Optimization of the flocculating capacity of natural coagulants in water treatment

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Abstract

The objective was optimize the flocculating capacity of three varities of cacti Echinopsis pachanoi (San Pedro), Neoraimondia arequipenses (Ulluquite) and Opuntia ficus (Tuna) in the artificial wastewater treatment. They were applied 1%, 2% and 3% coagulant doses of the three varieties of cactaceae extracted with 96% ethanol. It was evaluated the flocculating activity (FA) and removal percentage (%R); a significant increase was observed (p-value < 0.05) with the increase in the coagulant dose. The optimization was carried out considering as objective function the %R which were subjected to FA, pH, hardness, alkalinity and BOD5 of water treatment. Which were reported values of 99.09 %R for San Pedro variety, 92.42 %R for Ulluquite variety and 98.98 %R for tuna variety, for doses of 0.207%, 0.246% and 0.754% of coagulant respectively.

Keywords: artificial wastewater; flocculating activity; removal percentage.

1. Introduction

Cacti are one of the most abundant botanical families in Peru, being found in all altitudinal floors, in a large number of varieties. Thus, since ancient times cacti have been important and linked to a large number of Latin American cultures and peoples in many parts of the world. Cacti are used in very different ways and applications such as water clarification or as a natural polymer.

These polymers are complex in their chemical composition and are constituted mainly by several types of polysaccharides and proteins. Some of them have coagulant or flocculating properties and in many places, they are used
empirically to clarify turbid water with satisfactory results [20].

One of the cactaceae that has been widely used in coagulation is the genus Opuntia (family of cactaceae) which was characterized by the hydrocolloid production. It is known as mucilage, it forms molecular networks that retain large amounts of water [1]. Besides, it is a complex polymeric compound of glucidic nature with a highly branched structure [2]. Mucilage contains variable proportions of L-arabinose, D-galactose, L-rhamnose and D-xylose, as well as galacturonic acid in different proportions [3].

Another cactus that has coagulant properties is the Echinopsis pachanoi, which calls "San Pedro" as a common name in some areas of Peru. As well as the Neoraimondia arequipensis which receives the common name of Ulluquite. It is not really known whether it is related to the well-known Puyas de Raimondi, which grow in different parts of Peru including the Peruvian-Bolivian highlands.

Drinking water for human consumption must have quality characteristics such as free of turbidity, color and perceptible taste and other parameters regulated according to the regulations of the countries. Usually natural waters do not have satisfactory quality for human consumption or industrial use and generally should be treated [4], as well as wastewater according to their use.

Coagulation consists in the addition of chemical substances to mix the particles and some dissolved pollutants that can be agglutinated in larger particles and then being removed through solids removal processes or by sedimentation [5]. Coagulation as a physicochemical process destabilizes colloidal particles, precipitating and grouping suspended solids. This supplies their extraction by means of the flocs formation in water [6], reducing turbidity, color and to a lesser extent bacteria [7].

For coagulation, conventional chemical substances are used. However, there are disadvantages associated with the use of these coagulants such as high acquisition costs, large production volumes of sludge and the fact that they significantly affect the pH of the treated water [8,9]. Also, in some cases adverse neurological effects, such as the manifestation of Alzheimer's disease [10,11]. Therefore, it is necessary to carry out optimization processes to minimize the use of additives and chemical substances, and to maximize the parameters of water quality.

2. Materials and methods

2.1. Raw material

The Echinopsis pachanoi (San Pedro), Neoraimondia arequipensis (Ulluquite) and Opuntia ficus (Tuna) cacti varieties were obtained from wild crops located in Santa Rosa area from Talavera district at 3000 meters above sea level. At latitude 13° 36’07.89”S, length 73° 16’33.13”W. Andahuaylas province, Peru has an average temperature of 13 ºC and an average annual rainfall of 930 mm.

The cactaceae collection criteria were physiological maturity, morphology (external appearance and apparent color), size (length and width or diameter) and weight.

