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Incorporation of mineral phosphorus and potassium on leather waste (collagen): A new $N_{collagen}$PK-fertilizer with slow liberation

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ABSTRACT

The feasibility of using a solid waste (rich in nitrogen) from the leather industry, after chromium extraction, as adsorbent for P and K, for possible utilization as NPK fertilizer was evaluated. The materials, with and without the addition of P and K, were characterized by chemical analyses, infrared spectroscopy, EDS (energy dispersive X-ray spectrometry) and SEM (scanning electronic microscopy). Langmuir and Freundlich equations were used for analyzing the experimental data, which showed a better fit to the Freundlich model, thus suggesting a multilayer adsorption process on the surface of the adsorbent. A preliminary test in greenhouse demonstrates that the P and K incorporation on the matrix rich in nitrogen (collagen) is a interesting alternative to use such material as NPK fertilizer. The application of $N_{collagen}$PK formulations, as a source of nutrients for the growth of rice plants, showed promising agronomic results.

1. Introduction

The tanning treatments in the leather industry to produce the wet blue leather yield sludge containing approximately 30.000 mg kg^{-1}(w/w) of chromium [1]. The method commonly used for this waste disposal (landfill or incineration) presents high operational costs [2]. This material is classified by the Brazilian Environmental Council (CONAMA) as a category-one waste, one of the most dangerous and harmful wastes if discarded into the environment without any further treatment [3]. Because of this, such a material needs a special disposal, which is very expensive [4]. Chromium containing waste is considered category-one not because of the chromium content itself, but because of a possibility of its spontaneous oxidation to chromium VI. The patented process Br n. PI 001538 is a technique able to remove the CrIII from wet blue leather, with the recovery of a solid collagenic material (collagen), containing low chromium and high nitrogen levels, with potential use in agriculture.

In the past decades, a great part of the requirement of nitrogen by crops has been supplied by mineral sources. Nevertheless, the increased cost of these raw materials, in association with the growing concern about water and atmosphere pollution, which is caused by the indiscriminate use of nitrogen fertilizers, have stimulated the search for alternative sources of nitrogen that can enable the total or partial substitution of mineral fertilizers. Currently, most of the nitrogen fertilizers used in the world are produced from ammonia, which is obtained from the reaction of nitrogen (N_2) with hydrogen (H_2) with most of latter coming from natural gas, which is a “finite” natural resource [5]. The use of mineral fertilizers, especially those containing nitrogen, is variable and can cause environmental contamination. To increase the efficiency of mineral fertilizer it is necessary to carry out a greater number of applications, especially when it comes to nutrients as N and K. But this practice presents a significant increase in operational costs. Another alternative would be to use organic sources that release the nutrients slowly, which can reduce spending on labor, energy and also could be more efficient than the mineral fertilizers, as they release the nutrients in the soil solution at rates and concentrations more compatible with the demands of the plants throughout their growth cycle.

Chromium is chemically unique among the regulated toxic metals of the environment in that different species of Cr, especially trivalent (CrIII) and hexavalent (CrVI), are drastically different in their toxicities Chromium, in the trivalent form (CrIII), is an important component of a balanced human and animal diet and its deficiency causes disturbance to the glucose and lipids metabolism in humans and animals. In contrast, hexavalent Cr (CrVI) is highly

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Table 1
Chemical characterization of the collagen used in the preparation of the $N_{collagen}K$ and $N_{collagen}PK$ formulations and wet blue leather waste.

	N	P	K	Ca	Mg	S	Fe	Mn	Zn	Cr
	g kg^{-1}		mg kg^{-1}							
Wet blue	104	10	0.15	0.60	0.44	12	133	2	5	27,150
Collagen	140	26	0.14	0.48	0.08	3	70	1	10	84.7

toxic, carcinogenic and may cause death to animals and humans if ingested in large doses. Recently, concern about Cr as an environmental pollutant has been increasing due to its build up to toxic levels in the environment as a result of various industrial and agricultural activities [6,7]. This, together with a potential entrance of chromium into human body through skin, makes a combination that should not be ignored [8]. Re-destining the solid waste from the tanning industry as adsorbent of other contaminants is an interesting alternative [9,10]. However, if chromium is not extracted from this waste, its use can cause serious environmental problems.

