Leachate treatment: comparison of a bio-coagulant (Opuntia ficus mucilage) and conventional coagulants using multi-criteria decision analysis

Alfredo Martínez-Cruz, María Neftalí Rojas Valencia, Juan A. Araiza-Aguilar, Hugo A. Najera-Aguilar, Rubén F. Gutiérrez-Hernández

A) National Autonomous University of Mexico, Institute of Engineering, External Circuit, University City, Mexico City, Mexico
B) University of Science and Arts of Chiapas, School of Environmental Engineering, North beltway 1150, Lajas Maciel, 29039, Tuxtla Gutierrez, Chiapas, Mexico
C) National Technology of Mexico, Technological Institute of Tapachula, Department of Chemical and Biochemical Engineering, Km 2, Highway to Puerto Madero, Tapachula, Chiapas, 30700, Mexico

ARTICLE INFO

Keywords:
Bio-coagulants
Coagulation-Flocculation
Multi-criteria matrix
Opuntia ficus mucilage
Stabilized leachate

ABSTRACT

The main aim of this research was to compare a bio-coagulant, organic coagulant, and a conventional coagulant applied to the treatment of leachates. Coagulant options were Stage 1 FeCl₃, Stage 2 Polyamine, and Stage 3 Opuntia ficus mucilage (OFM). Optimal conditions for maximum chemical oxygen demand (COD) removal were determined by experimental data and Response Surface Methodology. The application of Multiple Criteria Decision Analysis using Multi-Criteria Matrix (MCM) was explored by evaluating the Coagulation-Flocculation processes. Maximum COD removal (%) and the best MCM scores (on a scale from 0 to 100) were: Stage 1: 69.2 ± 0.9 and 48.50, Stage 2: 37.8 ± 1.1 and 79.0, and Stage 3: 71.1 ± 1.7, and 81.5. Maximum COD removal using FeCl₃ and OFM was not statistically different (p < 0.05). OFM extraction process was evaluated (yield 0.70 ± 1.17%, carbohydrate content 32.6 ± 1.18%). MCM allows the evaluation of additional technical aspects, besides oxygen COD removal, as well as economic aspects, permitting a more comprehensive analysis. Significant COD removals indicate that the use of OFM as a coagulant in the treatment of stabilized leachate was effective. Opuntia ficus cladodes, a residue, were used to treat another residue (leachates).

1. Introduction

Landfill leachate is defined as a highly contaminated liquid that percolates through waste mass and is infused with dissolved and suspended matters (Ghani et al., 2017). It is well known that the inadequate treatment of leachates, together with poor operation of landfills and the resulting infiltration can lead to health and environmental issues (Martínez-Cruz et al., 2021; Yusoff et al., 2018). Table 1 reviews the classification of landfill leachate according to the composition changes.

Physico-Chemical treatments are recommended for stabilized leachate. In most cases, the separation of suspended particles from the liquid phase is usually accomplished by Coagulation-Flocculation Processes (CFP) (Amor et al., 2015; Liu et al., 2012). The use of iron salts as coagulants has been studied extensively, reporting optimal pH of 5.5–8.0 (Amor et al., 2015; Liu et al., 2012; Moradi and Ghanbari, 2014; Poblete et al., 2019; Tripathy & Kumar, 2019). Rajala et al. (2020) evaluated the use of polyamine as a coagulant in the removal of microplastics from wastewater. The inorganic salts Fe (III) have usually been used as a coagulant to reduce high molecular weight organic matter from various categories of water: surface water, brackish water, and landfill leachate (Singh et al., 2012). Numerous studies have been conducted on leachate treatment using FeCl₃ as a coagulant, and maximum COD removal values of 38% (Pi et al., 2009), 68% (Li et al., 2010), and 72% (Ntampou et al., 2006) have been obtained.

Because they are environmentally sustainable, plant-based bio-coagulants have emerged as low cost options (Tawakkoly et al., 2019), generating less sludge (Tawakkoly et al., 2019; Yin, 2010). In the case of leachate treatment, Rasool et al. (2016) evaluated Ocimum basilicum L as a natural coagulant in combination with alum, achieving 64.4% and 77.8% color and COD removals under optimal conditions. Yusoff et al. (2018) evaluated the flocculation process using the starch from a seed, Durio zibethinus, together with polyaluminium chloride, as a coagulant. According to their results, the use of the natural product makes it possible to lower the dose of coagulant, while achieving significantly better turbidity and COD reductions, as well as improved color removal, because of the more efficient flocculation obtained with starch.

* Corresponding author.
E-mail address: nrov@pumas.ingen.unam.mx (M.N. Rojas Valencia).

https://doi.org/10.1016/j.heliyon.2021.e07510
Received 7 December 2020; Received in revised form 26 March 2021; Accepted 5 July 2021
2405-8440/© 2021 The Author(s). Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
Tawakkoly et al. (2019) used a mucilaginous extract of *Salvia hispanica* (Chia) (40 g L⁻¹, pH 7) obtaining COD reduction of 39.8%.

