Mineralogical characterization of urban construction and demolition waste: potential use as a nutrient source for degraded soils

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Abstract

The consumption of raw materials in the construction industry is a non-sustainable activity because in this process large amounts of natural resources are consumed. Moreover, Construction and Demolition Waste (CDW) represents around 50% of waste produced in the urban region of world. For example, in the Medellin Metropolitan Area (MMA), 10,400 t.day^{-1} of CDW are produced, of which only 9.7% is recycled. It is for this reason that CDW management is currently unsustainable and generates significant adverse environmental impacts. It is today acknowledged that this waste can be used as a by-product material for the production of recycled coarse aggregate, showing industrial applicability. However, CDW with small particle sizes (less than 4 mm that represents around 16% of this waste), do not have applicability in these processes. Therefore, it is necessary to reduce CDW volume dumped. An alternative to the final disposal of finer CDW is to use it to improve the physical and chemical properties of degraded soils and improve vegetation and ecosystem services. This paper evaluated the potential use of CDW as a source of nutrients for degraded soils after it was submitted to bioacidulation process by *Aspergillus niger* and *Mortierella* sp. Insoluble minerals such as quartz, calcite, wollastonite, albite, anatase and actinolite were found in the CDW by mineralogical and chemical characterization

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techniques. CDW mesh could improve the physical properties of degraded soils since these particles are similar in size to silt and clay. Furthermore, after CDW were bioacidulated an increased concentration of Ca^{2+} were found, an essential nutrient for the growth and development of plants.
Keywords: construction and demolition waste (CDW), bioacidulation, degraded soil.

1 Introduction

The construction industry is significant to the growth and development of countries because it allows the development of buildings or infrastructures (roads, highways, bridges, among others) [1]. Thus, this growth enables to supply the demand generated by the population explosion and promotes the person's welfare [2]. Moreover, in the last decade, the construction industry has grown significantly and in this way it was generating an increase in raw material extraction. Where the extraction was preferred in the quarries, brick, gravel and sand quarries near of urban centers [2]. In this way, in 2010 consumption of aggregates was 37,400 Mt and this will increase to 48,000 Mt until 2015, the extraction is made of not removable mineral deposit [3].

Additionally, the construction and demolition waste process provide in the urban areas 50% of the total solid waste generate at the global level [4, 5]. Furthermore, its activity consumes 40% of the non-renewable natural resource [6, 7]. In the particular case of Medellin (city of Colombia) and its Metropolitan area (MMA), this kind of waste had not only arrived at dumps (4600 t/day) and legal landfills (2400 t/day) [8]. Also ends up in waterways and other areas not suited for it, as well as illegal dumps (3400 t/day) [7]. Unfortunately, in the MMA only approximately 1000 $t.day^{-1}$ of the construction and demolition waste (CDW) produced is recycled [9, 10]. Furthermore, in the MMA both the extraction of raw material used in civil works projects and the final disposal of CDW occur in the city's interior [9]. Together with an accelerated urban demand, high consumption of inert materials (gravel and sand) and the generation of CDW, this produces unsustainable development in the city [11, 12]. Thus, the extraction, construction and demolition of the building are considered unsustainable activity generating environmental impacts and system changes that may alter the biological balance [13, 14].

Therefore, it is necessary to research about new alternatives as using CDW. For example, as aggregates, it was proposed as a solution to the depletion of mineral deposits and generates decrease in the volume of spaces employees for disposal [15–17]. In this case, recycled aggregates of CDW present similar mechanical durability and non-structural concrete made from natural aggregates, where the degree of substitution required depends on the type of concrete [15, 18].

However, the use of fine recycled aggregates (size of less than 4 mm), in concrete products is not yet widely accepted. This limitation of fine recycled aggregate use is explained by the unpromising results of early research work, in particular because of high water absorption [12], a property that may create problems in both fresh and hardened state of concrete [19]. Therefore, these aggregates have been used mostly in bases and sub-bases of transport infrastructure and the recovery of former quarries by landscaping [5, 20].