Kolomaznik et al. (2008) showed that the probability of a spontaneous oxidizing process of CrIII into CrVI is real, as show by the Gibbs energy values for reactions in alkali medium and in acid medium. The negative values of both thermodynamic functions prove the possibility of spontaneous oxidation within a wide range of pH [6].

Nowadays, the production of solid wastes by industrial activity has been increasing and because of this, the use of such wastes as fertilizers has been an interesting alternative to environmental protection. Organic residues can contribute to slow release of N throughout the year. Due to high costs of industrial fertilizer in certain tropical areas, alternative solutions to increase the N availability for the crop have to be explored. Because of its high N content [11], the solid waste from leather industry, after chromium extraction and enrichment with mineral P and K, could be used as fertilizer.

The chromium extraction method, based on the process developed and patented (Br n. PI 001538) by Oliveira et al. [12] revealed, in the best condition of extraction, a reduction of approximately 99.6% of chromium in the waste, with a chromium content of 27,150 mg kg^{-1} (wet blue leather waste) being reduced to 84.7 mg kg^{-1} (collagen). This value is below the permitted value of this element in organic fertilizer marketed in Brazil (200 mg Cr kg^{-1}), according to the existing Normative Instruction number. 27, June 2006 the Brazilian Ministry of Agriculture [13]. The maximum levels of Cr compounds (total Cr) allowed in organic urban waste and sewage sludge for application on agricultural land, as established in some countries, in mg kg^{-1} (dry basis): Germany (100), Switzerland (150), EPA (1200), France (2000) and Austria (50–300) by Lutz (1984) [14] and USEPA (1993) [15]. Thus, the collagen displays a potential for application in agricultural soils as it not considered offensive to the environment.

The collagen was shown to be a good alternative source of nitrogen for the growth of elephant grass – *Pennisetum purpureum* Schumach. cv. Napier. The application of collagen supplied the need of nitrogen by elephant grass plants similarly to fertilization with mineral nitrogen [11].

In this work we propose to use the solid waste from the leather industry after the chromium extraction, as potential material for the mineral P and K adsorption and their application as a $N_{collagen}PK$ fertilizer.

2. Experimental

2.1. Materials and characterization

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 CrIII from wet blue leather was performed following the method developed by Oliveira et al. [12], which involves controlled temperature (50 °C) treatments with acid hydrolysis done with phosphoric acid, to avoid dissolution of the collagen.

The resulting material (collagen) 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 chromium in the collagen and wet blue waste samples was done according reference methods established by the United State Environment Protection Agency [16] (Table 1).

The reagents used in this experiment were all checked for purity and the quality control was assured by the Standard Reference Material (SRM) 1640 trace elements in natural water from NIST (National Institute of Standards and Technology) or the reference material Lab Performance Check Standard 1 (LPC-1-100/500) from SPEX (based on SRM from NIST). Most of the chemicals used in the experiment were trace metal-grade (TMG) and used without further purification.

The materials used in the adsorption tests were the wet blue leather waste (a Cr-containing leather waste) from the Áurea industry located in Erechim-RS, Brazil and the collagen, the waste material obtained after chromium extraction of the wet blue waste. In the adsorption tests, standard solutions of P and K were prepared using KH_2PO_4 and KCl, respectively. All reagents used were of high purity (Aldrich). The wet blue leather waste and the materials after Cr extraction were characterized by infrared spectroscopy (FTS 3000 Excalibur Series Digilab), EDS (energy dispersive X-ray spectrometry) and SEM (scanning electronic microscopy) analysis (LEO EVO-40XVP).

The wet blue leather waste is classified by the Brazilian Environmental Council (CONAMA) as a category-one waste, one of the most dangerous and harmful wastes if discarded on the environment without any further treatment [3]. Landfill or incineration are the recommended methods disposal, which are very expensive [17]. Chromium containing waste is considered category-one not because of the chromium content itself, but because of a possibility of its spontaneous oxidation to chromium VI. Therefore, a new alternative for the utilization of these materials is mandatory. Fig. 1 shows a pathway (I) to recover the material as adsorbent for K and P after chromium extraction in order to obtain a new fertilizer to avoid the expensive pathway (II).

2.2. P and K adsorption

Preliminary tests showed that sorption equilibrium was attained within 18 h, so that agitation for 24 h was performed in the sorption isotherms experiments.

