Extraction and Use of Plant Biopolymers for Water Treatment

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Abstract

The action of promoting the removal of particles in water requires coagulant substances, which destabilize the equilibrium of the mixture in aqueous solution; this is needed to perform the coagulation and flocculation operations, in the treatment of drinking water and wastewater; especially for the removal of solids with diameters smaller than 0.2 mm; this operation is carried out with chemical compounds capable of breaking the ionic stability of a mixture and segregating the solids that cannot be separated without this operation; The plants tested to be used as coagulants or flocculants have had a traditional use, which indicates their ability to carry out the separation of solids. The plants described in this chapter are *Melocactus* sp., *Opuntia* sp., *Stenocereus griseus*, *Cereus forbesii*, *Aloe arborescens*, *Aloe vera*, and Kabuli chickpea (*Cicer arietinum* L.), of these plants have been used different parts, either their stems, their fruits, or other parts of the plant that have demonstrated a coagulating or flocculating capacity.

Keywords: biopolymer, coagulation, flocculation, turbidity and color

1. Introduction

Conventional water treatment processes include coagulation and flocculation, especially that which is chemically assisted, for both drinking water and wastewater. The removal capacity of these operations is effective and with a speed that could have been used, especially with waters that have high concentrations of organic matter, for this purpose, reagents have been used such as aluminum sulfate, which is usually obtained from the reaction of aluminum hydroxide with sulfuric acid [1]. Another reagent used is ferric chloride, which is obtained by the reaction of chlorine gas on heated iron [2]; and a reagent used in recent years is the aluminum polychloride obtained by the reaction of aluminum with hydrochloric acid in aqueous solution [1].

The reactions associated with the coagulants are determined by some parameters such as the pH, the temperature of the water, and the concentrations of the solids that are going to be complexed to form flocs that can be separated by density difference inside the mixture. When the flocs are separated from the mixture, sludge is generated that must be thickened and then disposed of, within a waste management plan; these residues will have a high concentration of aluminum and iron, respectively, according to the type of coagulant used, whether it be aluminum sulfate, aluminum polychloride, or ferric chloride. The final disposal of these sludges is usually difficult, because of the load of aluminum or iron as they are considered toxic for the soil in high concentrations[3].

These disposal problems of the sludge, which generally has a high concentration of organic matter, generate environmental impacts when they are discharged into soils or bodies of water, changing the natural microbiota and affecting the species that have contact with high concentrations of aluminum and iron. To overcome this difficulty, different products of vegetable origin have been studied, which have properties similar to those of aluminum or iron compounds, generate coagulation and flocculation, but with organic compounds, are part of the natural components of plants come, as is the case of *Melocactus* sp., *Opuntia dillenii*, *Stenocereus griseus*, *Cereus forbesii*, *Aloe arborescens*, *Aloe vera*, and Kabuli chickpea (*Cicer arietinum* L.). These plants have shown an activity for the flocculation of substances with small particle size, below 0.2 mm, which generally cannot be separated by natural sedimentation [3].

The sludge derived from the coagulation and flocculation processes with plant extracts has a completely organic composition, which means that they can be digested by microorganisms and transformed into carbon, nitrogen, and phosphorus substances that can be incorporated into the corresponding biogeochemical cycles, with absence of toxic metals for the soil [4], or with safe concentrations for this vital resource. This technological alternative transforms water treatment into a less aggressive process with the environment, taking into account that most of the waste generated in drinking water and domestic waste treatment is sludge.

The extraction systems of plant biopolymers have different methodologies, which are easy to apply, proven, and are part of already standardized unit operations. Taking into account that different parts are harvested from each plant, we must understand that for most of the plants, their use is of the majority of the biomass, whereas when we speak of Kabuli chickpea (*Cicer arietinum* L), we are using only their seed, which diminishes its use, taking into account the weight ratio of the plant and the mass used for the preparation of the coagulant.

The operations developed to determine the efficiency of each plant extract in the coagulation and flocculation are defined within the established for jar tests and some of them have Z potential measurements (measure of the magnitude of the repulsion or attraction between the particles).

