and in the residual chips may be extremely harmful to the environment. In preliminary studies, the wet blue leather waste was previously submitted to chromium extraction and tested as a source of macronutrient nitrogen (N) for elephant grass (*Pennisetum purpureum* Schumach. cv. Napier.). It demonstrated to be a good alternative as a nitrogen source for the growth of this culture. Another important finding was that the nitrogen in wet blue leather

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residue (without the chromium extraction) was not taken up by the elephant grass culture, indicating that the chromium extraction is essential for the use of the leather residue as a nitrogen source for agricultural purposes [6]. These preliminary results suggested that after chromium extraction from wet blue leather waste, the resulting material can be considered as a viable alternative to reduce the use of mineral fertilizers and production costs. It can act as a soil conditioner because of its organic carbon content and mainly as a nitrogen source for plants [7].

In order to obtain a better use for the collagen and to aggregate its value, this work aimed at evaluating the efficiency of collagen (wet blue leather waste after chromium extraction) enriched with mineral P and K on the growth of rice plants in a typically Brazilian soil type. Pure collagen without P and K (used only as a source of N), and commercially available NPK inorganic fertilizers were compared.

2. Experimental

2.1. Characterization of the materials

All samples (leather waste and fertilizer leather) were characterized by scanning electron microscopy (SEM) using a JEOL analyzer coupled to an Oxford (EDS/INCA 350) energy dispersive X-ray analyzer.

2.2. Collagen enriched with mineral P and K

The total chromium contents in the wet blue leather and in the collagen were measured by atomic absorption spectrophotometry (Varian AA-175 series). The removal of Cr III from wet blue leather was performed following the method developed by Oliveira et al., which involves controlled temperature (50 °C) treatments with acid hydrolysis done with sulfuric acid (0.100 mol L^{-1}) to avoid dissolution of the collagen [8].

The resulting material (fertilizer leather) was submitted to physical and chemical analyses according to the official methodology of Brazilian Ministry of Agriculture (normative instruction number 28, July 2007). The determination of the elements chromium (Cr), arsenic (As), cadmium (Cd), lead (Pb), mercury (Hg), nickel (Ni) and selenium (Se) in the collagen samples was done according to reference methods established by the United State Environment Protection Agency (USEPA) (Table 1) [9].

The leather fertilizer containing an average amount of 140 g kg^{-1} of N (dry weight), was rinsed three times and immersed in P and/or K salt solutions in order to produce N$_{\text{leather}}$PK formulations. This mixture was agitated for 30 min and dried in a forced air oven for 12 h at 70 °C. Potassium chloride and KH_2PO_4 salts were used in this process. The formulations were then ground and selected according to grain-size analyses: 1.68–0.59 mm. The salt quantities added to the collagen for the N$_{\text{leather}}$PK formulations were based on the plant needs and on the recommendations for fertilization in greenhouses [10]. Fig. 1 shows a pathway (I) illustrating the chromium extraction and the preparation of the material enriched with K and P (pathway (II)).

Table 1

Chemical characterization of the collagen used in the preparation of the N$_{\text{collagen}}$K and N$_{\text{collagen}}$PK formulations.

Parameter	Unit[a]	
Volatile solids	% (w/w)	98.7
Organic carbon (C)	g kg^{-1}	481
Kjeldahl nitrogen (N)	g kg^{-1}	140
Aluminum (Al)	mg kg^{-1}	143
Arsenic (As)	mg kg^{-1}	<0.5[b]
Boron (B)	mg kg^{-1}	8.3
Cadmium (Cd)	mg kg^{-1}	<0.5[b]
Calcium (Ca)	g kg^{-1}	0.80
Lead (Pb)	mg kg^{-1}	17.6
Copper (Cu)	mg kg^{-1}	2.7
Chromium (Cr)	mg kg^{-1}	86
Sulfur (S)	g kg^{-1}	2.3
Iron (Fe)	mg kg^{-1}	1183
Phosphorus (P)	g kg^{-1}	0.1
Magnesium (Mg)	g kg^{-1}	0.2
Manganese (Mn)	mg kg^{-1}	13.2
Mercury (Hg)	mg kg^{-1}	<0.5[b]
Molybdenum (Mo)	mg kg^{-1}	<0.5[b]
Nickel (Ni)	mg kg^{-1}	13.2
Potassium (K)	mg kg^{-1}	670
Selenium (Se)	mg kg^{-1}	<0.5[b]
Sodium (Na)	mg kg^{-1}	1065
Zinc (Zn)	mg kg^{-1}	13.3
Neutralization power (NP)	%$CaCO_3$ equiv.	14.4
pH	–	7.0
Electrical conductivity	dS/m	495

[a] Results expressed from the dry base sample.