2.2. Preparation of artificial water

In order to simulate suspended particles in the artificial wastewater for its subsequent flocculation and coagulation. A stock solution was prepared by dissolving 25 g of kaolin (2SiO₂·Al₂O₃·2H₂O) in 500 ml of distilled water that was homogenized for 30 minutes manually. The solution was allowed to stand for 24 hours. Finally, 6 liters of drinking water was taken and 30 ml of kaolin stock solution was added to the solution.

2.3. Extraction of natural coagulant

The method proposed by Dujardin et al. [12] was modified. The thorns were completely eliminated from the cacti samples, then they were cut into small pieces and liquefied at high speed with distilled water in a 1:1 ratio. Afterward, the fine grinding was sifted in a 1000 micron mesh in order to eliminate the fiber and obtain only the mucilage (filtered juice). After that, a liquid - liquid extraction from the filtered juice was carried out by means of a solvent (96% Ethanol) in relation to 1 of juice:2 of solvent. Subsequently, as many changes of solvent as necessary were made until the color was eliminated and later the precipitate was dried at room temperature. After drying, the sample was finely ground and then sieved in a 300 micron mesh. A fine and crystallized coagulant powder was obtained.

2.4. Flocculant activity - FA

The methodology by Sánchez and Untiveros [13] was adapted. 0.25 ml at 1% natural coagulant solution, 4.50 ml of kaolin suspension and 0.25 ml at 1% iron (III) solution were poured into a test tube. Which was homogenized for 15 seconds with a Vortex and then left for 5 min. 2.5 ml of the supernatant was carefully removed from the top of the test tube with a pipette and the absorbance was measured at 550 nm (A) and a control (B). The flocculant activity was calculated using eq. (1). The test was repeated with 2% and 3% of natural coagulant.

\[
FA = \frac{1}{A} + \frac{1}{B}
\]  

(1)

2.5. Evaluation of the removal percentage

The process efficiency was determined by the percentage of turbidity removal (% R), according to eq. (2) [14]. For which the initial turbidity (T₀) and final turbidity (Tf) were determined with an Orbeco turbidimeter model TB300-IR from 0.01 to 1100 NTU range.

\[
%R = \frac{T₀ - T_f}{T₀} \times 100
\]  

(2)
2.6. Evaluation of physicochemical characteristics

The characterization of the treated water quality parameters was carried out, such as pH, total alkalinity, total hardness and BOD [15].

2.7. Optimization of flocculant capacity

The objective function for the optimization was the removal percentage of turbidity for each treatment. Which was evaluated through linear regression and nonlinear regression and taking as a convergence criterion the correlation coefficient $R^2$. It was considered restrictions to the limits established by the Peruvian technical standards and WHO for the parameters evaluated in the treated water. For the optimization, the Excel Solver utility was used.

2.8. Statistical analysis

Analysis of variance and Tukey's multiple comparison means test were performed at a significance level of 5%. The data were processed with the statistical package Statgraphics Centurion XV.

3. Results and discussion

In Table 1, it can see that the AF is in the range from 28 to 48; Ferreira et al. [23] reported similar results. It is also observed that the removal percentages are greater than 92%; similar results showed Jiménez et al. [22] when treating artificial wastewater with a mixture of coagulants based on Opuntia cochenillifera although with doses of the order of 20 ppm likewise Arismendi [21] using modified tannins. Sánchez and Untiveros [13] used pectin with concentration