Potassium adsorption was determined by the batch method using 25 mg of sample in 25 mL of a KCl solution with increasing concentrations of K (0, 25, 100, 250, 500, 1000, 2000, 3500 and 5000 mg L^{-1}) at pH 6. All adsorption flasks were kept for 24 h at 25 °C in a temperature-controlled batch. The equilibrium concentrations of K were measured using a flame photometer (Micronal B262) at wavelength 767 nm.

Phosphorous adsorption by the materials was also determined by the batch method using 25 mg of sample in 25 mL of a KH_2PO_4

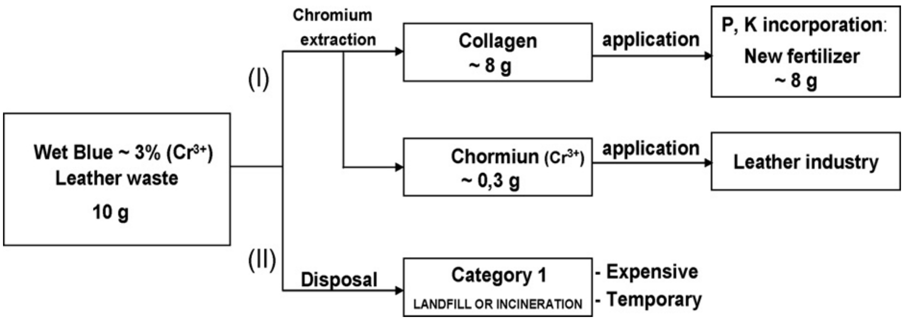

Fig. 1. Scheme of uses of the wet blue leather waste after chromium extraction.

and was performed under increasing concentrations of P (0, 50, 100, 250, 500, 1000, 2000, 3500 and 5000 mg L^{-1}) at pH 6. Phosphorous concentrations at equilibrium were determined by the colorimetric method, using a Shimadzu, UV-160 1 PC at wavelength 420 nm. All pH values were measured using a digital pH meter (TEC-3MP) and adjusted by adding either HCl or NaOH to the adsorption solutions. It is important to emphasize that the pH value used is due to its correlation with pH of soils commonly used in the cultivation of plants, i.e., which ensures better development of plants.

2.3. Fertilization experiments

The collagen, which contains an average amount of 140 g kg^{-1} of N (dry weight), was rinsed three times and then immersed in solutions with P and K salts in order to produce NK and NPK formulations. This mixture was agitated for 30 min and then dried in a dryer with forced air circulation for 12 h at 70 °C. KCl and KH_2PO_4 salts were used in this process. Then, the formulations were grounded and selected according to grain-size analyses: 5.68–1.68 mm – which will be denominated "$N_{collagen}$thick PK" and a 1.68–0.59 mm, which will be denominated "$N_{collagen}$thin PK". The salt quantities added to collagen for the NPK formulations were based on the necessities of the plants and on the recommendations for fertilization in greenhouses as follows: N—400 mg kg^{-1} soil; P—250 mg kg^{-1} soil and K—400 mg kg^{-1} soil (dry weight) as described by Malavolta [18].

The experiment with rice plants was carried out in a greenhouse at the Soil Science Department of the Federal University of Lavras. The soil utilized was a typical dystrophic Yellow-Red Latosol, clayey texture, Oxisol. The experiment was conducted in a completely randomized design, with three replicates, and consisted of six treatments. Pots with 5 kg of soil were used as experimental plots. The treatments were: 1. T1—collagen application + $_{mineral}$P (pre-planting) + parceled $_{mineral}$K; 2. T2—$N_{collagen}$PK formulation (N from collagen) with grain-size analysis ranging from 5.68 to 1.68 mm, denominated "thick $N_{collagen}$PK"; 3. T3—$N_{collagen}$PK for-