Despite of this, it is necessary to provide a new recycling process that permits generate an aggregate value for these kinds of wastes, which represent 16% of total solid waste produced in the world [21–23]. The proper management and recycling of CDW avoid that uncontrolled disposal in landfills, parks, roads separators, private lots; legal, and illegal dumps, among others [24].

One alternative that is being considered for the subsequent use of CDW consists in using it for the recuperation of soils degraded by urban mining. In this way, it was designed reinforced soil in order to improve physical properties [25, 26] and to improve chemical properties, such as decreased soil acidity [27]. However, to date, there has been no research on a viable way of speeding up the release of nutrients contained in CDW, which are commonly found in highly insoluble minerals. It is possible due in the desert rocks the microorganisms promote rocks dissolution for their nutrition and plant establishment [29]. On these residues, it can utilize biotechnological techniques to generate added value, which could be a more economical and environmental-friendly option for the management and disposal of CDW [22]. Thus, the use of CDW in the restoration of degraded lands can both reduce the environmental impact that has been generated and improve the disposal of the waste. For this reason, this study is in line with state policies and with the construction industry's new emphasis [28].

The objectives of this study are: (i) to perform a mineralogical characterization of CDW to determine its chemical and mineralogical composition, and estimates its potential as a source of nutrients for degraded soils and (ii) to evaluate the effect of CDW bioacidulation using soil microorganisms, to dissolve elements contained within the waste.

2 Materials and methods

2.1 CDW sources and preparation of the samples

The samples used for this study were provided by the dump CONASFALTOS S.A., a local company, where three sample types were obtained: (i) concrete and brick, (ii) pavement and (iii) sand from excavation. These are representative of the CDW commonly produced in the MMA.

The samples were individually subjected to a crushing and grinding process with the aim of reducing the particle size. Initially, the CDW was passed separately through a jaw crusher of the BAN TRANNS brand, and fragments were obtained of approximately ¼ inch (0.635 cm). This was followed by a secondary crushing, in a roller crusher (0.01778 cm). After this process, samples were dried in an oven at 65°C for 24 h with the aim of eliminating residual moisture. Finally, the samples were passed through a disc pulverizer of the BICO brand (0.014986 cm). Using the Jones box method, a quartering of the samples was performed. Finally, in an Agate mortar, the samples were ground separately to ensure that they could pass through Tyler 200 mesh.

2.2 X-ray diffraction

The analysis was carried out using an X-ray diffractometer of the Panalytical Reference X'Pert PRO MPD brand with Cu radiation of the wavelength $K\alpha 1$ = 1.5406 Å. Power: 45 kV and 40 mA. Swept by a step-size of 0.013° at a rate of 59 s per step with constant sweeping.

2.3 Chemical analysis of minor elements

The concentrations of Pb, Fe, Cu, Zn and Ni in the solution were evaluated by atomic absorption, using an AA Spectrometer S Series Thermo Electron Corporation machine under the norm ENT 5526, 2007.

2.4 X-ray fluorescence

It was measured with an energy dispersive X-ray fluorescence spectrometer, with direct excitation in 2D. PANalytical MiniPal 2 brand, 9 w (30 KW, 1 mA) chrome irradiation tube, Si-PIN detector, 12-position sample changer, 100–240 V, 45–65 HZ.

2.5 Optical microscopy of plane polarized light (OMPPL)

The samples crushing were mounted in an epoxy resin with a catalyst of the ARALDITE brand. Subsequently, they were sanded with thick abrasives, then polished with a series of sandpapers of 200, 400, 600 and 1000 grit, and finally polished with an alumina of 3, 1, 0.3, and 0.05 μm on a fiber cloth. The procedure was performed using the standard practice ASTM D2797-2009. Then, the thin sections were analyzed using OMPPL, in the reflected light mode, with an optic microscope of the Carl Zeiss AXIO brand and objective lenses of 4, 50, and 100X in air.

Additionally, to determine the percentage of brick, plaster and concrete, as well as the average particle size, a point-count was performed using the ASTM C1356M-2010 standard test method.