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2. Selection of plants with the potential to produce biopolymers for coagulation and water flocculation

Plants with the capacity to generate biopolymers with coagulant and flocculant uses have been under study during the last decades, especially *Moringa oleifera*, *Opuntia* spp., *Cicer arietinum* [5], and others that have demonstrated coagulant capacity, as part of the traditional empirical knowledge of indigenous communities [6].

Figure 1. *Stenocereus griseus*. Source: http://cactiguide.com/cactus/?genus=Stenocereus&species=griseus.

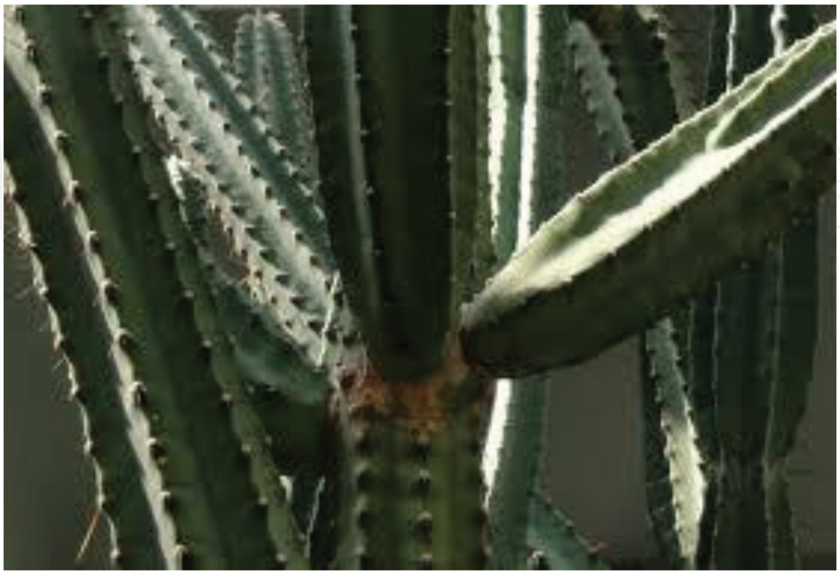

Figure 2. Cereus forbesii. Source: http://www.kakteensammlungholzheu.de/en/cereus_forbesii.html.

Figure 3. *Aloe arborescens*.

The selected plants took a part of those referenced and others of those present in semi-arid regions in Colombia, such as La Guajira in northern Colombia and the banks of the Chicamocha River, in the northeastern region. The species not studied are *Stenocereus griseus* (**Figure 1**), *Cereus forbesii* (**Figure 2**), *Aloe arborescens*, and *Aloe vera*; and one already studied is the Kabuli chickpea (*Cicer arietinum* L.) [6].

In the case of *Opuntia* sp., they are used to be present in the Colombian regions already named and sufficiently studied, in the same way *Aloe vera* and *Aloe arborescens* were selected (**Figure 3**). Kabuli chickpea (*Cicer arietinum*) is reviewed with studies already elaborated by other authors [7]. It should be noted that some species of *Opuntia* spp. are used as part of the animal and human diet in communities of northeastern Colombia, in semidesert areas [8].

To have a better selection, we reviewed the massive presence of these plants and that they were not part of the list of plants in danger of extinction, to be able to access their manipulation.

3. Biopolymer extraction methodologies

3.1. Extraction of the plants *Melocactus* sp., *Opuntia dillenii*, *Stenocereus griseus*, *Cereus forbesii*, *Aloe arborescens*, and *Aloe vera*

The extractions of each plant have particularities, taking into account the usable parts in the search of their coagulating capacity. The extractions are segregated into two types: the plants that are used in all their foliage are *Melocactus* sp. (**Figure 4**), *Opuntia dillenii* (**Figure 5**) [9], *Stenocereus griseus*, *Cereus forbesii*, being belonging to the family Cactaceae and the other part corresponds to *Aloe arborescens* and *Aloe vera*, belonging to the Xanthorrhoeaceae family, with superior *Aloe* classification.

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Figure 4. *Opuntia* sp. Source: http://www.fichas.suculentas.es/Almacenfichas/903/903.html.

