Compositional, thermal and microstructural characterization of the Nopal (*opuntia ficus indica*), for addition in commercial cement mixtures

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Abstract. The Nopal (*opuntia ficus indica*) from remote times has contributed like food and additive product in prehispanic constructions; although it grows in all the Colombian territory is very little used and its contribution in mixtures of Colombian cement is unknown. In order to evaluate the hydration characteristics of Nopal, several Thermogravimetric Analysis (TGA) were performed to evaluate the optimal temperature of dehydration. Initially, the results show that around 175°C the weight loss is approximately 95%, this mass loss corresponds to the process of physical removal, suggesting that at least a remaining amount of 5% (w/w) has the ability to retain large amounts of water which is stored in the micro-structural deposits of Nopal. The evaluation by means Scanning Electron Microscopy (SEM), confirm that the whole cactus structure enables the water storage at cellular level. The results of infrared spectroscopy (FT-IR) and Energy Dispersive X-ray (EDX) analysis allowed the qualitative and semi-quantitative evaluation of the presence of functional groups and elemental chemical composition of Nopal respectively, mainly related with polysaccharide functional groups, which corresponds to 85% of the total composition. Other functional groups, are related with protein and mineral components. This found characteristics are relevant for the water retention in process that require the decrease of water consumption and the reinforcing of mechanical properties and durability, due to ability of Nopal mucilage to restore its hydration characteristics.

1. Introduction

The cement is one of the most durable and versatile building materials known to date, economical and the most used in the world, its production follows a trend of growth reaching $2.8 \times 10^9$ tons worldwide and an increase of $4 \times 10^9$ tons is expected by 2050 [1,2]. In Colombia, the production of cement in 2015 reached 12,100 tons with a constant problem related with the excessive water consume, which increases the handling characteristic but leads to an increase in porosity, as consequence the final material exhibits a reduction in the mechanical resistance and a high permeability inducing to the decrease of durability [3,4]. However, if the water content is insufficient a decrease in workability appear, causing strong damage effects as excessive water content [5]. Although this phenomenon has been solved from pre-Columbian times due to the incorporation of derivatives of plant species as Cactus Genus *Opuntia*, also known as Nopal in cement mixtures, mainly concentrated in the region of Mexico with the Aztec culture in the construction process of the pre-Hispanic buildings [6,7]. This xerophytic plant characteristic of subtropical dry climate regions, originated in tropical and subtropical America, nowadays this vegetative specie is present in a great variety of agro-climatic conditions, where it could be cultivated. This cactus specie have a strong ability to withstand prolonged periods of dryness, due to the presence of a gelatinous...
body called “mucilage” that form three-dimensional molecular networks capable of retaining large amounts of water in a stable cellular arrangement [8,9], reason that justify its use in cement mixtures, representing the objective of current work as one of the most relevant studies in this field, due to hydration effect that could be improved as well as another physicochemical properties. This vegetal product is used in form of a complex carbohydrate or gel with high molecular weight, which behaves like negatively charged polyelectrolytes, delaying the hydration of the cement because of the presence of hydroxyl and carboxyl groups along the chains of Nopal’s mucilage binding to water molecules by polar interactions specifically by hydrogen bonds [2,10], tending to form stable hydrocolloids causing greater cross linking between macromolecular bonds in a calcium rich system such as the cements, this increases thickening in this type of mixtures [11,12], provide excellent results in the water absorption capacity; the Nopal has been used in the actual food industry as emulsifiers, water purifiers, comestible adhesives, plasticizers in mortars, among others [13,14]. To achieve this purpose, the work evaluates several percentage mixtures (w/w) and different setting times as been reported previously [6,15,16], contributing to provide a physicochemical characterization of native Nopal specie of Tunja city (Colombia), in order to evaluate its thermal behaviour, microstructural arrangement and its elemental composition, responsible for the improvement of properties in cement mixtures.

2. Materials and method
Initially, the Nopal specie was characterized with the help of the Botanical Garden of the Universidad Pedagógica y Tecnológica de Colombia, comparing and establishing qualitative similarities of the structural units of the plant such as stem, leaves, thorns and fruits, in order to determine its main characteristics related with the interest specie, because almost 300 species of Nopal are known, however, there are only 10 or 12 of the same are used as hydrating material [17,18]. For the preparation of the sample, was necessary to start from a sample of 2 years of age, which was treated to isolate the mucilage from the rest of Nopal plant in longitudinal sections with intervals of approximately 1cm, the outer cuticle was removed. The resultant material was dried in an electric oven at 40°C for 3 days, after which a sample was recollected to be grounded and sieved at 200 US standard before characterization process. Initially the dried mucilage was evaluated by infrared spectroscopy, using a Perkin-Elmer FTIR equipment between 4700-500 cm⁻¹, using the ATR configuration. The TGA-DTA analysis was performed in a thermostatic balance SDT Q600 equipment, using 50mg of sample, at a heating rate of 25°Cmin⁻¹ from room temperature to 500°C under air flow (50mLmin⁻¹). The percentage of weight as a function of temperature was analysed in terms of endothermic and exothermic processes. The microstructural properties were evaluated by means SEM and EDX on a Zeiss-Evo MA 10 equipment. For the analysis, the samples were coated with platinum for a better resolution images in a sputtering QUORUM Q150R ES instrument.

3. Results and discussion
The botanical classification of Nopal is shown in Figure 1 and summarized in table 1; it allows to identify the best Nopal specie in the Tunja region for hydration process in cement mixtures, revealing that is a very common cactus without evidence of commercial exploitation with a high degree of proliferation in arid areas.