2.6 Culture medium and solubilization conditions

Two soil fungi with the capacity to produce organic acids were used in the study, with the aim of determining CDW bio-dissolution. The fungi were *Mortierella* sp, provided by the Universidad Nacional of Colombia's Biogeochemistry Laboratory (Osorio and Habte [38]), and *Aspergillus niger*, provided by Universidad Nacional de Colombia Microtoxinas y venenos naturales Laboratory.

The fungi were cultured in the potato-dextrose-agar (PDA) medium at 25°C for 5 days. Then they were Subculture in the culture medium with bromothymol blue as a pH indicator, used to verify their production of acids.

Before using the fungi, a count of colony forming units in the PDA medium was performed at 25°C after 48 h. After verifying the ability of both fungi to lower pH, they were cultured in the PDA medium for 5 days at 25°C and the mycelia were suspended in distilled sterile water and conserved at 4°C for experimental use.

For the in vitro CDW dissolution tests, the basic composition of the experimental culture medium was (g.L-1): glucose 10, NH4Cl 1.0, and CDW 3.5 as the sole nutrient source. 100 mL of this medium was placed in 250 mL Erlenmeyer flasks and sterilized in an autoclave at 120°C, 0.1 MPa for 20 minutes. After the Erlenmeyer flasks were inoculated with 1 mL of the *Mortierella* sp. suspension and 7 mL of *A. niger*, they were agitated continually at 100 rpm, 28°C for 7 days.

After the incubation period, the pH of the solution was determined, along with their P and Ca2+ concentrations. The pH was measured using a potentiometer (WTW electrode Sentix 81). The P concentration (mg.L-1) was determined using the blue-molybdate method [39] at 890 nm (Genesys 20 Thermo Spectronic spectrophotometer), prior to filtration through Whatman No. 42 filter paper and centrifugation (Jouan MR 1812 centrifuge) at 4000 rpm (1520xg) for 10 minutes. The Ca2+ concentration in solution was evaluated using atomic absorption in an AA Perkin Elmer 2380 spectrometer by direct reading.

2.7 Experimental design and data analysis

The in vitro CDW bioacidulation experiment was performed separately for each fungus and a completely randomized statistical design was employed. The treatments consisted in inoculation with each microorganism, with an uninoculated control included as a reference point. Every treatment had four tests. The effect of the treatments was evaluated using variance analysis and when this was significant, the Duncan's multiple range test was used for mean separation. Both tests were conducted with a significance level of (p) ≤ 0.05, using STATGRAPHICS software, version Centurion XVI.

3 Results and discussion

3.1 Mineralogical characterization

The concrete and brick samples presented the following mineral phases: quartz, calcite, sodium feldspar, wollastonite, actinolite and anatase; these phases may belong to the concrete aggregate (Figure 1). These minerals masked the most of the constituent phases of the cementitious matrix due to their lower quantity, size and degree of crystallinity [30]. It should also be noted that the cementitious matrix phases were rich in calcium silicates, calcium aluminosilicates and calcium ferroaluminates. All phases are hydrated, as well as calcium hydroxide and calcium sulfoaluminate hydrates [5]. For the pavement samples, the phases found were quartz, actinolite, albite and calcite (Figure 2). These samples also showed lifting in the spectrum, suggesting the presence of amorphous materials, which could be petroleum-based polymers. On the other hand, quartz and calcite were found for the sand samples (Figure 3). It is important to emphasize that the minerals identified in all the samples are present as primary or secondary minerals in the clayey part of soils. Thus, if these minerals were used in degraded soil, this would not affect its composition [29].