Figure 5. *Aloe vera*. Source: http://www.fichas.suculentas.es/Almacenfichas/903/903.html.

For the *Cactus* and *Aloe* species, an extraction methodology was used with different operations that are:

- Selection of parts of the plant for cutting: The operation of cutting parts of the plant is done taking into account mature parts, with the presence of thorns in the case of cacti, with a hard external surface, similar to the criteria used for the animal or human consumption of

Opuntia spp. [10]. In the case of *Aloe* species, the maturity of the leaves is considered, with the presence of perimeter spines. This shows the possibility of isolating the crystals of the plant.

Figure 5 shows a part of the penca or cladodes of a cactus *Opuntia* sp., with skin and thorns, but the part to be used is the vascular tissue of the plant, eliminating skin and spines [11].

For the sampling of the species of *Aloe* (**Figure 6**), garden plants were considered, which are cultivated in a homemade way, taking into account the age of the plant, as it must have enough leaves with enough crystals, and it must not present any evidence of contamination or parasites, especially the characteristics of the green color of the leaves, absence of external insects, and total absence of organisms associated with diseases of the plant.

- Cut and transport to the laboratory: The cutting of the parts of the plant takes measurements (**Figure 7**), to then make a transport to the site of obtaining the coagulant. The transport must be carried out in refrigeration, to avoid possible contamination with environmental fungi or other organisms that can significantly change the composition of the parts obtained.
- Weighing of the gross material: The weighing of the material is carried out on a 25-kg scale, to determine the weight of the sample taken and then determine its performance according to its humidity.
- Cutting of thorns and removal of the bark: To perform the extraction of the coagulant, the cut parts are taken and the thorns are removed (**Figure 8**), and the skin of the cacti, also

Figure 6. *Melocactus* sp. Source: http://www.tephroweb.ch/kuas/melo.htm.

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Figure 7. *Opuntia* sp. and *Cereus forbesii* samples. Source: authors.

Figure 8. Removal of thorns. Source: authors.

called epidermis, which is the external hard part of the pads or cladodes, in the case of cactus and leaves in the case of *Aloe* species.

- Cutting of clean material: In order to follow the extraction process, the tissue of the plants is cut. This is done to improve the moisture loss of the plant, increasing the contact surface with the atmosphere (**Figure 9**).

- Drying the pieces: The drying of the material is carried out outdoors (**Figure 10**). It is important to note that the region in which these operations are carried out is of a warm tropical climate with low humidity, in which the temperature ranges between 20 and 35°C with relative humidities between 50 and 70% on average.
- Weighing of dehydrated material: The material is kept outdoors, taking care that it is not hydrated by rain, the drying time is between 48 and 96 h depending on the temperature and relative humidity of the place where they are dried.
- Grinding of the material: The grinding of the dried material is done with a food processing device and then it is passed through a mill that pulverizes the material.

Figure 9. Cutting of the plants. Source: authors.

Figure 10. Desiccation of the specimens. Source: authors.

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The final characteristics of the material are similar to the raw materials used in the coagulation and flocculation process, that is, a presentation similar to the presentation of type A and B aluminum sulfate and aluminum polychloride, in their solid presentations, the liquid presentation is not sought because it is an organic material with nutritional characteristics for filamentous fungi and bacteria, which would require a procedure for its sterilization, and any application of excessive heat, a degradation of the biopolymers will be carried out, condition that impairs its performance in coagulation.

- Material screening: The material after being macerated is taken to a 1-mm sieve (**Figure 11**), which separates the thick parts that cannot be diluted efficiently in aqueous solution. This characteristic is based on the solubility of complex organic substances, such as the vascular tissue of these cacti and *Aloe* plants.
- Weighing of the material of interest: The material obtained from the plants *Melocactus* sp., *Opuntia dillenii*, *Stenocereus griseus*, *Cereus forbesii*, *Aloe arborescens*, and *Aloe vera* is weighed to have a reference of its performance in relation to weight to weight, with respect to its use.