[b] Not determined, lower concentrations than the quantification limit.

2.3. Installation and conduction of the experiment

To evaluate the capacity of the mineral P and K enriched collagen to supply the N, P and K to plants, experiments using rice cultivar (*Oriza sativa* L.) were carried out.

The soil used, classified as RED LATOSOL, typically dystrophic, very clayey texture (Oxisoil) [11], was collected from the 0–0.2 m layer, and had the following physical and chemical characteristics: pH in water (1:2.5) 5.1; 0; 0.03; 1.2; 0.1; 2.9 cmolc dm^{-3} of Al^{3+}, K^{+}, Ca^{2+}, Mg^{2+} and (H^{+}+Al^{3+}); 31.4% base saturation rate (V); 4.0 dag kg^{-1} of O.M. (organic matter); 0.4 mg dm^{-3} of P; 1.2; 35.7; 2.5; 0.9 and 1.5 mg dm^{-3} of Cu, Fe, Mn, Zn and Cr (Mehlich 1); 250 mg dm^{-3} of Cr (USEPA, 3051); 780; 30 and 190 g dm^{-3} of clay, silt and sand. The soil analyses were performed according to

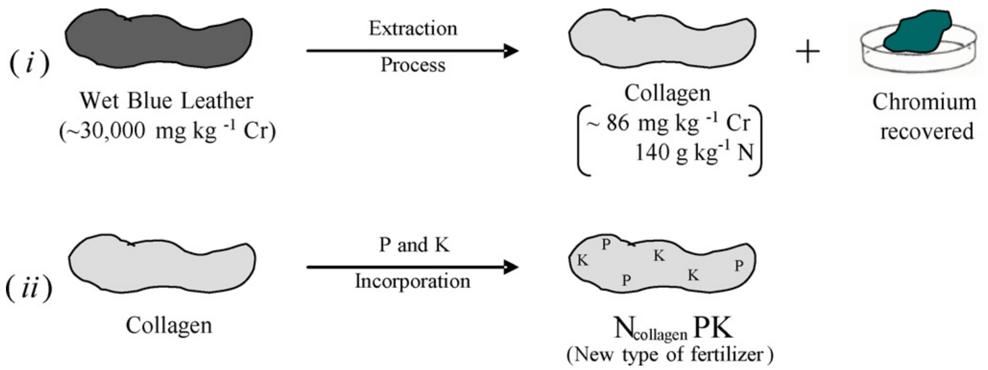

Fig. 1. Disposal steps for the wet blue leather waste.

Embrapa methodology [12], and the Cr content (USEPA 3051) followed USEPA methodology [9]. The experiment was conducted in a completely randomized design, with four repetitions, and five treatments. Pots with 5 kg of soil were used. The treatments were: (1) T1 – collagen application + $_{\text{mineral}}$P (pre-planting) + parceled $_{\text{mineral}}$K; (2) T2 – N$_{\text{leather}}$PK formulation (N from collagen) with grain-size analysis ranging from 1.68 to 0.59 mm – which will be denominated N$_{\text{leather}}$PK; (3) T3 – N$_{\text{collagen}}$K formulation (N from collagen), with grain-size analysis ranging from 1.68 to 0.59 mm and $_{\text{mineral}}$P pre-planting; (4) T4 – conventional fertilization with $_{\text{mineral}}$N (urea) + $_{\text{mineral}}$P (pre planting) + parceled K; (5) T5 – fertilization with NPK commercial formulation (corresponding to the application of N – 400 mg kg^{-1} soil; P – 250 mg kg^{-1} soil and K – 400 mg kg^{-1} soil).