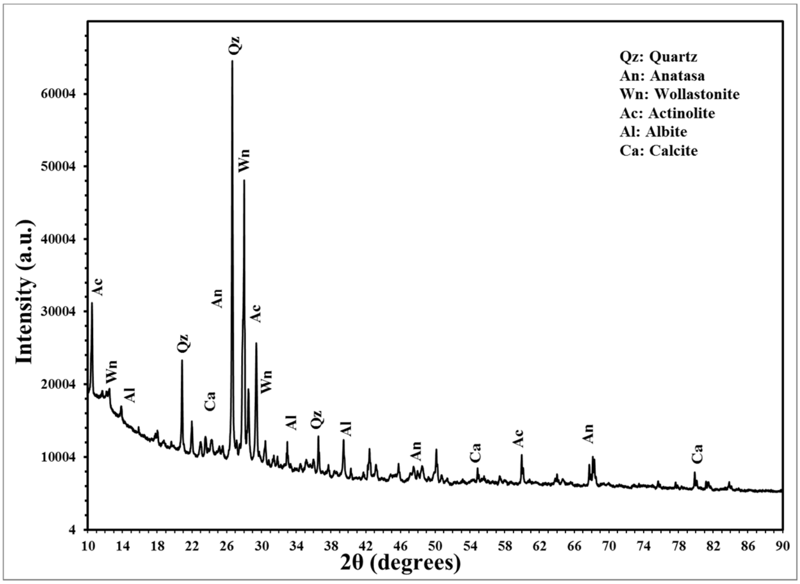

Figure 1: X-ray diffractogram of the concrete, brick and cement samples.

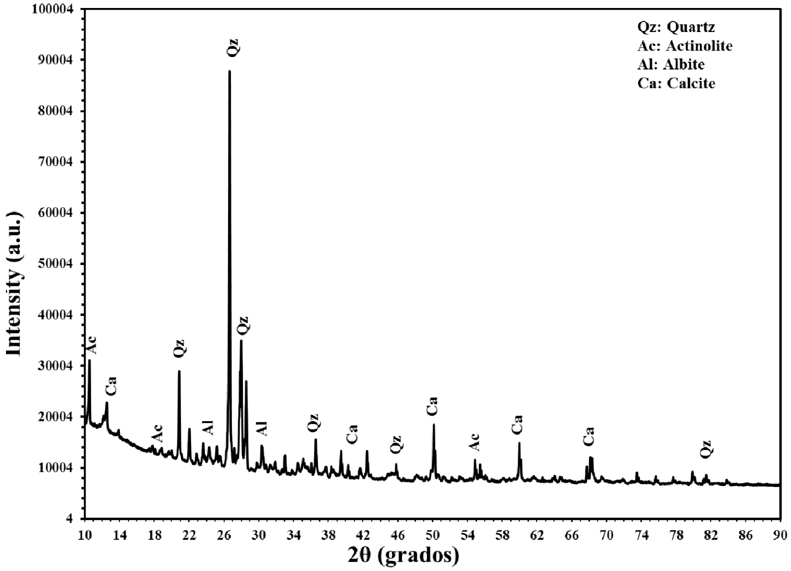

Figure 2: X-ray diffractogram of the pavement sample.

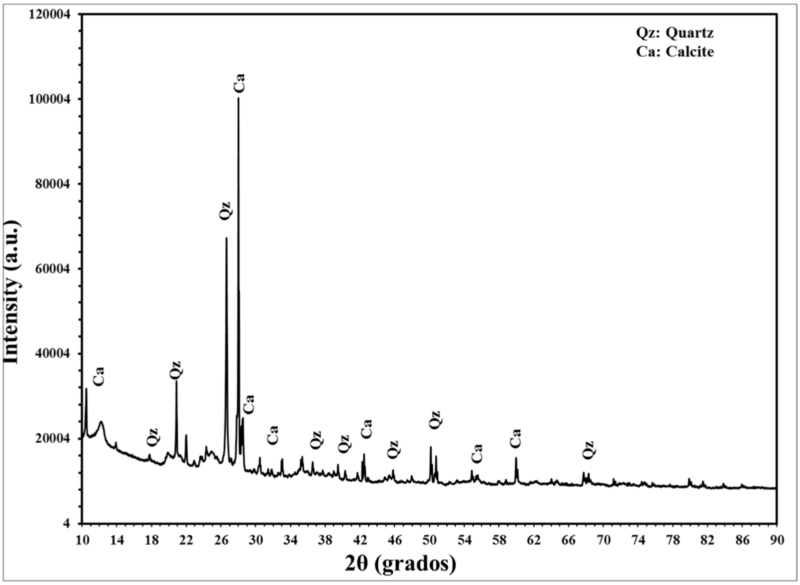

Figure 3: X-ray diffractogram of the excavation sand sample.

