Cactus Cladode Juice as Bioflocculant in the Flocculation-Thickening Process for Phosphate Washing Plant: A Comparative Study with Anionic Polyacrylamide

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Abstract: In the phosphate industry, the thickening process is vital to increasing the solid slurry concentration and to recovering water that is as clear as possible. The performance of the thickening process depends mainly on the coagulation–flocculation effect. The thickening process is based on flocculant agents to concentrate particles: flotation and washing plant rejects as large flocs, which accelerate their sedimentation velocity. The phosphate industry worldwide uses syntethical flocculants such as polyacrylamides. These flocculants are non-biodegradable, limiting the process efficiency regarding cost and harmful effects on the environment. This study proposes cactus cladodes juice as an eco-friendly alternative to industrial flocculants. The particle size of the phosphate samples ranges from 0 µm to 160 µm, with a solid concentration of 8%. This bioflocculant allowed for an increase in sedimentation velocity of 95% compared with the case without flocculant. The optimal amount of cactus bioflocculant for decanting 1 tonne of phosphate pulp at pH 7–8 is 1.12 kg. Special attention is paid to understanding the flocculation mechanism. The results of the physicochemical characterization show that the flocculant biopolymers have similar characteristics to anionic polyacrylamide. This work indicates the promising application of the cactus juice bioflocculant in phosphate washing plants.

Keywords: thickening process; flocculation process; sedimentation velocity; bioflocculant; phosphates; phosphate washing plant

1. Introduction

Recently, significant advances have been achieved in the development of alternative green and sustainable technologies in chemical engineering [1,2]. Sustainable chemistry has emerged as a new concept aimed at developing efficient chemical products and services with natural resources. It includes different areas such as bio-renewable resources, alternative energies, and energy storage [3,4].

The thickening process is important in the phosphate industry to increase the solid sludge concentration and to recover water that is as clear as possible. The performance of the thickening operation depends mainly on the flocculation impact. Indeed, the thickening process involves the separation of two immiscible liquid or liquid–solid phases. This process is most frequently used to separate suspended solids and flocs of the liquid phase. Many factors govern solid–liquid separation. The main ones are the nature of the particles (size, distribution, shape, density, mineralogical, chemical properties, and others), the solid
concentration, the physical/chemical effects (flocculation, heating, and cooling), and the viscosity of the liquid [5].

The particle settling depends on different regimes related to the behavior of each particle, which depends on both the suspension dilution and the inter-particles interactions. The agglomeration of the particles can cause the sedimentation of the flocs through the addition of flocculant agents. Then, a progressive clarification without a clear interface between the liquid and the solid particles is observed [6]. Flocculants have been extensively used in industrial processes such as wastewater treatment, pulp treatment in mineralogy and hydrometallurgy [7], downstream treatment in the biopharmaceutical industry [8], and fermentation and food processes [9]. The flocculants are classified into two types, mainly synthetic and natural. The classification of flocculant types is illustrated in Figure 1.

**Figure 1.** Classification of flocculants.

The demand for synthetic flocculants increases continuously due to the rapid growth of the phosphate industry. Industrial flocculants, such as Polyacrylamide (PAM), are usually employed in thickening processes. These materials are cost-effective; however, they are derived from synthetic polymers, which are not degradable and hazardous to health and to the environment [6,7]. Recently, biopolymers have received much attention as flocculants, as they are an efficient, cheap, and environmentally friendly resource. Organic biodegradable polymers are chemical macromolecules (metabolites) secreted by microorganisms (bacteria) or made from natural products: algae, fungi, yeasts, and others. Extracellular biopolymers include polysaccharides, proteins, glycoproteins, lipids, and glycolipids [10–12]. Recently, research has focused on extracting bioflocculants from natural and sustainable resources (plants and microorganisms) [13]. These studies have sorted out the best bioflocculants and explored their culture conditions, flocculation mechanisms, chemical structures, and others [14–16].