Treatment 1 (T1) corresponded to the application of 5 t ha^{-1} of collagen equivalent to 13.3 g pot^{-1}. This collage application rate was calculated according to the total nitrogen content from the collagen and the average mineralization rate for an organic compound (50% year^{-1}). The quantity of 400 mg kg^{-1} of total N from recycled leather, which corresponds to 200 mg kg^{-1} of mineral N per year, was applied. The rate of 5 t ha^{-1} (corresponding to 400 mg dm^{-3} – based on a mineralization rate of 50% per year) is the recommended rate for fertilization in greenhouse experiments, which can be maintained until the grains are formed, as described by Malavolta [10].

The salt quantities which were added to collagen for the N$_{\text{leather}}$PK (T2 and T3) formulations were based on the plant needs and on the recommendations for greenhouse experiments: N – 400 mg kg^{-1} soil; P – 250 mg kg^{-1} soil (8 mmol L^{-1}) and K – 400 mg kg^{-1} soil (10 mmol L^{-1}). The quantity of 400 mg dm^{-3} of N was added to the mineral nitrogen fertilization (T4 and T5).

Before the rice planting, calcium and magnesium carbonate p.a. (3:1 ratio) were applied in order to increase the base saturation of the soil to 50%, as was recommended by Venegas and Ribeiro [13]. The leather fertilizer (T1) was applied together with the lime, which were both mixed in the soil in the pot. The other treatments were used as pre-planting applications. The pots were incubated for 15 days under approximately 60% humidity of its total pore volume (TPV). Then, the macronutrients (Ca: 80, Mg: 30 and S: 50) and the micronutrients (B: 0.5; Cu: 1.5; Zn: 5.0 and Mo: 0.1), in the form of aqueous reagent solutions of p.a. reagents were added, with the values referring to mg dm^{-3} of soil, according to recommendations of Malavolta [10]. The nitrogen (only in T4) and potassium were parceled in four equal applications: at planting and at 30, 45 and 75 days after sowing. The leather fertilizer (T1) was added before the planting and mixed with the soil in the pot.

On the 60th day of germination, at the beginning of the flowering period, one plant from each pot was cut at the base for the chemical analysis. The dry matter weight was obtained and the chemical analysis of leaf samples (from the first cut) was carried out. The shoots were rinsed in deionized distilled water, dried until constant weight in a ventilated oven at 60 °C, and then weighed and subsequently ground in a Wiley type grinder.

The remaining plants were kept in the pots until the end of the cycle in order to evaluate their grain production (second cut). After the cut, the shoots were separated into leaves, stems and panicles. After cutting the shoots, the roots were kept in the pot and soil samples were collected. The evaluations performed (dry matter weight and the determination of the N and Cr levels in different parts of the plant) were similar to those from the first cut. The data obtained from different crops related to the dry matter yield, level and accumulation of N and Cr were submitted to a variance analysis. As there were significant differences by the *F*-test, comparisons among the treatment averages were performed through the Tukey test, at a level of 5% of probability, with the aid of the statistical analysis software SISVAR [14].

3. Results and discussion

3.1. Characterization of the materials

To investigate the morphology of the materials, a scanning electron microscope analysis was carried out before and after the incorporation of potassium and phosphorous in the collagen structure. Fig. 2 shows the characterization of the adsorbent by SEM.

The micrograph of the wet blue leather waste (Fig. 2a) presented a different morphology from the natural leather (without chromium) related in the literature. The fibrous aspect of the wet blue waste is probably due to the presence of chromium in the leather [7]. It is interesting to observe that after P and K incorporation (Fig. 2c) and chromium extraction, a strong modification in the morphology was observed, suggesting that this was caused by the chromium extraction.

Moreover, the respective EDS analyses showed interesting results for the amounts of chromium, potassium and phosphorous. A high chromium content was observed in the wet blue leather waste (Fig. 2b), but after the Cr extraction treatment, the signal from that element disappears (Fig. 2d) suggesting its total removal from collagen, producing the NPK-fertilizer leather (N$_{\text{leather}}$PK). The EDS analyses also showed the potassium and phosphorous incorporated within the collagen structure (Fig. 2d).