The use of bio-coagulants and inorganic coagulants in leachate treatment, using Response Surface Methodology (RSM) to achieve optimal conditions, has been explored previously. Liu et al. (2012) used FeCl₃ (10 g L⁻¹, pH 8) achieving COD reduction of 39.8%. Rasool et al. (2016) evaluated the use of *Ocimum basilicum* L. in combination with aluminum sulfate (1:1, ratio, pH 7), obtaining COD reduction of 64.4%.

Because bio-coagulants are based on locally-sourced plants, their use has the potential to enhance the living standards of rural communities while further lowering costs (Oladoja, 2015). The use of *Opuntia* species as a coagulant is interesting. It is a genus in the Cactaceae, characterized by the production of a hydrocolloid—known as mucilage—which forms molecular networks that can retain large amounts of water (Saeng et al., 1975). High COD removal efficiency could be obtained (50-60%) using *Opuntia* species to treat sewage water, potable water source, and high turbidity seawater (Zhang et al., 2006). A different approach to assessing CFP will be the use of Multiple Criteria Decision Analysis (MCDA) using Multi-Criteria Matrix (MCM). It could be determined from all the combinations of factors evaluated which of those obtains the best evaluation through the use of weighted criteria—criteria that in addition to COD removal or some other parameter value could include technical and economic factors—so that the optimization could be approached more comprehensively (García-Cáceres, 2020).

The main aim of this research was to compare a bio-coagulant with *Opuntia ficus* mucilage (OFM), organic coagulant (polyamine), and a conventional coagulant (FeCl₃), using jar test and RSM. Besides, the use of MCDA using MCM will be explored evaluating technical and economic aspects of the processes. Three different Coagulant-Flocculant options were evaluated: FeCl₃-Polyacrylamide, Polyamine-Polyacrylamide, and OMF-Sodium bentonite. Additionally, optimal conditions of greater COD removal were determined by jar test and using RSM. Supplementary, the best results generated in MCM were compared with these optimal conditions. To our knowledge, this is the first attempt to use MCM in the evaluation of CFP applied to the treatment of stabilized leachates.

2. **Methodology**

2.1. Landfill leachate collection, characterization, and other materials

The leachate samples used in this investigation were taken from “Bordo Poniente sanitary landfill”. Bordo Poniente sanitary landfill is in the eastern part of Mexico City (longitude: 99° 00’ west, latitude: 19° 26’ north). Bordo Poniente sanitary landfill is currently closed and received 6.9 megatons of municipal solid waste from 1991 to 1994. The samples were collected in the main pumping sump of the so-called Section III (Figure 1). Around 80 L of leachate samples were accumulated and transported to the laboratory. The recommendation for preserving the sample at 4°C was taken. The leachate samples were characterized: pH, BOD₅, COD, color, and turbidity following standardized methods (APHA, 2012). Table 2 shows the methodology used for the characterization of leachates and effluents. FeCl₃ 6H₂O (called FeCl3 in this research report), denatured CH3–CH2 OH, and Sodium bentonite (analytical grade) were purchased from Merck Company Mexico. The synthetic organic coagulant (Polyamine FL3249) and the organic flocculant (Polyacrylamide FO 4800SSH) were donated by SNF Floerger Company Mexico. The pH conditioning of the leachates was achieved with the addition of H2SO4 or NaOH 1 N. The other chemicals used for sample analysis were of analytical grade and were supplied by Merck Company Mexico. *Opuntia ficus* cladodes (OFM) were purchased in a public market in the western area of Mexico City.

2.2. Extraction and characterization of *Opuntia ficus mucilage*

Considering the proposals for the extraction of OFM indicated by Figueroa et al. (2011), Rodríguez-González et al. (2011), and Sepúlveda et al. (2007) the following methodology was used—consisting of simple stages of unit operations—: selection, cleaning, peeling, grinding, scalding, filtration, sedimentation, centrifugation, precipitation, and drying (Figure 2). OFM of at least three months were selected to realize the extraction of the OFM since these sheets are thicker than the OFC that are normally marketed. This increased thickness facilitated the stripping and cleaning steps in the extraction procedure. The conditions for each stage of mucilage extraction were as follows:

- The OFC were washed with potable water. The cladodes were brushed to remove the spines, making them easier to handle, and then peeled with a knife, removing as little pulp as possible.
- The cladodes were then cut in 2 cm pieces.
- Mixing equal parts of nopal and distilled water, the cladodes were ground in a commercial blender at 3000 RPM.
- The ground product was scalded at 80°C for 5 min.
- Large solids were removed by passage through a 1 cm aperture sieve.
- The solution obtained was centrifuged at five thousand RPM for 20 min.
- The mucilage of the aqueous phase was precipitated with the incorporation of denatured ethyl alcohol -ratio 1:3, solution: alcohol-causing the insolubilization of mucilage.
- The mucilage was separated by decantation –prior 4-hour sedimentation- and centrifugation at two thousand RPM for 20 min.
- The pellets were dried to remove the organic solvent, adapting a vacuum system to a Kitazato flask for 4 h.