Based on the XRD results obtained, it can be concluded that the concrete and brick samples had the highest potential for being a nutrient source for degraded land because it contains elements as Ca^{2+}, Si and P that are deficient in degraded soil. However, the elements are in minerals that are insoluble. Therefore, if its constituent minerals are, subjected to a bioacidulation process. It could result in a solution of elements such as Si, S, P, Ca, Mg, Fe, Mn and Zn from alumisilicates, silicates or carbonates. These elements are considered to be essential nutrients and beneficial to plant growth [31, 32]. Although some minerals were present in the pavement sample with elements that could be released and promote soil restoration, pavement may contain some derivatives of petroleum, which is potentially toxic to plants.

In all the materials were detected trace elements (Cu, Fe, Pb, Zn and Ni), which were measured by atomic absorption (Table 1). Although they were present, they were found in small concentrations that would not be toxic to plants [2].

Table 1: Content of elements in CDW determined by atomic absorption.

Sample	Cu	Fe	Pb	Zn	Ni
	mg kg^{-1}				
Concrete and brick	60	33700	170	230	90
Pavement	60	34200	140	190	180
Excavated sand	60	4760	130	240	40

The chemical characterization of CDW using X-ray fluorescence (XRF), showed that the all samples contained the following elements: Si, Ca, Al, Fe, Ti, Mg, Na, K, Mn, Cr and S (Table 2). Additionally, these elements were present in minerals had a low solubility in water. However, the dissolution of CDW can be promoted through bioacidulation processes using mineral-solubilizing microorganisms, such as those found in plants established in desert rocks [33]. These could be used in the process of bioacidulation for these minerals, thus permitting the release of those elements as nutrient sources for soils.

Table 2: Content of elements in CDW determined by X-ray fluorescence.

Oxides	Concrete and brick (%)	Pavement (%)	Excavation sand (%)
SiO_2	44.3	47.5	55.39
CaO	20.47	3.47	5.63
Al_2O_3	15.76	19.96	13.9
Fe_2O_3	5.35	14.91	10.22
P_2O_5	1.9	0.69	0.78
TiO_2	1.01	1.67	1
MgO	<0.10	<0.10	<0.10
Na_2O	0.1	2.64	1.16
K_2O	1.04	1.27	1.32
MnO	0.13	0.2	0.19
Cr_2O_3	0.05	0.05	0.14
SO_3	0.49	0.1	0.62

With the aim of verifying that, the various types of minerals contained in the samples equated to a higher quantity of potential nutrients for soils (concrete and brick sample). Thin sections analyzed by OMPPL exhibited displayed sub-rounded heterogeneous forms that ranged from medium sphericity to subangular and subelongate forms, which were also heterogeneous. The important phases included: monocrystalline quartz (38.4%), polycrystalline quartz (23.9%) and lithics (7.3%). Grains of polycrystalline quartz and lithic fragments of igneous rocks were observed, which alterations such as oxidation. The principal minerals in the sample(s) were amphibole (possibly hornblende), quartz, plagioclase, pyroxene, carbonates, iron oxides, aluminum oxides and muscovite. Additionally, through a point count the sample was composed of concrete (55.8% with average particle size 84.2 μm), plaster (26.6% with average particle size 74.6 μm) and brick (17.6% with average particle size 68 μm). The particle size of the constituent elements in the concrete and brick samples was within the values corresponding to silt and fine sand in the soil. The results confirmed that CDW has the potential to be use as a nutrient source in degraded soil since it can provide some of the nutrients necessary for plant growth [33]. Degraded urban soil exhibits compaction problems and a decrease in the essentially nutrients for plant growth, thus impeding the establishment of plants [22]. The results showed that the CDW samples contained a large percentage of quartz, an inert mineral that is useful for improving physical properties such as texture and water filtration in soil [28]. Furthermore, the presence of calcite, wollastonite and anatase was evident. These minerals can improve the chemical properties of soil [22], increase pH (in the case of calcite and wollastonite), and provide essential nutrients such as Ca, P, Mg, Mn and Fe, as well as others such as Na and Al, which are present in feldspar and actinolite. These minerals were found in greater proportion in the concrete and brick sample.