3.2. Rice plant yield

The variance analysis showed significant differences in the studied treatments. In general terms, the PK enriched collagen (fertilizer leather) formulations provided rice yields similar to those observed in the treatments with commercial NPK and urea (Table 2).

The yields observed with the application of PK enriched collagen (fertilizer leather) formulations (T2 and T3) and with fertilizer leather (T1) were achieved by the organic N release and the subsequent transformation in content sufficient for the normal development of the plants. Moreover, these formulations were highly effective for the grain yield. Although they produced less dry matter, it is reasonable to state that the N collagen was released in a way that enabled the plant roots to obtained better benefit from both N and P and K, which resulted in a higher grain yield.

It is important to emphasize that although the commercial NPK formulation (T5) showed a higher shoot dry matter yield at tilling and harvesting, the same was not observed regarding grain yield. The number of panicles per each unit area is the component which most influences the grain yield regarding the nitrogen. On the other hand, there is a tendency towards a decrease in the number of grains/panicle and an increase in the number of panicles per each unit area. This indicates that there is a negative correlation between these two components [15]. Thus, the greater number of panicles which was found in the commercial NPK (T5) formulation was not observed in the grain yields either. The urea fertilization (T4) showed satisfactory results and they were somewhat similar to the fertilization which contained collagen in terms of grain yield.

3.3. Nitrogen in the plants

No significant differences regarding the N contents at tilling and harvesting were verified (Table 3) among the different treatments. It was also observed that the contents observed in the different treatments did not result in grain yield limitations, except for $_{\text{commercial}}$NPK (T5).

The accumulation of N followed a similar tendency observed for the dry matter yield, that is, greater accumulations of N were detected in the vegetative part when $_{\text{commercial}}$NPK was applied, whereas the opposite occurred in the grains. The PK enriched col-