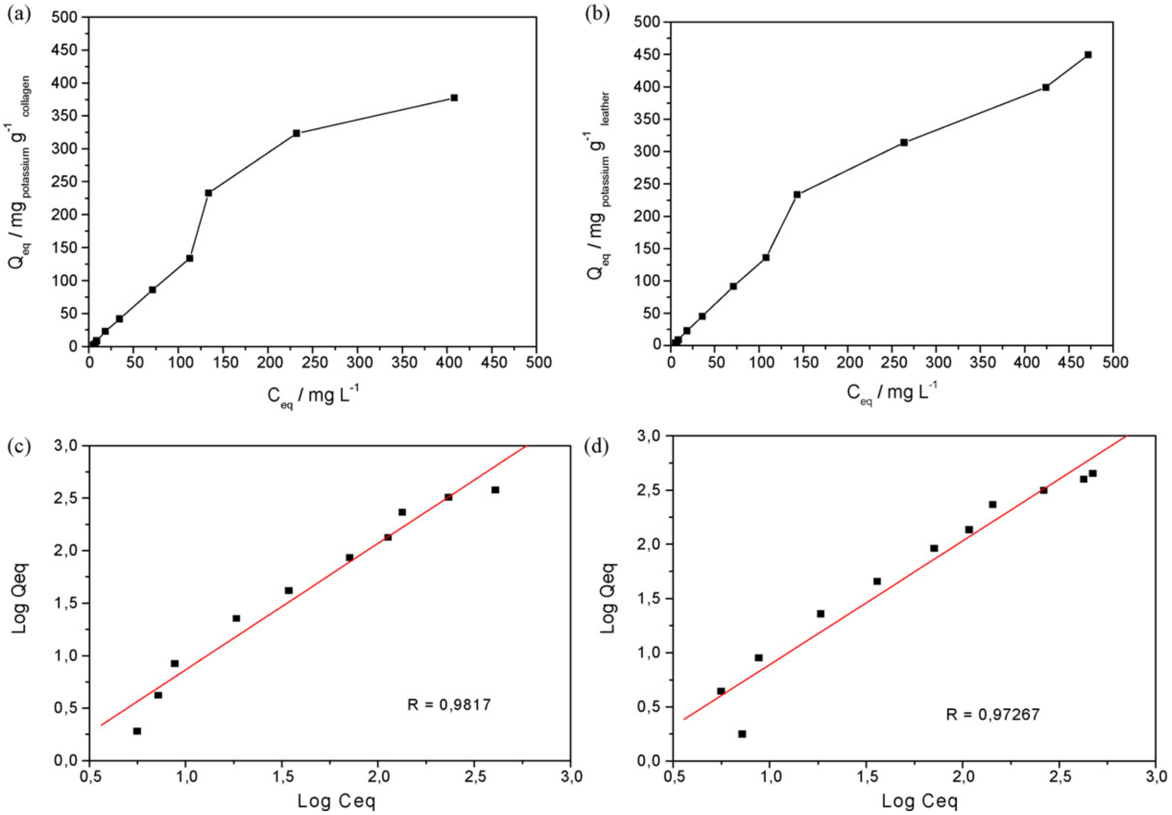

Fig. 2. Adsorption isotherm of potassium by materials (a) after chromium extraction (collagen) and leather waste (wet blue leather waste) with chromium (b), linear regression coefficient (*R*) collagen (c) linear regression coefficient (*R*) leather wet blue.