Although CDW may contain traces of elements toxic to plants, these are found in low concentrations, and are unlikely to pose a risk to any plants that ultimately establish in degraded soils. These elements are, in fact, necessary in small concentrations for the development of many biochemical processes of soil and plant microorganisms [34]. However, it is worth noting that a posterior study should be performed to measure the impact on bioavailability and the potential phytotoxicity of these elements following their application in soils degraded by urban mining.

3.2 CDW bioacidulation

In vitro CDW bioacidulation tests showed the production of acids by both fungi, evidenced by decrease in the pH values of the solution (Figure 4). The control presented a pH of 8, while the pH of the inoculated samples fell to 6.0 with *Mortierella* sp. and 3.6 with *A. niger*. The production of acid by *A. niger* was statistically significant with respect to the control. These results indicate that fungus acidification could be to neutralize the dissolution of carbonates and hydrate calcium aluminosilicates to increase the pH. Their dissolution reactions in an acidic environment are thermodynamically favorable as illustrated by [35] in equations 1–4 for albite, chlorite, quartz and calcite:

$$NaAlSi_3O_8 + 4H^+ + 4H_2O \leftrightarrow Na^+ + Al^{3+} + 3H_4SiO_4 \quad (LogK^\circ = 2.74,\ \Delta G^\circ = -887.41\ {}^{Kcal}/_{mol}) \tag{1}$$

$$Mg_5Al_2Si_3O_{10}(OH)_8 + 16H^+ \leftrightarrow 2Al^{3+} + 3H_4SiO_4 + 6H_2O \quad (LogK^\circ = 60.30,\ \Delta G^\circ = -1975.56\ {}^{Kcal}/_{mol}) \tag{2}$$

$$SiO_2 + 2H_2O \leftrightarrow H_4SiO_4 \ (LogK^\circ = 10.41,\ \Delta G^\circ = -203.51\ {}^{Kcal}/_{mol}) \tag{3}$$

$$CaCO_3 + 2H^+ \leftrightarrow CO_{2(g)} + H_2O \quad (LogK^\circ = 9.74,\ \Delta G^\circ = -270.18\ {}^{Kcal}/_{mol}) \tag{4}$$

Based on the minerals contained in CDW, the potential to solubilize P and Ca can be highlighted, which is very important because these two elements are necessary nutrients for plant establishment. The levels of P in solution after bioacidulation (Figure 5) did not present significant differences with respect to the control. This may be because CDW contains small quantities of this element (<2%). However, the amount that fungi can immobilize, which could be significant, was not measured.

The concentration of Ca significantly increased in *A. niger* (262.6 mg L^{-1}) and *Mortierella* sp. (275.37 mg L-1) with respect to the white (141.25 mg L-1) (Figure 5).