The extraction procedure was performed on three batches of OFC, each batch was harvested from the same plot, but on different dates. OFM characterization was determined following official analysis methods (AOAC, 1990), including the parameters listed in Table 3. The carbohydrate content was determined by the difference at 100% of the parameters indicated in Table 3 (FAO, 2012; Sepúlveda et al., 2007).

2.3. Experimental procedure

CFP tests were executed in a jar test kit (Phipps™), adapting six 1 L beakers, using 0.5 L of leachate. CFP tests were performed in three stages using different Coagulant-Flocculant: Stage 1 FeCl₃- Polyacrylamide, Stage 2 Polyamine - Polyacrylamide, and Stage 3 OFM-Sodium bentonite. Besides, the sample collected at the end of the jar test was analyzed. Optimal conditions to maximize COD removal were defined using two different ways: Firstly, jar test (according to Standard Methods) (APHA, 2012) based on the experimental outcome; and second, using RSM. The correlation coefficient (R2) was obtained and the Durbin Watson's Test

| Parameter | Type of leachate | Young | Intermediate | Mature |
|-----------|-----------------|-------|--------------|-------|
| Age (Years) | <5.0 | 5.0-10.0 | >10.0 |
| COD (g L⁻¹) | >10.0 | 4.0-10.0 | <4.0 |
| BOD₅/COD | 0.5-1.0 | 01-0.5 | <0.1 |
| pH | <6.5 | 6.5-7.5 | >7.5 |

BOD₅: Biological oxygen demand. COD: Chemical oxygen demand. BI: Biodegradability index.
was performed to validate the models obtained. Table 4 indicates the conditions of Coagulation-Flocculation experiments.

A full factorial type of experiment was developed. Independent variables were coagulant dose, flocculant dose, and pH. COD removal was the response variable. 18 experiments were made by every stage of experimentation with three repetitions. To obtain a narrower and more effective range of studied factors, some preliminary studies with wide Coagulant-Flocculant doses and initial pH ranges were made. Table 5 shows the values of the independent variables in the Coagulation-Flocculation experiments. The values of the means between the different treatments were compared using t-test or Welch’s t-test, previously verifying the equality of the data variances. All data analysis was conducted using the IBM SPSS Statistics Version 20.

2.4. Multi-Criteria Matrix

MCDA was used as an alternative to the evaluation of the CFP applying MCM. The technical and economic evaluations were considered. A weighted weight of 50% was assigned for each one with a maximum possible grade being 100 points. Eqs. (1), (2), and (3) were used (Romero, 1993):

\[
B = \sum_{i=1}^{n} n_i A_{\text{max}}
\]

\[
W_{ri} = \frac{A_i}{B} W_{ea}
\]

\[
D = \sum_{i=1}^{n} W_{ri}
\]

Where:
- \( n \): Aspects evaluated for each criterion.
- \( i \): Criterion evaluated.
- \( A_{\text{max}} \): Maximum possible rating.
- \( B \): Arithmetic product of \( n_i \) and \( A_{\text{max}} \).
- \( W_r \): Weighted rating.
- \( A_i \): Number of aspects evaluated by each criterion \( i \).
- \( D \): Final grade for the reagent combination evaluated.
- \( W_{ea} \): Weighting to the economic aspect or technical aspect.

2.4.1. Technical evaluation

Technical criteria used were % removal of the physicochemical parameters (COD, turbidity, and color), final pH value, amount of generated sludge, flocc sedimentation time, manageability of generated sludge, and requirement of chemical products. The criteria for assigning weight to each criterion were described. COD, turbidity, and color removal percentage: 5, optimal (>70.0%); 4, particularly good (50.0–70.0%); 3, good (40.0–50.0%); 2, regular (30.0–40.0%); 1, bad (0.0–30.0%); and 0, too bad (<0.0%). Final pH value: 5, excellent (6.0–8.0); 3, good (2.0–6.0 or 8.0–12.5); and 0, bad (any other pH value). Flocc sedimentation times (minutes): 5, excellent fast (0–3 min); 3, fast (3–5 min); 1, regular (5–10 min); and 0, slow (>10 min). Amount of sludge generated (ASG) (kg m\(^{-3}\)): 5, excellent (<20.0 kg m\(^{-3}\)); 3, good (20.0–30.0 kg m\(^{-3}\)); and 1, bad (>30.0 kg m\(^{-3}\)). Ease of handling of generated sludge (the most favorable option will be that in which the sludge can be processed more easily): 5, excellent (sludges of natural organic origin); 3, regular (sludges from a synthetic polymer); and 1, bad (sludges generated by an inorganic coagulant). The requirement of chemical inputs and/or additives (the most favorable technology was one that has a minimum or no requirement): 1, bad (two or more requirements); 3, regular (one requirement); and 5, excellent (no requirement).

