

Synthesis of natural coagulant from *Anacardium occidentale* and application to remove metallic pollutants from water

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The removal of metallic pollutants from water or wastewater requires the application of specific methods and processes such as chemical precipitation, ion exchange, adsorption, membrane filtration, electrochemical treatment technologies, among others.

Ang and Mohammad (2020) state that natural coagulants have shown its coagulation efficiency. However, some important technological bottlenecks need to be overcome to ensure reliability and full-scale application. When compared to synthetic coagulants based on trivalent iron and aluminium salts, tannins have stood out as natural coagulants since they present some advantages such as the possibility of synthesis at a local level and the high efficiency of pollutant removal in a wide range of values of pH.

Anacardium occidentale (Cajueiro) is a deciduous plant abundant in the north and northeast regions of Brazil and easily found throughout tropical America. The Brazilian variety is popular for its ease of culture and has a great economic and social importance for vulnerable populations in the Brazilian poorest regions. The main product is the kernel that participates in a world market that moves over 2.4 billion-dollars per year and employs approximately 1.2 million people.

Another important aspect is the search for eco-friendly coagulants that could reduce the environmental impacts from cradle to grave. Some LCA studies have shown that the synthesis and use of natural coagulants results in a reduction of potential environmental impacts. Amante et al. (2015) showed that the carbon dioxide emissions associated with sulphate aluminium coagulant are 80% higher than those of the *Moringa oleifera*-based coagulant.

Therefore, this study presents the process of synthesizing and obtaining a natural coagulant from tannins extracted from the *Anacardium occidentale* bark and the results of its use to remove metallic species from water.

The raw material was the bark of the *Anacardium occidentale* collected in the municipality of Camaçari, north coast of the state of Bahia, Brazil, geographic coordinates -12.697968, -38.128461 of latitude and longitude, respectively. The chips were removed from the bark of the *Anacardium occidentale* between 25 cm from the base and 1.30 m high carefully in order to not reach the vascular cambium. The chips were washed to remove sand and dust. Subsequently, the material was dried in an oven at 70 °C for 24 hours. After the cleaning step, the chips were reduced to smaller fragments with the aid of an analytical mill (Quimis® model Q298A21). The milling process was carried out with regular stops to avoid overheating the mill knives, which could cause changes in the chemical composition of the tannins. The ground material was sieved and the fraction that passed through the 1.00 mm sieve (16 mesh) and which was retained in the 0.25 mm sieve (60 mesh) was selected. The powder obtained was stored in a desiccator avoiding moisture and protected from the light.

The morphological analysis of the natural coagulant surface was obtained through scanning electron microscopy (SEM), performed in a Jeol® model JSM-6610LV equipment with gold deposition on the sample surface performed in a Denton® Vacuum DeskV metallizer. The content of hemicellulose, cellulose and lignin was determined using a methodology based on the determination of insoluble fibres in neutral detergent developed by Soest and Wine (1967). Thermogravimetric analysis (TG) were performed using a Shimadzu® model TGA-50 equipment, in a nitrogen atmosphere and heating rate of 10 °C per minute in a temperature range from 30 to 1,000 °C. The thermal behaviour of the material was observed using the differential scanning calorimetric (DSC) technique, performed in a Shimadzu® model DSC-50 equipment, in a nitrogen atmosphere and a heating rate of 10 °C per minute in a range of 30 to 600 °C. For analysis of the functional groups, infrared spectra with Fourier transform were obtained in an IRPrestige-21 Shimadzu® instrument, using scanning in the spectral range from 4,000 to 400 cm⁻¹. In order to determine the metal concentration present in the powder, its acid digestion was carried out, followed by the quantification of the metals by reading the samples using optical emission spectrometry.

The tannins were extracted from the powder obtained from the chips of the *Anacardium occidentale* (PCAO) by connecting a volumetric flask containing the powder diluted in ultrapure water to a reflux condenser and it was kept under heating at 100 °C and stirring for 2 hours. The extracted liquid was centrifuged in a Quimis® model Q222T204 centrifuge and kept under 4 °C to protected from the light and to prevent the degradation of tannins. Each sample was subjected to two extractions in order to increase the amount of extracted tannins. At the end, each 2 g of PCAO produced 25 mL of extract with *Anacardium occidentale* tannins (EAOT).

Synthetic water contaminated with known amounts of the metallic species was prepared using analytical grade reagents (Merck®) and ultrapure water with a specific resistivity of 18.2 MΩcm from an Elga LabWater® purification system (Option-Q, UK). The tests were carried out in a Jar Test apparatus. The tests were performed in duplicate using volumes of 0.5; 1.0; 2.0; 3.0; 4.0 and 5.0 mL of extract with tannins to a volume of 500 mL of synthetic water. The quantification of metallic species was carried out using the inductively coupled argon plasma optical emission spectrometer (ICP-OES), Shimadzu® ICPE-9820.

The EAOT density was approximately equal to 1.0 g.cm⁻³. The FTIR results revealed an intense band between 3,343-3,252 cm⁻¹, a band around 2,356 cm⁻¹, another at 2,136cm⁻¹, a well-defined band at 1,633 cm⁻¹ and smaller bands at 1,321 cm⁻¹ and 1,212 cm⁻¹. The preliminary tests revealed removal efficiencies of metallic species ranged between 2 and 25%. Among the investigated metals, the one that presented the lowest affinity with EAOT was Sn and Cu presented the highest affinity.

References

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