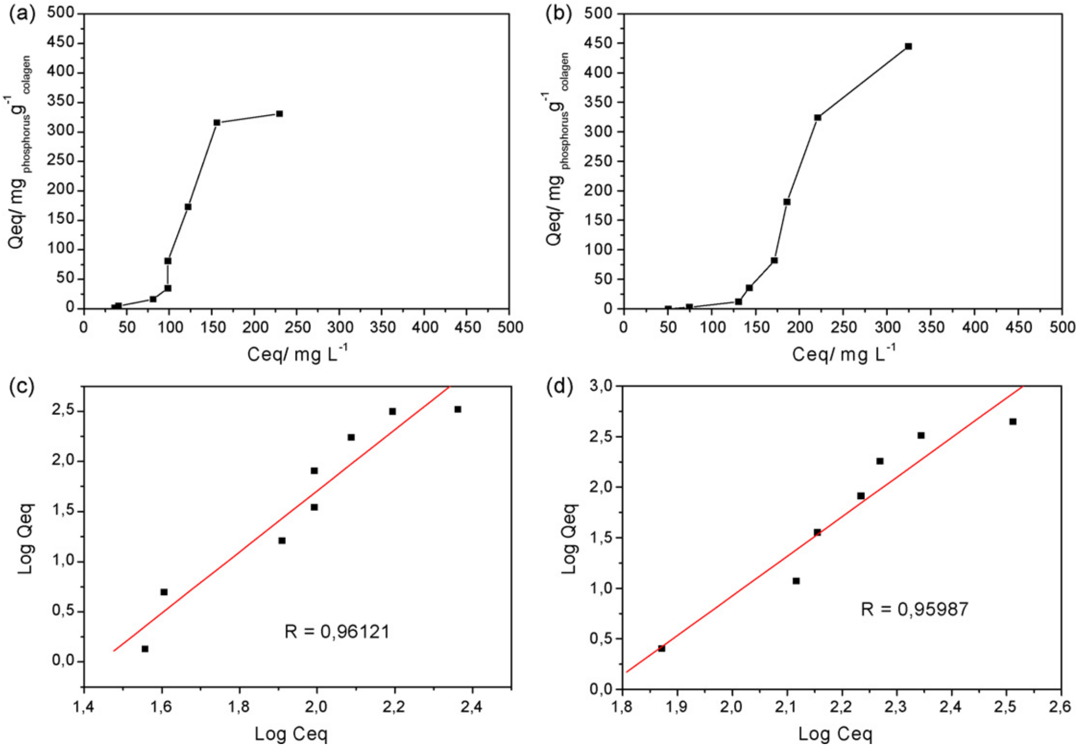

Fig. 3. Adsorption isotherm of phosphorous by materials (a) after chromium extraction (collagen) and leather waste (wet blue leather waste) with chromium (b) linear regression coefficient (*R*) for the collagen (c) linear regression coefficient for wet blue (d).

mulation (N from collagen) with grain-size analysis ranging from 1.68 to 0.59 mm – which will be denominated "thin $N_{collagen}$PK"; 4. T4—$N_{collagen}$K formulation (N from collagen), with grain-size analysis ranging from 1.68 to 0.59 mm and $_{mineral}$P pre-planting; 5. T5—conventional fertilization with $_{mineral}$N (urea) + $_{mineral}$P (pre-planting) + parceled K; 6. T6—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).

3. Results and discussion

3.1. Adsorption tests

3.1.1. Potassium adsorption

The results showed that the Freundlich model fits better than the Langmuir (not shown here) model to the experimental data. The results of tests of retention of metals carried out in batch, which are a function of initial concentration of metal (Ci) and the equilibrium concentration of metal (Ce) after 24 h under agitation. A Fig. 2 shows the adsorption isotherms of potassium in the material after the extraction of chromium (collagen) (Fig. 2a) and the wet blue leather waste (Fig. 2b).

Leather wet blue showed higher adsorption capacity when compared to collagen (377 mg g^{-1} – collagen and 449 mg g^{-1} – wet blue waste). This value is greater than previous adsorption capacities reported in the literature for other materials [19]. Therefore, the higher values of adsorption capacities for the leather waste at pH 6 can be explained by two possibilities: (I) complexation with the surface hydroxyl groups [17] and (II) electrostatic interaction due the presence of chromium (mainly on wet blue leather waste) in the protein structure [19].

A power function was able to fit the data with a high degree of correlation (R = 0.9726 for wet blue and R = 0.9817 for collagen). The linear regression analysis of the log q_{eq} versus log C_{eq} plot is shown in Fig. 2d and c.

3.1.2. Phosphorous adsorption

Fig. 3 shows the adsorption isotherms of phosphorous on the collagen (Fig. 3a) and wet blue waste (Fig. 3b). It was observed a rare profile of the adsorption, with significant incorporation of P with high concentrations of phosphate. At high concentrations, an efficient removal capacity was obtained for both materials with an adsorption capacity of approximately 332 mg g^{-1} and 445 mg g^{-1} for the collagen and wet blue waste, respectively. In this case the adsorption probably occurs by complexation with the hydroxyl groups [17] in the protein structure. The P and K incorporation on the matrix rich in nitrogen can be a interesting alternative to use the materials as NPK fertilizer. In fact, the literature describes the use of this waste as N-organic fertilizer, but only after many physical and chemistry process to obtain a protein hydrolyzates [6].

The affinity between the materials (collagen and wet blue) with the phosphorus element was quantified by fitting the obtained adsorption values for the Freundlinch isotherm. The Freundlinch model fitted very well for the collagen and wet blue, with regression coefficients R = 0.9596 for the leather wet blue and R = 0.9612 for the collagen (Fig. 3c, d). In all cases studied the linear fits obtained with the Langmuir model were lower than those found for the Freunlinch model (data not shown).

3.2. Characterization of the material

To investigate the morphology of the materials, scan electronic microscopy analyses were carried out before and after the incorporation of potassium and phosphorous in the collagen structure. Fig. 4 shows the characterization of the adsorbent by SEM.