![Figure 1](image-url) (a) Schematic images of the Nopal plant (Opuntia ficus indica). (b) Photographic images of the Nopal plant in Tunja, Colombia.
Table 1. Botanical classification of the Nopal (Opuntia ficus indica).

| Structural unit of the plant | Description |
|-----------------------------|-------------|
| Stem                        | Plants from shrub to arborescent, from 1.7 to 3m in height, with a primary stem, well defined. Dark chestnut, green or grey, cylindrical stem, 45cm long, 20cm in diameter. |
| Leaf                        | Cladodes usually elliptic, but also, oval, circular, oblong or rhombic 27 to 32cm wide and 44 to 63cm high when they reach 2 to 3 years of age. |
| Thorn                       | Thorns are usually absent, but sometimes there are few cladodes with a spine, usually acicular, sunken, and white. |
| Fruit                       | The fruit is usually turbid, sometimes spherical, cylindrical or elliptical, often bright yellow or red |

The infrared spectroscopy results shown in Figure 2, allow to evaluate of qualitative form the presence of amide functional groups associated with polysaccharides, responsible for the higher water retention as has been established by the literature in which, this vegetative specie have been used as additive in cement mixtures [19]. The vibrating signals at approximately 1640 and 3280cm⁻¹ could be identified with polysaccharide molecules in which the signals were compared with the corresponding SDBS database. The signals around 1600cm⁻¹ identify the amide group corresponding with the amide vibration, composed by the coupled vibrations of the C=O, NH and CN bonds [20]. The presence of secondary amines could be identified by the signal around 1400cm⁻¹, corresponding with the N-H deformation and C-N deformation bonds [20]. Chandra [19] observed this behaviour in vegetative samples derived from cactus species with strong signals around 1400cm⁻¹, related with amines and amides. Other authors [20-22] associate these signals with the carboxylic acid group and the peptide bond linked with the C-H deformation vibrations of the polysaccharides. In other studies Bayar [18] determined that the area between 1200 and 950cm⁻¹ is the region for carbohydrates fingerprint and it allows the identification of some functional groups of polysaccharides such as stretching C-O-C, bending O-H, and deforming (CH₃) vibrations. Finally, the band located at 2920cm⁻¹ is associated with the vibrational bond C-H present in all organic samples with a strong signal around 3500cm⁻¹ related with the hydroxyl group (O-H) [19,20,22], a characteristic band present in proteins, carbohydrates and polysaccharides in general.

Figure 2. Infrared spectrum of dry mucilage extracted from Nopal specie.
The thermal analysis shown in Figure 3 evidence the progress of several exothermic reactions with weight loss around 90% of the initial mass, and related with the presence of water, which begins to evaporate around 50°C and progressively increase until a maximum value of 105°C and finish around 210°C in accordance with Pansu and Villegas [23,24]; this behaviour is common in organic samples and some research applied to cements has shown that the water retention capacity is slightly better when the mucilage is added dry at low doses and when is pre-mixed with the water in the place of mixing it as a dry powder in the other solid phases of the blends of cement as usual [11], Therefore by thermogravimetric analysis it was determined that the temperature of 50°C or less are optimal for a good dehydration of the Nopal in order to obtain better results when mixing it with cement.

![Figure 3. Thermal analysis (TGA-DTA) of the Nopal specie.](image1)

It is evident that the evaporation process is carried out in a single stage, clearly identified in which occur a weight loss around 95%, after the mass begins to stabilize. The corresponding heat flow is concordant with a process of physical removal of water retained in the material, after which exist a slight variation of mass related with the combustion of organic compounds (250-350°C) and the final loss of mass stabilizes around 350-500°C, implying that at least a remaining amount of 5% (w/w) has the capacity to retain large amounts of water for potential applications. The morphological evaluation of mucilage by SEM shown in Figure 4, confirm the morphological characteristics of the vegetative specie, determining that dry process produce an open cell morphology in which the plant stored the cellular water to fulfil its vital functions. The images reveal that all the lattice of the cactus focuses on water storage at the cellular level without evidence of another kind of another water storage mechanism in accordance with TGA results.

![Figure 4. Scanning electron microscopy images of Nopal dry specie, (a), Nopal microstructure at 500x, (b) Nopal microstructure at 800x.](image2)
With the help of EDX analysis and energy dispersion, it was possible to provide an elemental composition of mucilage, determining that the majority of the components correspond to oxygen and carbon with at least 85% of the total composition and other elements such as sulphur, iron potassium and calcium in small amounts. There is no evidence of mineral elements that assist in the water retention process according to the results derived from FT-IR. It is therefore evident that in this case most of the carbon and oxygen contents are due to the presence of polysaccharide chains, as well as components such as sulphur in proteins and other organic compounds are responsible for the high water storage capacity. In the Nopal plant, in this respect, the work done by Cardenas [8] determined that the Nopal has the capacity to withstand prolonged drought due to the presence of mucilage that form molecular networks capable of retaining large amounts of water, this property works like an additive for good hydration in cement mixtures [25].

4. Conclusions

Based on the characterization by FT-IR and SEM-EDX, it was possible to determine that the morphology, molecular and elemental composition of Nopal are responsible for the retention of large amounts of water with small amounts of this plant's mass corroborated by TGA-DTA analysis; this is due to the fact that all the microstructure allows the storage of water at the cellular level supported by the presence of hydroxyl functional groups belonging to polysaccharide chains which, through chemical bonds, allow the retention and rheological changes at the molecular level in the water; this type of species could help in the obtaining of new cements and improve the process of hydration, durability and mechanical resistance in conventional cements with a low environmental impact.

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