<table>
<thead>
<tr>
<th>Variety</th>
<th>Coagulant solution (%)</th>
<th>Flocculant activity</th>
<th>Removal percentage</th>
<th>pH</th>
<th>Hardness (ppm CaCO$_3$)</th>
<th>BOD (mg O$_2$/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E.P.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>47.39     ± 0.46</td>
<td>99.21     ± 0.06</td>
<td>6.98   ± 0.04</td>
<td>266.3 ± 1.5</td>
<td>2.41 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>48.39     ± 0.19</td>
<td>99.31     ± 0.06</td>
<td>7.25   ± 0.02</td>
<td>268  ± 1.0</td>
<td>2.65 ± 0.04</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>48.58     ± 0.06</td>
<td>99.44     ± 0.06</td>
<td>7.28   ± 0.01</td>
<td>269  ± 1.0</td>
<td>2.72 ± 0.04</td>
<td></td>
</tr>
<tr>
<td>N. A.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>28.41     ± 0.94</td>
<td>92.64     ± 0.33</td>
<td>6.75   ± 0.03</td>
<td>262  ± 1.0</td>
<td>3.08 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>30.36     ± 0.11</td>
<td>92.79     ± 0.18</td>
<td>6.93   ± 0.04</td>
<td>263.7 ± 0.6</td>
<td>3.32 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>30.38     ± 0.11</td>
<td>92.78     ± 0.09</td>
<td>7.02   ± 0.01</td>
<td>263.7 ± 1.5</td>
<td>3.34 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>O. F.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>46.13     ± 0.39</td>
<td>99.02     ± 0.15</td>
<td>6.68   ± 0.03</td>
<td>269.3 ± 1.2</td>
<td>3.35 ± 0.11</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>46.41     ± 0.11</td>
<td>99.11     ± 0.18</td>
<td>6.9    ± 0.02</td>
<td>270.7 ± 0.6</td>
<td>3.64 ± 0.11</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>46.48     ± 0.22</td>
<td>99.15     ± 0.06</td>
<td>6.96   ± 0.02</td>
<td>271  ± 1.0</td>
<td>3.66 ± 0.05</td>
<td></td>
</tr>
<tr>
<td>Initial value</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>6.61</td>
<td>260</td>
</tr>
</tbody>
</table>

Where: E.P. is *Echinopsis pachanoi*; N.A. is *Neoraimondia arequipensis*; O.F. is *Opuntia ficus*; $\bar{x}$ is the average; $s$ is the standard deviation. * Equal letters mean that there is no significant difference evaluated through the Tukey test, with $\alpha = 5\%$. Source: The Authors.

<table>
<thead>
<tr>
<th>Model</th>
<th>R$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Echinopsis pachanoi</em> (San Pedro) variety</td>
<td></td>
</tr>
<tr>
<td>$%\text{R}$</td>
<td>$%\text{R} = 0.108 \cdot \ln \text{C} + 99.218$</td>
</tr>
<tr>
<td>$\text{AF}$</td>
<td>$%\text{AF} = 1.119 \cdot \ln \text{C} + 47.456$</td>
</tr>
<tr>
<td>$\text{pH}$</td>
<td>$\text{pH} = 0.282 \cdot \ln \text{C} + 6.999$</td>
</tr>
<tr>
<td>$\text{D}$</td>
<td>$\text{D} = 2.425 \cdot \ln \text{C} + 266.33$</td>
</tr>
<tr>
<td>$\text{A}$</td>
<td>$A = 50.113 \cdot \exp(0.0055 \cdot \text{C})$</td>
</tr>
<tr>
<td>$\text{BOD}$</td>
<td>$\text{BOD} = 0.293 \cdot \ln \text{C} + 6.415$</td>
</tr>
<tr>
<td><em>Neoraimondia arequipensis</em> (Ulluquite) variety</td>
<td></td>
</tr>
<tr>
<td>$%\text{R}$</td>
<td>$%\text{R} = 0.138 \cdot \ln \text{C} + 92.65$</td>
</tr>
<tr>
<td>$\text{AF}$</td>
<td>$%\text{AF} = 1.907 \cdot \ln \text{C} + 28.576$</td>
</tr>
<tr>
<td>$\text{pH}$</td>
<td>$\text{pH} = 0.247 \cdot \ln \text{C} + 6.756$</td>
</tr>
<tr>
<td>$\text{D}$</td>
<td>$\text{D} = 1.613 \cdot \ln \text{C} + 262.15$</td>
</tr>
<tr>
<td>$\text{A}$</td>
<td>$A = 1.561 \cdot \ln \text{C} + 31.734$</td>
</tr>
<tr>
<td>$\text{BOD}$</td>
<td>$\text{BOD} = 0.249 \cdot \ln \text{C} + 3.098$</td>
</tr>
<tr>
<td><em>Opuntia ficus</em> (Tuna) variety</td>
<td></td>
</tr>
<tr>
<td>$%\text{R}$</td>
<td>$%\text{R} = 0.117 \cdot \ln \text{C} + 99.024$</td>
</tr>
<tr>
<td>$\text{AF}$</td>
<td>$%\text{AF} = 0.324 \cdot \ln \text{C} + 46.143$</td>
</tr>
<tr>
<td>$\text{pH}$</td>
<td>$\text{pH} = 0.265 \cdot \ln \text{C} + 6.691$</td>
</tr>
<tr>
<td>$\text{D}$</td>
<td>$\text{D} = 1.561 \cdot \ln \text{C} + 269.40$</td>
</tr>
<tr>
<td>$\text{A}$</td>
<td>$A = 2.206 \cdot \ln \text{C} + 36.46$</td>
</tr>
<tr>
<td>$\text{BOD}$</td>
<td>$\text{BOD} = 0.302 \cdot \ln \text{C} + 3.368$</td>
</tr>
</tbody>
</table>