Wen-Xin Gong et al. [17] developed a new bioflocculant, SF-1, produced by the bacterium Serratia Ficaria. The chemical analysis showed that the product contained polysaccharides without amino acids. The zeta potential of the bioflocculant produced showed that the charge neutralization had an important effect on the flocculation. Additionally, they distinguished that Mg$^{2+}$ and Ca$^{2+}$ increased the flocculation activity but were reduced by Al$^{3+}$, Na$^+$, and Fe$^{3+}$. SF-1 exhibited good efficiency when flocculating a kaolin suspension in an acidic pH range (5–7). Moreover, it showed an excellent performance when flocculating wastewater, such as brewery wastewater, river water, meat processing wastewater, and soy sauce brewing wastewater. Lastly, the wastewater removal efficiency with SF-1 is similar to that of PAM and polyaluminum chloride (PAC). Wen-Yu Lu et al. [18] developed a new bioflocculant produced by Enterobacter aerogenes Bactrim to treat alkaline trona suspension. The trona is mainly composed of soluble salts (NaHCO$_3$, Na$_2$CO$_3$, Na$_2$SO$_4$, and NaCl) and insoluble materials (CaCO$_3$, mud, quartz, clay, and calcite). They studied the influence of temperature, bioflocculant dosage, and concentration of positive ions on flocculation activity. The optimal conditions are 45 °C, 90 mg/L of WF-1, and 0.03 mol/L of Zn$^{2+}$, on a sedimentation velocity of $2.96 \times 10^{-4}$ m/s. The bioflocculant efficiency was better than conventional chemically synthesized flocculants, such as non-ionic PAM or anionic PAC. Fujita et al. [19] produced a new bioflocculant from low molecular weight fatty acids...
as an innovative strategy for the recovery of waste sludge digestion fluid. Additionally, it is applied to various inorganic and organic suspended particles, including kaolin, diatomite, bentonite, activated charcoal, soils, and activated sludge. They identified the chitosan biopolymer with a high molecular weight as the flocculation agent, easily concentrated by ultrafiltration to improve recovery efficiency. Interestingly, the bioflocculant performance is comparable with synthetic flocculants.

De Souza et al. [20] studied the coagulant activity of OFI biopolymers extracted from the cactus Opuntia Ficus-Indica. They revealed that the OFI has a significant coagulant activity and is an effective alternative for the treatment of textile effluents. After optimization, the OFI was efficient for Chemical Oxygen Demand (COD) removal and percent turbidity removal for both effluents. Abid et al. [17] employed a cactus juice extract for the treatment of industrial waste. It was also used for the physicochemical treatment ‘coagulation–flocculation’ of pseudo-industrial and industrial wastewater loaded with chromium (VI) from a surface treatment unit (chrome plating). They compared the organic flocculant and the industrial flocculant PPRQESTOLR 2515. The results show that the bioflocculant leads to satisfactory results in terms of flocculation power because it reduced the turbidity of the industrial effluent from 100 NTU to 2 NTU. Bouatay et al. [21] tested the Opuntia Ficus Indica mucilage cactus as a natural flocculant combined with Aluminum Sulfate as a coagulant for textile wastewater treatment. They carried out a comparative study between the flocculation performance of commercial flocculants (EPENWATE EXP 31/1, Polyacrylamide A100PWG) and the bioflocculant. The results showed that the cactus has the most effective pollution removal. At optimal conditions, decoloration, COD removal, and turbidity reduction are 99.84%, 88.76%, and 91.66%, respectively.

Based on the aforementioned discussion, it is concluded that the bio-degradable flocculants have an enormous potential for the flocculation-thickening process. The cactus juice bioflocculant has been tested to be effective for wastewater treatment. To the authors’ best knowledge, this is the first study investigating the potential to replace industrial flocculants in the flocculation-thickening process of phosphate washing plants. Thus, the flocculent activity of Moroccan Opuntia cactus is compared with the industrial anionic polyacrylamide. The Opuntia cactus used is grown in arid climates in the common Skhour Rhamna, on more than 26,000 ha [22]. The physical and chemical properties and the flocculation potential of the cactus juice are analyzed. The details of the methods and results are presented and discussed in the following sections.

2. Materials and Methods

2.1. Industrial Flocculant

The industrial flocculant used in this study is the anionic polyacrylamide [-CH₂-CH(-CONH₂)]ₙ, with a concentration of 5 g/L (Figure 2). The PAM is a white powder and miscible with water, a viscous liquid with white color. According to the functional and technical specifications of the industrial decanting unit, the initial flocculant solution must be diluted ten times under agitation for 15 to 20 min.

![Anionic polyacrylamide powder and solution.](image-url)

Figure 2. Anionic polyacrylamide powder and solution.
The basic physical and chemical properties of industrial flocculant are listed in Table 1.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Industrial Flocculant</th>
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<tbody>
<tr>
<td>Polymer type</td>
<td>Polyacrylamide</td>
</tr>
<tr>
<td>Approximate bulk density</td>
<td>0.80</td>
</tr>
<tr>
<td>Stability of DI water solution (days)</td>
<td>1</td>
</tr>
<tr>
<td>Color</td>
<td>White</td>
</tr>
<tr>
<td>Ionic character</td>
<td>Anionic</td>
</tr>
<tr>
<td>Molecular</td>
<td>Very high</td>
</tr>
<tr>
<td>Soluble in water</td>
<td>Yes</td>
</tr>
</tbody>
</table>

### 2.2. Bioflocculant Preparation

The Moroccan Opuntia cactus is used as raw material to prepare cactus juices. The bioflocculant preparation protocol is shown in Figure 3. This approach is based on the work of B. Othmani et al. [23] establishing the preparation steps of the cactus juice bioflocculant.