The micrograph of the wet blue leather waste (Fig. 4a) presented a different morphology from the natural leather (without chromium) related in the literature [20]. The fibrous aspect of the wet blue waste is probably due to presence of chromium in the leather [19]. It is interesting to observe that after P and K incorporation (Fig. 4b and d) a significant modification in the morphology

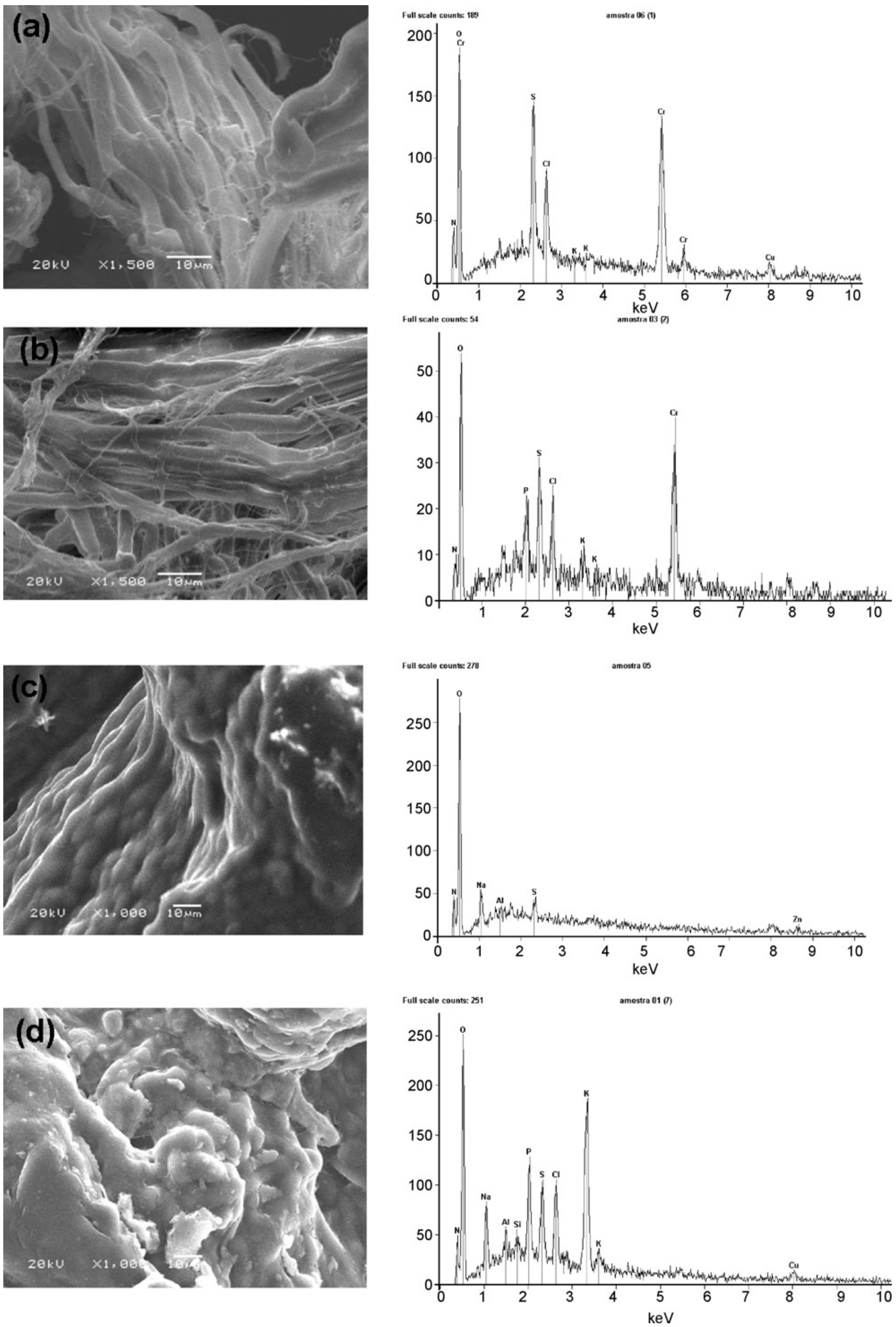

Fig. 4. Characterization of the adsorbent by SEM. (a) Wet blue leather waste; (b) wet blue leather waste incorporated with mineral K and P; (c) collagen (after the chromium extraction process); (d) collagen (after the chromium extraction process) incorporated with mineral K and P.

did not take place. On the other hand, comparing the wet blue waste (Fig. 4a) and the collagen (Fig. 4c), a strong modification in the morphology was observed, suggesting that this was caused by the chromium extraction. Moreover, the respective EDS analyses show interesting results about the amounts of chromium, potassium and phosphorous. It was observed high chromium content in the wet blue leather waste (Fig. 4a and b), but after the treatment of Cr extraction the signal form that element disappears (Fig. 4c and d) suggesting their total removal from collagen. The EDS analyses also showed the potassium and phosphorous incorporated in the collagen structure (Fig. 4b–d).