3.2. Extraction of Kabuli chickpea coagulant (*Cicer arietinum* L.)

The seeds of the anionic coagulant Kabuli Garbanzo (*Cicer arietinum* L.) were selected and then the following procedures were performed.

- Washed: The seeds selected without evidence of the presence of fungi or yeasts were washed with large amounts of water to eliminate impurities related to bulk handling and then in their fractionation and packaging that can take other materials such as small sand stones or other grain waste.

Figure 11. Maceration of the material. Source: authors.

- Drying: After washing, it was dried for 2 days in the sun, taking into account that they cannot be wetted by rain or other water source.
- Crushed: The material was crushed using a mixer (Oster). The resulting powder was sieved with a No. 200 sieve to obtain a very fine powder for storage in plastic containers to avoid hydration and subsequent use in the preparation of the solutions of the coagulant.

4. Tests of the biopolymers obtained

After obtaining the biopolymers, we proceed to prepare solutions of these extracts, to perform jar tests, and thus to determine the coagulant and flocculant capacity of natural biopolymers.

The tests are carried out with water of natural characteristics with different types of solids, which include natural tannins, solids smaller than 0.2 mm, organic matter, and other substances typical of raw or residual waters.

4.1. Preparation of the solutions for coagulation and flocculation of *Melocactus* sp., *Opuntia dillenii*, *Stenocereus griseus*, *Cereus forbesii*, *Aloe arborescens*, and *Aloe vera*

After obtaining the biopolymers of the plants *Melocactus* sp., *Opuntia dillenii*, *Stenocereus griseus*, *Cereus forbesii*, *Aloe arborescens*, and *Aloe vera*, the preparation of the solutions is carried out to realize the tests of jars, which prove the action of coagulant and flocculant.

The flocculant preparation process was weighed 1 g of biopolymer, then 1000 ml of distilled water was added and manual agitation was carried out until completely diluted.

4.2. Preparation of coagulation solutions of Kabuli chickpea (*Cicer arietinum* L.)

About 1% solution was prepared by adding 10 g of the anionic coagulant in 1000 ml with Milli-Q® water, obtaining a solution of 10,000 mg/l, after which stirring was carried out for 1 h to homogenize the mixture. In this solution, the tests were carried out to know the adequate doses to treat the synthetic water prepared in the laboratory.

To prepare the synthetic water, laboratory clay was used for the preparation of samples of turbid water for all the experiments. About 20 g of clay were added to 1 l of distilled water. The suspension was gently stirred for 1 h on a magnetic stirrer in order to achieve a uniform dispersion of the clay particles. The suspension was allowed to stand for 24 h to achieve complete hydration of the clay. This clay suspension served as a stock solution using distilled water to prepare water samples with a turbidity of 200 NTU.

4.3. Control parameters in rockrose tests

To test the coagulating and flocculating effect of the biopolymers of *Melocactus* sp., *Opuntia dillenii*, *Stenocereus griseus*, *Cereus forbesii*, *Aloe arborescens*, *Aloe vera*, and Kabuli chickpea (*Cicer arietinum* L.), jug tests were performed as provided in ASTM D2035: 08 [12].

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The control parameters normally used in the efficiency of a coagulant are pH, turbidity, and color, which are governed by standardized methodologies [13], which determine the ability to remove solids from water based on their behavior, pH, and with its spectrophotometric absorbance, turbidity and color at different wavelengths.

In accordance with the regulations in force in Colombia, the tests were carried out taking into account the technical standards adopted by the country for each test [14].

The removal obtained is processed in terms of percentages, to be able to compare. In the case of pH, it is observed that it complies with the provisions of the national standard for this parameter [15]; and in the case of turbidity and color, the percentage of removal is taken into account, which is directly proportional to the decrease in absorbance in each test.

5. Results of jar tests with natural coagulant biopolymers

The results of the tests of the biopolymers, natural coagulants, are collected in four main tests, the first ones refer to the pH, the turbidity, and the color; the last one takes the coagulants with good performance and measures the Z potential.

Turbidity and color in water is related to the presence of substances or microorganisms, which is directly related to its quality to be consumed or used in other ways; the results offer an overview of the potentialities of all the plants for the coagulation and flocculation processes, with different degree of efficiency.