The cactus cladodes are harvested and then netted to remove the thorns and the pusher. Then, the cactus cladode is cut into small pieces to grind 9 g in one liter of water, so the initial concentration of the extracted juice is 0.9 g/L. Lastly, the mixture is filtered through a 1 mm cloth to obtain the cactus juice. Indeed, the cactus cladode juice is diluted in 10% water and homogenized by shaking for 15 to 20 min.

![Cactus cladodes recovery](image1)

![Cleaning station](image2)

![Cutting station](image3)

![Grinding filtration](image4)

![Cactus cladodes cleaned](image5)

![Pieces of cactus cladodes](image6)

![Bioflocculant](image7)

Figure 3. Schematic diagram of the extraction process of cactus juice bioflocculant.

The basic physical and chemical properties of bioflocculant are listed in Table 2.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Bioflocculant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer type</td>
<td>Polygalacturonic acid</td>
</tr>
<tr>
<td>Approximate bulk density</td>
<td>1</td>
</tr>
<tr>
<td>Stability of DI water solution (days)</td>
<td>2</td>
</tr>
<tr>
<td>Color</td>
<td>Green</td>
</tr>
<tr>
<td>Ionic character</td>
<td>Anionic</td>
</tr>
<tr>
<td>Molecular</td>
<td>Very high</td>
</tr>
<tr>
<td>Soluble in water</td>
<td>Yes</td>
</tr>
</tbody>
</table>

The cladode juice is a green viscous liquid, miscible with water, and has a stability duration of two days.
2.3. Preparation of the Phosphate Sample

The experiments were performed under the same industrial conditions. Hence, flocculation tests were performed on phosphate samples recovered before injection into the scrubber decanter (flotation unit discharge and scrubber discharge).

Based on particle size analyses of the phosphate samples, the particle size was between 0 $\mu$m and 160 $\mu$m, and the value of solid concentration was 8%. The pH of phosphate pulp was between 7 and 8.

2.4. Sedimentation Test

The sedimentation tests were performed in a 46.5 cm long and 10.5 cm diameter column to investigate the effectiveness of the flocculating agents (Figure 4). The sedimentation velocity of each test was calculated using the conventional method:

$$ v = \frac{\Delta d}{\Delta t} $$

where $v$ is the velocity of sedimentation (cm/s), $\Delta d$ is the distance between the two levels (cm), and $\Delta t$ is the duration required for sedimentation of all of the phosphate particles (s).

![Figure 4. Sedimentation test bench.](image)

Three tests were carried out: (1) decantation without flocculant representing the reference test, (2) decantation with industrial flocculant, and (3) decantation with bioflocculant. The repeatability of the tests was verified by repeating each experiment three times.

3. Results and Discussion

3.1. Bioflocculant Activity

The sedimentation velocity was compared for three cases: without flocculant (the reference case), with polyacrylamide industrial flocculant, and with cactus juice bioflocculant. The average sedimentation velocities of the three cases are illustrated in Figure 5.
Flocculants have a significant effect on the sedimentation velocity of phosphate particles. It increases from 0.1 cm/s without flocculant to 2.56 and 2.29 cm/s for industrial and cactus flocculants. The cactus extract increased the velocity of phosphate sedimentation to 95.6%.

In addition, the rheological behavior of industrial flocculant and bioflocculant is compared. Figure 6 illustrates the evolution of the dynamic viscosity as a function of the shear stress (\(\gamma\)). The results show that the rheological behavior of industrial flocculant is similar to that of water; the Newtonian and equal water viscosity was \(10^{-3}\) Pa.s. Additionally, the rheological behavior of cactus cladode juice is similar to that of an industrial flocculant.

The viscosity of both flocculants does not decrease with agitation. Then, it becomes low as the shear value increases, so the stability of both solutions decreases as a function of time.

3.2. Optimal Specific Consumption of the Bioflocculant

The specific consumption is defined as the amount of flocculant required to sediment a specified amount of phosphate particles. The objective is to determine the optimal specific consumption of the bioflocculant to enhance the maximum sedimentation velocity of the phosphate. It is one of the operating parameters of the settling unit at the plant that was
very important in the optimization studies of these operating parameters. Figure 7 shows the evolution of the sedimentation velocity as a function of the bioflocculant volume.

![Figure 7. Variation in the sedimentation velocity as a function of the added volume of the bioflocculant.](image)

The maximum sedimentation velocity of the phosphate particles is obtained with a volume of 10 mL of bioflocculant and a concentration of 0.8 g/L. The specific consumption is determined by calculating the mass of the cactus used to flocculate 8 g of phosphate.