The infrared spectroscopy analyses were carried out for the all materials and the results are shown in Fig. 5. The protein-like structure of the material is evidenced by the signals in 1655 cm^{-1} relative to the carbonyl group (C=O) and in 1540 cm^{-1} to the N–H group in all materials [19]. Moreover, the chromium extraction and also the incorporation of the potassium and phosphorous did not modify strongly the collagen structure.

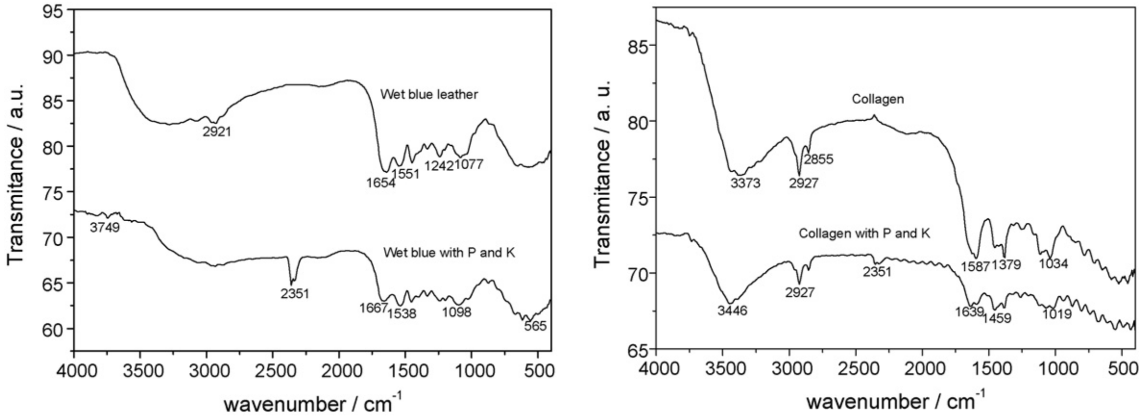

Fig. 5. Characterization of the infrared spectroscopy analyses for the all materials. (a) Wet blue leather waste and wet blue leather waste incorporated with mineral K and P; (b) collagen (after the chromium extraction process) and collagen (after the chromium extraction process) incorporated with mineral K and P.

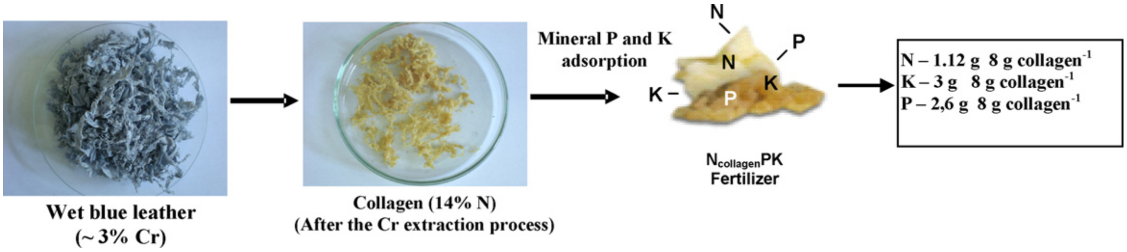

Fig. 6. Scheme of obtaining of the $N_{collagen}$PK fertilizer.

3.3. Tests as $N_{collagen}$PK fertilizer

In Fig. 6 shows the steps of obtaining the fertilizer $N_{collagen}$PK from the extraction of Cr wet blue leather.