To control the efficiency of coagulation and flocculation as a function of pH, the pH was taken after coagulation, taking into account that the initial pH of the water is 7.2. The pH results are shown in **Graph 1**, showing that the coagulant that most affected the final pH was the biopolymer of *Melocactus* sp., which brought the pH up to 6.2. The data show a standard deviation of 0.3.

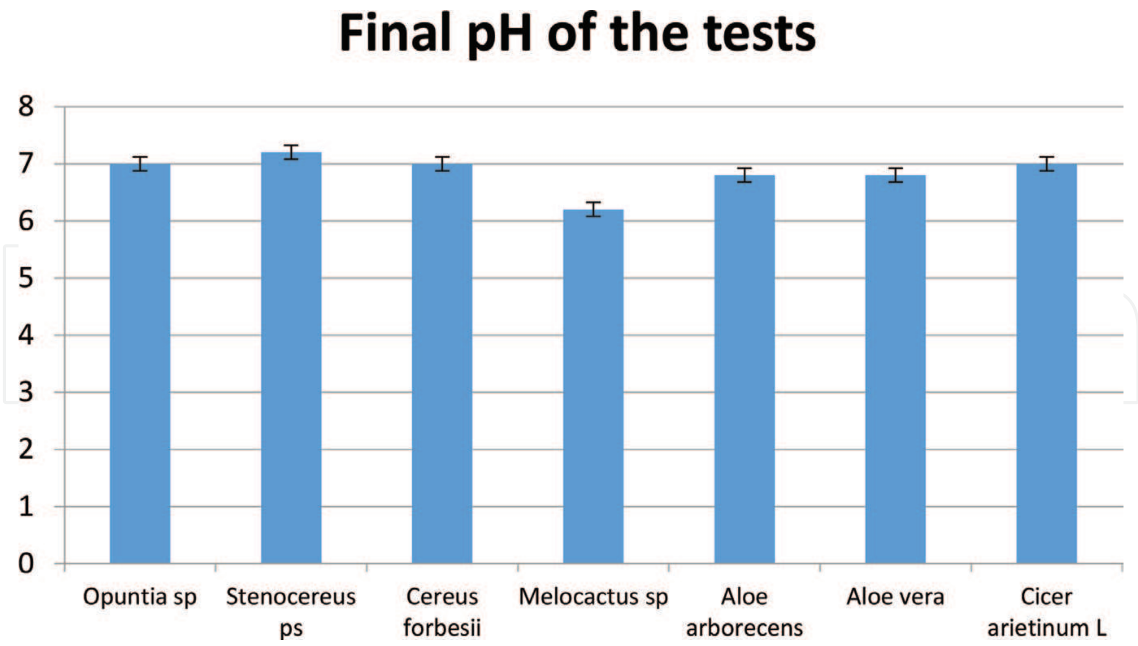
Graph 1 shows that the only one that did not affect the pH in the jar test was *Stenocereus* spp.; the others lowered the pH moderately to values of 7 or 6.8.

The turbidity results (**Graph 2**) showed that the best biopolymers to remove these solids associated with turbidity were *Melocactus* spp. and Kabuli chickpea (*Cicer arietinum* L.), which showed turbidity removals greater than 95 and 97%, respectively. The data show a standard deviation of 3.1.