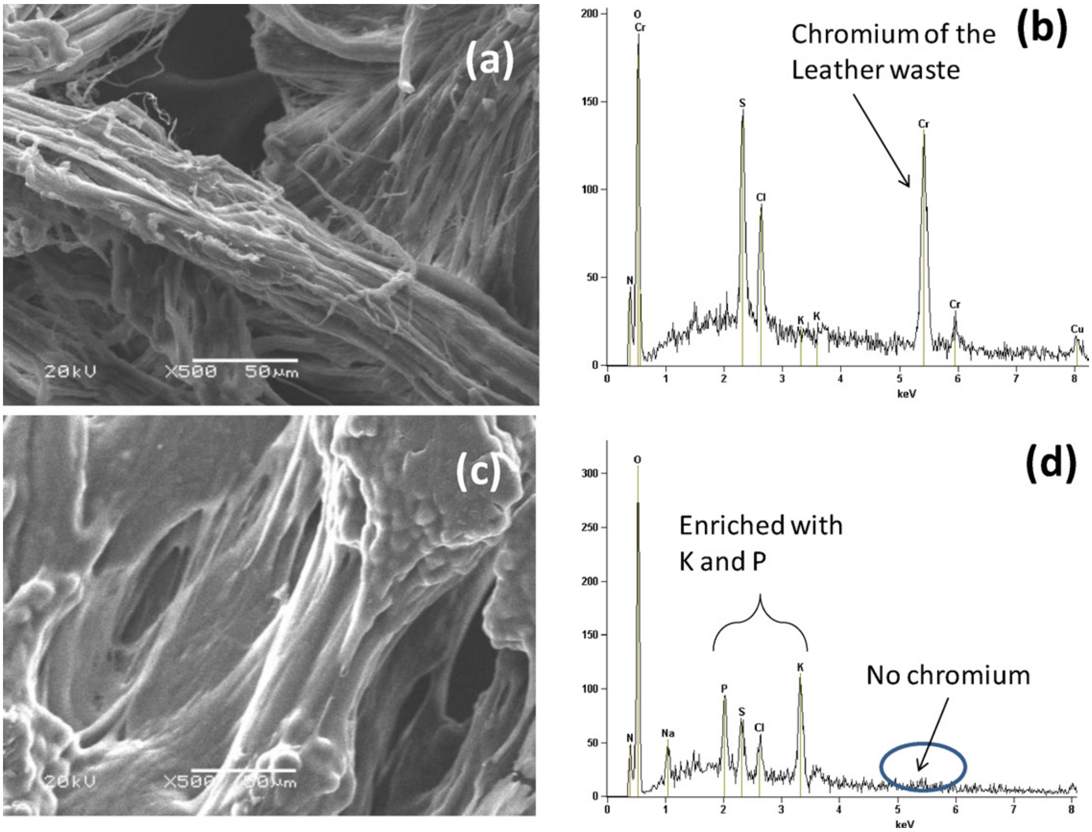

Fig. 2. Characterization of the adsorbent by SEM and EDS. (a) Wet blue leather waste; (b) EDS spectra obtained for wet blue leather waste; (c) collagen (after the chromium extraction process); (d) EDS spectra obtained for collagen (after the chromium extraction process) incorporated with mineral K and P.

lagen application with grain-size of 1.68–0.59 mm (T2) showed better accumulation results (Table 3).

Oliveira et al. verified a positive effect on the collagen application in the elephant grass, which demonstrated to be a good source of nitrogen [6]. They concluded that the collagen application supplied the necessary nitrogen to elephant grass plants similar to fertilization with mineral nitrogen. The nitrogen concentrations in plants are higher during the first growth phase and they subsequently decrease slightly. They begin to increase until the differentiation of floral primordia, and then they decrease until the grain filling period, after which the concentrations show little variation until the full maturity of the grains [16]. Higher supplies of N to the plants through leather residues applied to the soil were also observed in studies developed by [4,17–19].

3.4. *P and K leaching studies*

The chemical composition and the decomposition speed of the organic residues in soil have important implications in the liberation of nutrients for the plants and, therefore, are determinants of the predominance of the immobilization or liquid mineralization processes in the soil. Over the short term, if there is predominance of the immobilization over the mineralization, there is a risk of there being a nutrient deficiency in the soil, mainly of N. Thus, with the intention of studying the incorporation of P and K to the collagen without the influence of the plant, leaching experiments of those elements were conducted. We hoped to assess the efficiency of the collagen in maintaining (adsorption force) P and K within its structure, seeking to reduce the loss of those macronutrients, which would increase the absorption possibility for the plant. Fig. 3

Table 2
Weight of shoot dry matter yield at tilling (SDMTIL), shoot dry matter at harvest (SDMH), grains and roots, and number of panicles of rice plants submitted to the different treatments.

	Treatment	Dry matter (g pot^{-1}) (means of four replications)								Number of panicles per pot	
		SDMTIL		SDMH		GRAINS		ROOTS			
T1	Leather + ${}_{\text{mineral}}$ P + ${}_{\text{mineral}}$K	5.03	b	20.28	c	15.84	ab	20.64	ab	11.67	ab
T2	$N_{\text{leather}}P_{\text{mineral}}K_{\text{mineral}}$	6.34	ab	27.35	c	21.84	a	15.93	b	9.33	b
T3	$N_{\text{leather}}K_{\text{mineral}} + P_{\text{mineral}}$	2.90	b	25.12	c	14.10	ab	15.42	b	9.00	b
T4	Urea + ${}_{\text{mineral}}P_{\text{mineral}}K$	6.23	ab	29.35	bc	15.43	ab	38.42	a	11.00	b
T5	Commercial NPK	10.94	a	51.49	a	11.21	b	34.27	ab	17.33	a
	C.V. (%)	17.88		11.22		19.05		19.00		18.8	

T1 – leather application + ${}_{\text{mineral}}$P (pre-planting) + parceled ${}_{\text{mineral}}$K; T2 – N_{leather}PK formulation; T3 – N_{leather}K formulation and ${}_{\text{mineral}}$P pre-planting; T4 – conventional fertilization with ${}_{\text{mineral}}$N (urea) + ${}_{\text{mineral}}$P (pre planting) + parceled K; T5 – fertilization with NPK commercial formulation (corresponding to the application of N – 400 mg kg^{-1} soil; P – 250 mg kg^{-1} soil and K – 400 mg kg^{-1} soil). Means followed by distinct lower case (columns) letters, are different ($P < .05$) by Tukey test.