Where: $%\text{R}$, Removal percentage; $\text{AF}$, flocculant activity; $\text{D}$, Hardness; $\text{A}$, Alkalinity, BOD, Biochemical Oxygen Demand; $\text{C}$ is the percentage of coagulant application; $R^2$ is correlation coefficient. Source: The Authors.
of 30 ppm (0.003%) in artificial wastewater formulated with kaolin and iron (III). Yagual and Torres [14] found removal percentages between 95% to 99.6% for river water samples when using coagulants such as aluminum sulphate, floater praestol 650 TR and artisanal chemical flocculant. Quiros et al. [16] found a solids removal of 83% with coagulant extracted from Moringa at 400 ppm.

On the other hand, slight variation of the pH in the treated water is observed for all the cases with basic tendencies. Solís et al. [17]. However, Miranda et al. [19] showed a slight increase when adding cal and kollpa coagulants (Alum from Altiplano).

The coagulant addition increases significantly the BOD₅ of the artificial water due to the tests were realized in solution with the coagulant, which showed that its composition is made up by proteins and carbohydrates.

The objective function to optimize the flocculant capacity was the removal percentage of solids in artificial treated water for three coagulant varieties of cacti, thus, mathematical models or equations were determined, which are shown in Table 2, which show R² > 0.9.

Table 3 shows the results for coagulant Echinopsis pachanoi (San Pedro) variety with its respective restrictions. It is observed that optimum removal percentage is 99.092% for an application percentage of 0.27% coagulant at 1% in the solution. Thus, achieving values of the flocculant activity of 46.01%, pH of 6.6, Hardness of 264.536 ppm of CaCO₃, Alkalinity 30.00 ppm of CaCO₃ and BOD of 2.097 mg O₂/L.

On the other hand, the coagulant from Neoraimondia arequipensis variety shows a 92.42% of removal percentage, it must be applied 0.246% of coagulant at 1% in solution. Being that, under this condition the flocculant activity will be 46.01%, pH of 6.6, Hardness of 264.536 ppm of CaCO₃, Alkalinity 30.00 ppm of CaCO₃ and BOD of 2.097 mg O₂/L.

4. Conclusions

The optimization of the flocculant capacity of three natural coagulants in the artificial treated water evaluated through the removal percentage shows values of 99.09% for Echinopsis pachanoi (San pedro) variety, 92.419% for Neoraimondia arequipensis (Ulluquite) variety and 98.98% for Opuntia ficus (Tuna) variety. For dosages of 0.207%, 0.246% and 0.754% respectively in coagulant solution at 1%.

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