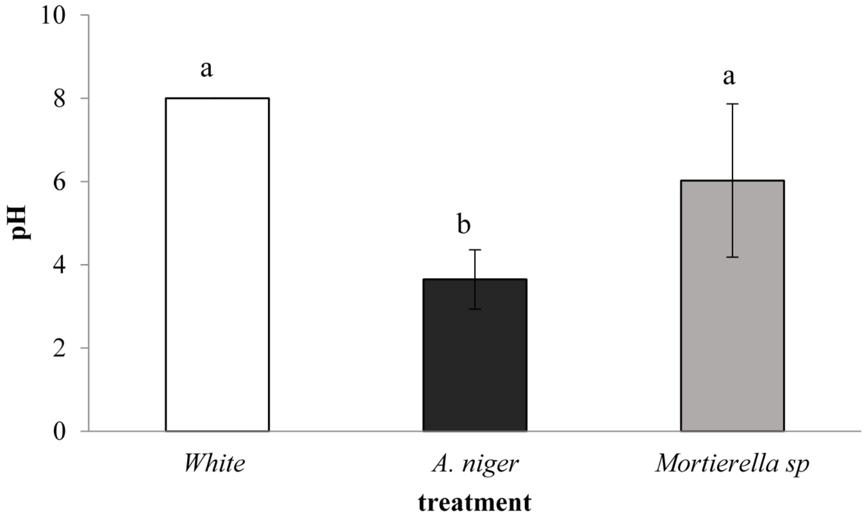

Figure 4: Changes in pH values in solutions inoculated with the fungi. Each bar represents the average of the four repetitions. Standard deviations are represented at top of each bar. Different lowercase letters indicate significant differences among the treatments according to the Duncan test ($p \leq 0.05$).

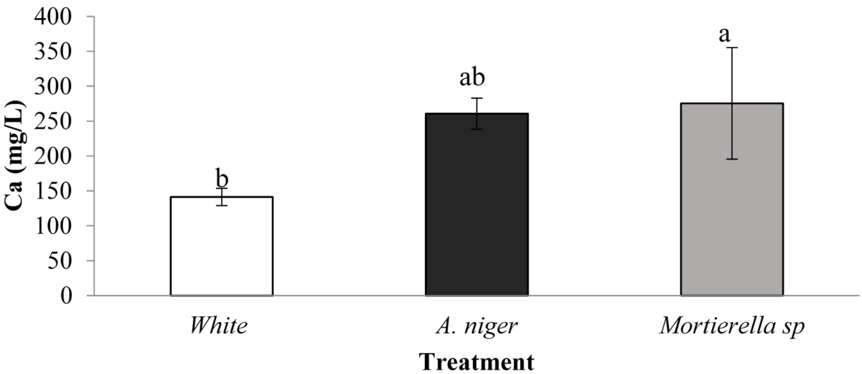

Figure 5: Calcium concentration in solution ($mg.L^{-1}$) of the solution as a function of inoculation with the fungi.

Each column represents the average of four repetitions. The bars indicate standard deviation. Columns with different lowercase letters indicate significant - differences in the treatments according to the Duncan test ($p \leq 0.05$).

Both fungi produced acids in the medium. *A. niger* produced citric acid in a greater quantity [36] and *Mortierella* sp. produced oxalic acid [37] in a greater quantity. Both acids caused comparable reactions in terms of dissolving CDW. This was evidenced by a decrease in pH and the release of Ca.

Both other researchers' results [38, 39] and the results of this study show the apparent existence of a proportional inverse relationship between medium pH and nutrient concentration in solution as a result of CDW dissolution.

From the results obtained, it can be inferred that despite the fact that CDW is stable in natural conditions in accordance with the mineralogy found, upon being exposed to mediums with microorganisms that exude organic acids, it undergoes changes to its physical, chemical and mineralogical properties. This favors the dissolution of elements such as calcium, which is comparable to the results that have been found [40, 41] in the case of urban structures and sculptures.

The deterioration, or degradation, of CDW is caused by the organic acids produced by the fungi *Mortierella* sp. and *A. niger*, leading to instability and the dissolution of minerals like carbonates, calcium silicates, and phosphates, among others [42], thus releasing Ca and P in solution. In studies carried out by other authors, one of the predominant factors in the dissolution processes of rocks, minerals, and urban structures is microbial activity. This is supported by the findings of the present study [43].

4 Conclusions

This study has shown how CDW can potentially be used in the remediation of soils degraded by urban mining, since it contains elements needed for plant nutrition and soil microorganisms that can be left in solution after a bioacidulation process. Although these elements are present in insoluble minerals in the most cases, they can be solubilized by the actions of fungi. Furthermore, due to the size of CDW particles, it can change the physical properties of the soil, thus improving texture, filtration, drainage, aeration and other properties.

Although CDW presents traces of elements that in high quantities can be toxic, these are found in very low levels, and are thus not expected to generate phytotoxic effects; to the contrary, they may benefit biochemical processes of plants and microorganisms.

The concrete and brick sample is that which may provide the greatest contribution of nutrients to the soil. This is due to its high Ca and P content, as well as the absence of petroleum-based materials present in the pavement, which can be harmful to plants.

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