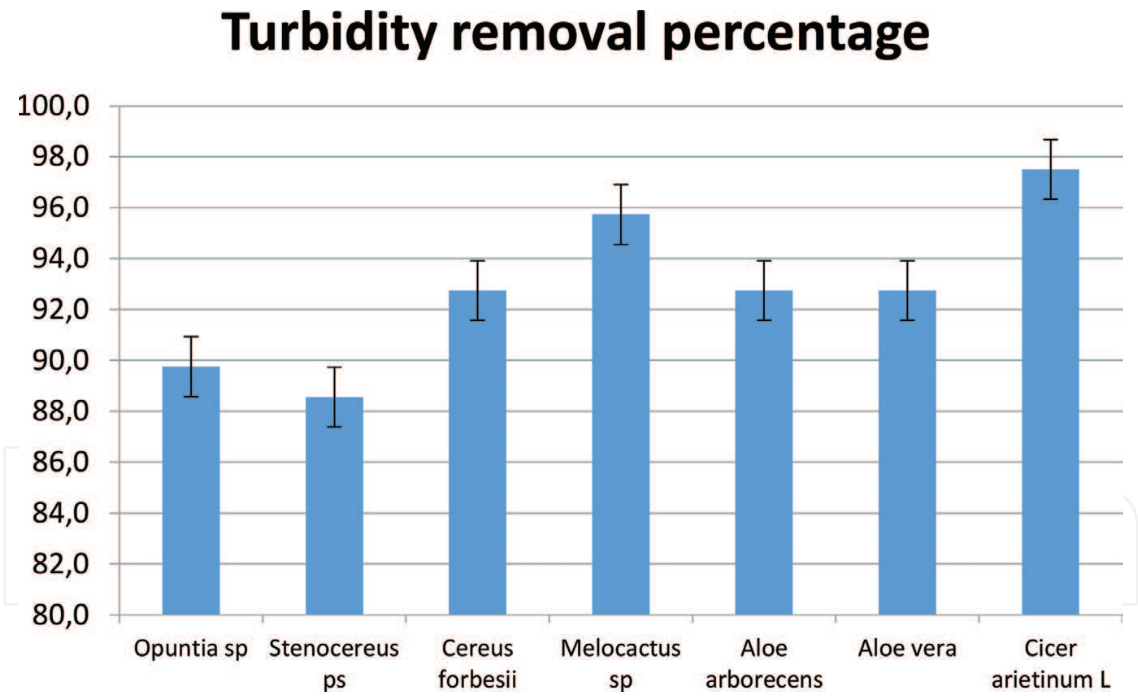
The results of the other biopolymers showed a removal capacity greater than 88 and up to 92%, which shows the effectiveness of these biopolymers with water that has a neutral pH.

All the biopolymers tested showed effective action in the removal of turbidity, in a range between 88 and 97%, with some differences and affectations to the pH of the sample at the final moment of the jar test.

For the case of the color results (**Graph 3**), we can see a good activity of all the biopolymers, taking into account that the one that showed the best performance in the removal of the