Laboratory tests have shown that 9 mg of cactus can sediment 8 g of phosphate. Thus, at the industrial level, 1.12 kg of cactus must be added to decant one ton of phosphate. After optimization, the sedimentation velocity was increased to 2.60 cm/s, similar to that of PAM.

### 3.3. Bioflocculant Characterization

The FTIR spectra presented in Figure 8 illustrated information about the main functional groups of cactus cladode juice and anionic polyacrylamide.

![Figure 8. Fourier transform infrared spectroscopy spectra of flocculants: (a) anionic polyacrylamide; (b) cladode cactus juice.](image)
The FTIR spectra show that cladode juice and anionic polyacrylamide are similar. Indeed, the functional carboxyl groups (–COOH), hydroxyl (–OH), and amino or amine (–NH₂) groups, as well as hydrogen bonds, are presented in both flocculants (Table 3). The existence of the carboxylic group may be related to the presence of galacturonic acid.

Table 3. Main functional groups in cactus juice: FTIR spectrum analysis.

<table>
<thead>
<tr>
<th>Vibration Type</th>
<th>Molecules/Components</th>
<th>Wave Number (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroxyl and Amines (O–H and N–H stretching)</td>
<td>Carbohydrates, Glycoproteins</td>
<td>3400</td>
</tr>
<tr>
<td>Alkyl (C–H stretching)</td>
<td>Carbohydrates, Glycoproteins</td>
<td>2931</td>
</tr>
<tr>
<td>Asymmetric and symmetric stretching vibrations of ionized carboxylic acid groups (COO⁻),</td>
<td>Galacturonic Acid</td>
<td>1623 and 1425</td>
</tr>
<tr>
<td>Carboxyl (C=O stretching of non-ionized COOH groups)</td>
<td>Galacturonic Acid</td>
<td>1730</td>
</tr>
<tr>
<td>Methoxyl (C–O stretching alcohol/ether groups)</td>
<td>Carbohydrates</td>
<td>1050–1150</td>
</tr>
</tbody>
</table>

The percentage of cladode carbohydrates are as follows: l-arabinose (24.60–42%), d-galactose (21–40.10%), l-rhamnose (7–13.10%), d-xylose (22–22.20%), and galacturonic acid (8–12.70%) [24].

The proposed flocculation mechanism of cactus juice is presented in Figure 9. Indeed, the bioflocculant makes contact with the solid particles; some of its functional groups are adsorbed onto the particle surface, while other bioflocculant regions remain free in solution. Then, this leads to adsorption of the bioflocculant in “loop series” (segments coming out in solution) and in “trains” (segments adsorbed on the surface). Thus, the extended segments of the bioflocculant are adsorbed onto other solid particles within the solution to form particle–polymer–particle aggregates in which the bioflocculant acts as a bridge.

Figure 9. Mechanism of flocculation by physicochemical adsorption: (a) adsorption of PAM to solid particles; (b) aggregation and binding of particles via PAM; (c) flocculation.
Indeed, the galacturonic acid exists predominantly in the polymeric form (polygalacturonic acid) that provides a ‘bridge’ for particles. Polygalacturonic acid is composed of a long anionic chain, including carboxyl (–COOH), carbonyl (–C=O), and hydroxyl (–OH) groups. It is anionic due to partial deprotonation of the carboxylic functional group in the aqueous solution. Moreover, the presence of –OH groups along the polymeric chain of polygalacturonic acid assumes possible intra-molecular interactions that may distort the relative linearity of the chain [25].

4. Conclusions

Polyacrylamide (PAM) is the most widely used flocculant in the thickening process of phosphate washing plants. It has a high efficiency at a low cost; however, it is based upon synthetic polymers, which are dangerous for health and for the environment. This research studied the production and characterization of bioflocculant isolated from cactus cladodes. This work proposes cactus cladode juice as an efficient and cost-effective alternative to conventional flocculants. Thereby, the two flocculants are compared for the phosphate-thickening process. The results show that the sedimentation velocity of the cactus juice-based bioflocculant was 2.29 cm/s. After optimization, the sedimentation velocity was increased to 2.60 cm/s, similar to that of PAM. The chemical analysis revealed that the pure bioflocculant consisted of carbohydrates, glycoproteins, and galacturonic acid. The flocculation mechanism of cactus biopolymers is similar to that of the PAM. The proposed flocculation mechanism of cactus juice is a combination of adsorption and particle–polymer–particle bridging. In future work, further physical and chemical analyses should be performed to confirm the proposed bioflocculation mechanism. Additionally, the flocculation parameters should be optimized and tested at the pilot level. Finally, an economic study should be conducted to explore the possibility of replacing PAM with cactus juice.


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