The observed yields with the application of $N_{collagen}$PK formulations (T2, T3 and T4) and of the isolated collagen (T1) were sanctioned, mainly by the organic N release and the subsequent transformation in sufficient contents for the normal development

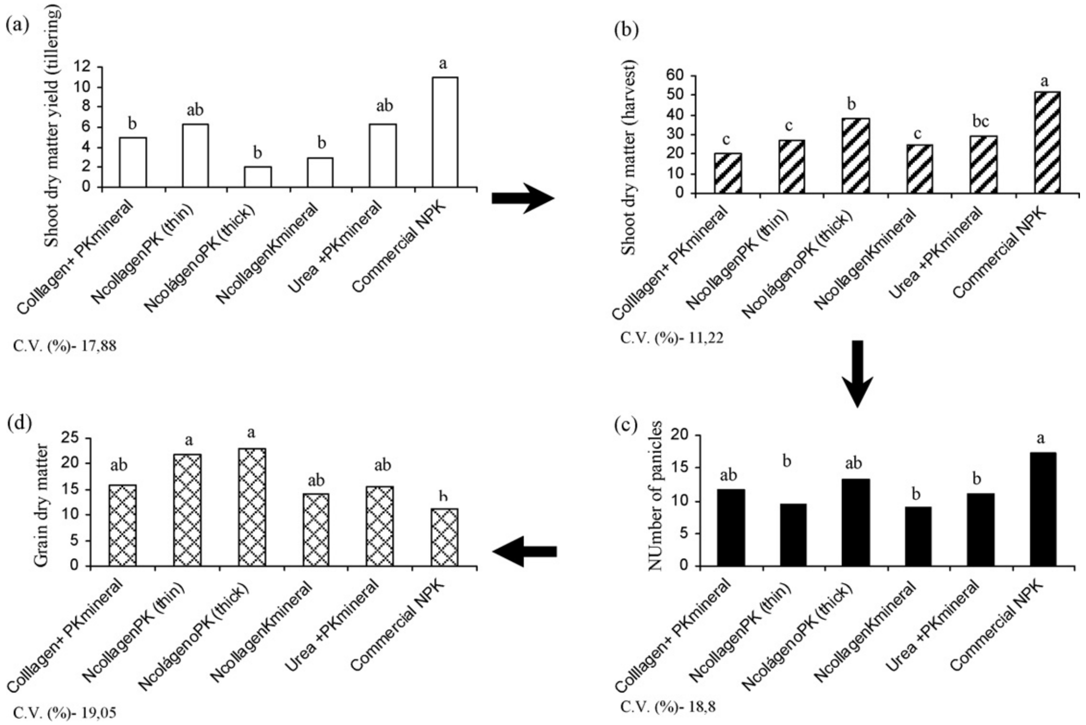

Fig. 7. Weights of shoot dry matter yield tillering (a), shoot dry matter the harvest (b), number of panicles (c) and weights of grains dry matter (d) of rice plants submitted to the different treatments.

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 collagen N was released in a way that the roots of the plants obtained better benefit from both N and P and K, which resulted in a higher grain yield (Fig. 7).

It is important to emphasize that although the $_{\text{commercial}}$NPK (T6) showed a higher weights of shoot dry matter because of tillering (Fig. 7a) and harvesting (Fig. 7b). The same results were not observed regarding grain yields (Fig. 7d). The number of panicles per each area unit is the component which mostly influences the grain yield regarding the nitrogen. On the other hand, there is a decrease tendency 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. Thus, the greater number of panicles which was found in the $_{\text{commercial}}$NPK (T6) formulation was not observed in the grain yield either (Fig. 7c). The urea fertilization (T5) showed satisfactory results and they were somewhat similar to the fertilization which contained collagen in terms of grain yield.

4. Conclusions

Phosphorus and potassium adsorption on leather industry wastes was well described by Freundlich models over the studied range of P and K concentrations, thus suggesting a multilayer adsorption process on surface of the adsorbent.

In the concentration range studied, both materials showed considerable adsorption capacity. The adsorption capacity values for potassium were 377 mg g^{-1} (collagen) and 449 mg g^{-1} (wet blue waste). For phosphorus, adsorption capacity values were 332 mg g^{-1} and 445 mg g^{-1}, for the collagen and leather waste, respectively.

The P and K incorporation on the collagen was shown be an interesting alternative to use this material as NPK fertilizer. The application of N$_{\text{collagen}}$PK formulations, as a source of nutrients to rice plants, showed promising agronomic results.

Due to the relatively high adsorption capacity of the collagen and also the high amounts of this material that are being produced worldwide, we believe that the leather waste can be used for adsorption of phosphorus and potassium for the production of fertilizers.

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