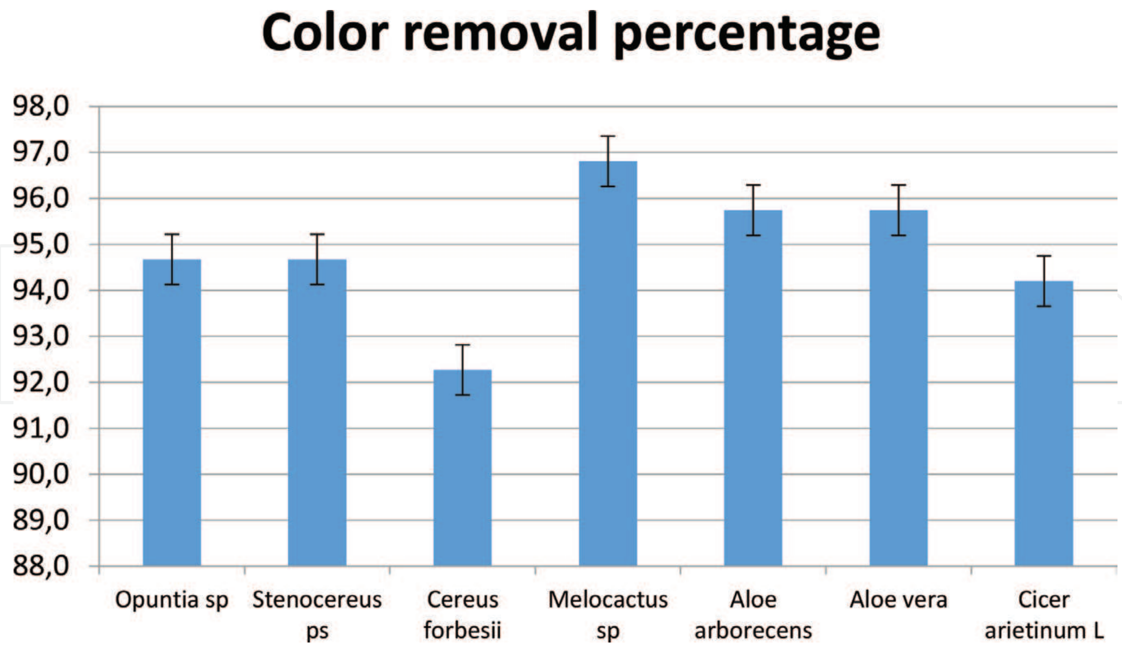


Graph 1. Results of the pH test for studied coagulants. Source: authors.



Graph 2. Turbidity removal with each coagulant studied. Source: authors.

color was the biopolymer of *Melocactus* sp., with a performance greater than 96%, and then it was appreciated that the two species of *Aloe* sp. with a removal greater than 95%; then there are *Opuntia* sp., *Stenocereus* sp., and Kabuli chickpea (*Cicer arietinum* L.), with performances greater than 94% and the last one was evidenced by *Cereus forbesii* with a performance greater than 92%. The data show a standard deviation of 1.4.



Graph 3. Color removal with each coagulant studied. Source: authors.

The results show a greater efficiency in the removal of color. The best performance of these tests lies in the *Melocactus* that was the best removing species in case of both turbidity and color, but with the highest incidence in the pH. The other biopolymer with high performance is the Kabuli chickpea (*Cicer arietinum* L.), which showed a good turbidity and color removal capacity with very little pH affectation.

Z potential measurements were made to the biopolymers with better performance, which showed the following results.

Table 1 shows the results of the Z potential of the *Melocactus* sp. and Kabuli chickpea (*Cicer arietinum* L.), with pH between 3 and 10.

pH	Zeta potential (mv) *Melocactus* sp.	Zeta potential (mV) Kabuli chickpea
3	−1.7	15.1
4	−3.9	−2.5
5	−12.9	−11.8
6	−19.6	−19.8
7	−22.9	−21.9
8	−22.9	−21.9
9	−27.1	−24.5
10	−29.4	−27.1

Source: authors.

Table 1. Z potential of *Melocactus* sp. and Kabuli chickpea (*Cicer arietinum* L.).

The Zeta potential of the biopolymers shows similar values in the range of pH 4 and 10, which may indicate a similar activity with solid particles of small size, such as those that generate turbidity and color in the water.

It is important to note that all plants used have the potential to treat water; and that the efficiency differences can be associated to the affinity for different particles and their extraction form.

6. Conclusions

All the extracts showed turbidity and color removal, with efficiencies higher than 88%, which indicates that the extraction methodologies conserve the coagulant and flocculant capacity of each plant.

The biopolymers of *Melocactus* sp., *Opuntia* sp., *Stenocereus griseus*, *Cereus forbesii*, *Aloe arborescens*, *Aloe vera*, and Kabuli chickpea (*Cicer arietinum* L.) have an activity for coagulation and water flocculation.

The plants with the best performance in the removal of turbidity and color were *Melocactus* sp., and Kabuli chickpea (*Cicer arietinum* L.), with the best percentages of elimination of solids of small size of water.

The Z potential measured to the extracts of *Melocactus* sp. and Kabuli chickpea (*Cicer arietinum* L.) has similar values in the range of pH 4–10, which shows a similar activity for the suspended particles of the water used in the tests.

The biopolymers of the plants *Melocactus* sp., *Opuntia* sp., *Stenocereus griseus*, *Cereus forbesii*, *Aloe arborescens*, *Aloe vera*, and Kabuli chickpea (*Cicer arietinum* L.) can be a viable alternative for the treatment of drinking and residual water, in replacement of sulfate of aluminum, aluminum polychloride, and ferric chloride; decreasing the amounts of dissolved metals in drinking water of humans and animals, especially with the aluminum residues associated with diseases such as autism and Alzheimer [16-23].

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Conflict of interest

The authors declare that there is no conflict of interests regarding the publication of this document.

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