Table 3
Levels and accumulations of nitrogen in the shoot dry matter at tilling (NSDMTIL), at harvesting (NSDMH), and in the grains (NGRAINS) produced by the rice plants submitted to the different treatments (average of four replications).

	Treatment	Levels of N in the plant (g kg^{-1}) (means of four replications)					
		NSDMTIL		NSDMH		NGRAINS	
T1	Collagen + $_{\text{mineral}}$P + $_{\text{mineral}}$K	23.00	a	15.73	a	18.87	a
T2	N$_{\text{collagen}}$P$_{\text{mineral}}$K$_{\text{mineral}}$ (thin)	23.73	a	16.87	a	17.97	ab
T3	N$_{\text{collagen}}$K$_{\text{mineral}}$ + P$_{\text{mineral}}$	23.97	a	14.87	a	18.10	ab
T4	Urea + $_{\text{mineral}}$P$_{\text{mineral}}$K	26.53	a	13.73	a	18.47	a
T5	Commercial NPK	23.63	a	16.13	a	15.03	c
	C.V. (%)	12.17		14.42		6.61	

	Treatment	Accumulation of N in the plant (mg pot^{-1}) (means of four replications)					
		NSDMTIL		NSDMH		NGRAINS	
T1	Collagen + $_{\text{mineral}}$P + $_{\text{mineral}}$K	137.57	b	317.27	b	316.72	b
T2	N$_{\text{collagen}}$P$_{\text{mineral}}$K$_{\text{mineral}}$ (thin)	183.83	b	422.26	b	405.89	a
T3	N$_{\text{collagen}}$K$_{\text{mineral}}$ + P$_{\text{mineral}}$	80.38	cd	341.25	b	218.81	c
T4	Urea + $_{\text{mineral}}$P$_{\text{mineral}}$K	132.33	bc	339.45	b	313.68	b
T5	Commercial NPK	308.49	a	671.15	a	194.21	c
	C.V. (%)	13.45		8.68		5.37	

T1 – collagen application + $_{\text{mineral}}$P (pre-planting) + parceled $_{\text{mineral}}$K; T2 – N$_{\text{collagen}}$PK formulation (N from collagen) with grain-size analysis ranging from 1.68 to 0.59 mm – which will be denominated "thin N$_{\text{collagen}}$PK"; T3 – N$_{\text{collagen}}$K formulation (N from collagen), with grain-size analysis ranging from 1.68 to 0.59 mm and $_{\text{mineral}}$P pre-planting; T4 – conventional fertilization with $_{\text{mineral}}$N (urea) + $_{\text{mineral}}$P (pre planting) + parceled K; T5 – fertilization with NPK commercial formulation (corresponding to the application of N – 400 mg kg^{-1} soil; P – 250 mg kg^{-1} soil and K – 400 mg kg^{-1} soil). Means followed by distinct lower case (columns) letters, are different ($P < .05$) by Tukey test.

presents the photograph of the experimental assembly employed in the nutrient leaching studies.

3.4.1. *Potassium leaching assay*

In Fig. 4, considering the $_{\text{commercial}}$NPK material in the first 15 days, a high level of K being leached can be observed. That behavior was expected, since in those commercial formulations, the potassium is available. For N$_{\text{leather}}$PK, the leaching of K occurred in a more significant way, liberating K to the medium after only 60 days of experiment, the necessary period for the collagen mineralization to occur. That result suggests that there was a relatively strong chemical interaction between the collagen and K in the preparation of the N$_{\text{leather}}$PK formulation, showing that the liberation of K to the culture will also be able to be controlled by the decomposition of the collagen, as happens with the nitrogen. In the control (without addition of the $_{\text{commercial}}$NPK and N$_{\text{leather}}$PK formulations), there was no significant variation in the K level during the studied period.

Another important factor to be mentioned is the K level in the soil after the end of the experiment. It is observed that, for N$_{\text{leather}}$PK, the potassium level found in the soil (234 mg dm^{-3}) is superior to that found in the $_{\text{commercial}}$NPK (144 mg dm^{-3}). Those values corroborate the leaching data presented in Fig. 4, in other words, there is a slower availability of the element when originating from the organic material, showing that the N$_{\text{leather}}$PK material can be used as a slow-release fertilizer because the organic matrix (collagen) adsorbs K in an efficient way.

Fig. 3. Partial photograph of the P and K leaching experiment.

3.4.2. *Phosphorus leaching assay*

A study similar to that conducted for K was conducted for P (Fig. 5). As the phosphorus in the soil is in the anionic form, it tends to be immobilized, explaining the low level of that element found in the leaching studies carried out for both materials (N$_{\text{leather}}$PK and $_{\text{commercial}}$NPK). In spite of the low P values, the behavior is similar to that found for K, in other words, the collagen retains P efficiently, liberating it gradually for the plant, again evidencing

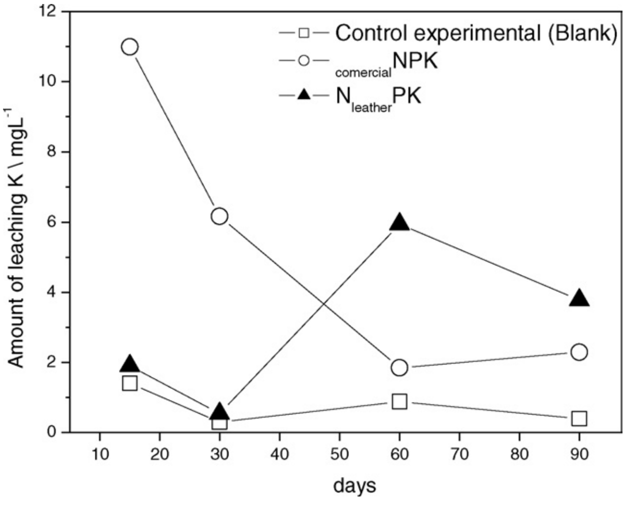

Fig. 4. Leaching profile of K previously incorporated in the collagen (N$_{\text{leather}}$PK) and $_{\text{commercial}}$NPK.

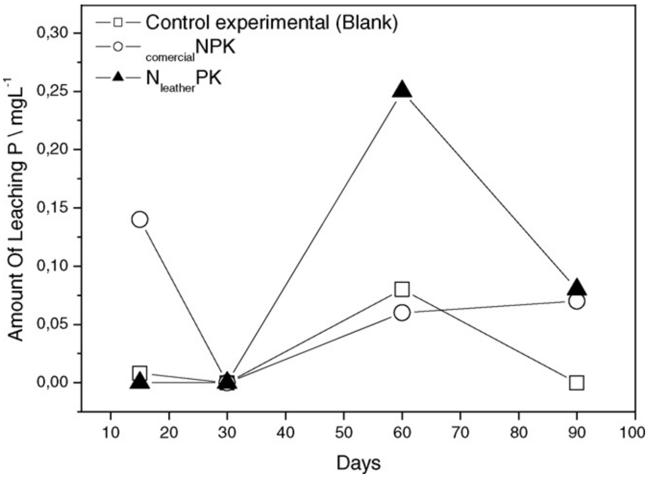

Fig. 5. Leaching profile of P previously incorporated in the collagen and $_{commercial}$NPK.

the formation of a chemical interaction between the collagen and the chemical element P during the preparation of the formulation $N_{leather}$PK.

The results obtained in the leaching study in the absence of the plant and also the rice growth tests show that industrial wet blue leather reject can be transformed in NPK fertilizers with different formulations to be applied in different cultures. Those results open a new perspective in the application of industrial rejects in the fertilizer industry for the production of fertilizers using leather industry rejects, because the chrome is removed in an efficient way as described by the patent [8].

4. Conclusions

The application of PK enriched-collagen formulations resulted in N, P and K contents in the vegetative parts and in grains of rice plants equivalent or superior to those obtained with urea using and commercial NPK formulations. The application of collagen-based formulations, as a nutrient source for rice plants, showed promising agronomic results. Under the conditions of the present study, the Cr contents in the leaves and grains of the rice plants are were within the maximum acceptable limits, according to established technical criteria. The Cr level in the soil through the USEPA method was statistically similar to those of urea and commercial NPK formulation, indicating that there was no restriction in the use of this type of residue concerning Cr problems in the soil.

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