2.4.2. Economic evaluation

Economic criteria used were the following costs: coagulant dose, flocculant dose, sludge final disposal, consumption of H\(_2\)SO\(_4\), and NaOH.

| Parameter         | Method (APHA, 2012) | Principle (Method) |
|-------------------|---------------------|--------------------|
| COD               | 5220 D              | Colorimetric -closed reflux |
| BOD               | 5210 D              | Respirometric      |
| pH                | 4500-H\(^+\) B      | Electrometric      |
| Color             | 2120 C              | Spectrometric      |
| Turbidity         | 2130 B              | Nephelometric      |
The weight allocation for each criterion was assigned considering the maximum and minimum costs, generating five equal intervals. Zero weight was given for the maximum cost and five for the minimum cost. Table 6 indicates the rating assigned for each criterion.

### 3. Results and discussion

#### 3.1. Landfill leachate characteristics

Results obtained of leachate characterization were COD: 2.11 ± 0.087 g L⁻¹, BOD₅: 0.0348 ± 0.0.002 g L⁻¹, IB: 0.02 ± 0.001, and pH 8.9 ± 0.2. Considering the IB value below 0.1, the sampled leachate belongs to the stabilized type (Foo and Hameed, 2009), which was expected since the landfill was closed in 1994, so leachates are older than 10 years. Low IB values recommend the use of physicochemical methods for the adequate treatment of this type of leachate. In comparison to other stabilized leachates, differences were found: Aftab et al. (2020) (landfill site located in South Korea, closed in the year 2000 after eight years of operation) obtained COD 0.536 g L⁻¹ and pH 8.2; and Poblete et al. (2019) (landfill situated in Chile) found COD 12.3 g L⁻¹ and pH 8.9. The reason for these notable differences was the variability in the production and composition of leachates in landfills (Deng and Englehardt, 2006; Mandal et al., 2017; Martínez-Cruz et al., 2020).

![Figure 2. Stages of the extraction process of Opuntia ficus mucilage.](image-url)
The leachates have a dark brown color and a slightly unpleasant odor, mainly due to the presence of organic acids stemming from the high concentration of decomposing organic matter (Tripathy & Kumar, 2019). The leachate had a high color concentration (4110.0/C6 79.4 Pt–Co U), a particular characteristic of stabilized leachates, which can be associated with the presence of high organic substances (Aziz et al., 2007), such as humic and fluvic compounds (Ibrahim and Yaser, 2019; Tripathy & Kumar, 2019). Turbidity value found (50/C6 3.5 NTU) can be associated with the presence of volatile fatty acids (amino acid and other low molecular compounds), which although they are present in low concentrations in the stabilized leachates, are still present (Bhalla et al., 2013).

3.2. Extraction and characterization of the Opuntia ficus mucilage

Starting from 10 kg of OFC, the OFM extraction process generated the following results: after peeling (OFC without cuticle): 5.63/C6 0.17 kg, after grinding and bleaching (water and OFM solution): 5.55/C6 0.20 L. The average OFM yield after drying was 0.70/C6 1.17% based on fresh weight. Although at a first stay, it might seem that the yield obtained to produce mucilage is low, it is necessary to compare the result with other investigations. Contrasting to other research papers the performance obtained was lower. Matsuhiro et al. (2006) got 3.8%, Sepúlveda et al.
(2007) obtained 1.48%, Rodríguez-González et al. (2011) derive 0.9%, and Sáenz and Sepulveda (1993) achieved 1.2%. This result could be influenced by the different methods used for the extraction of OFM, as well as the different origins of OFC. In the case of the extraction method proposed in this research, it should be considered that material was lost in the stages of peeling and mucilage precipitation.

Table 7 shows the characterization of OFM used in this research. Moisture values above 50% are highlighted. The carbohydrate content of the mucilage obtained in this experiment was 33.23 ± 1.7%. This content could not be compared with other researches since, according to the consulted bibliography, this is the first research that examined this parameter. Considering the statement of Matsuhiro et al. (2006) that mucilage’s are complex polymeric substances of carbohydrate nature with a highly branched structure, the carbohydrate content could be considered as the component present in mucilage to which its coagulant capacity is associated.

### 3.3. Multi-Criteria Matrix

Using the criteria established in the methodology, MCM was formulated for the technical and economic aspects of each of the proposed combinations of pH, coagulant dose, and flocculant dose. Supplementary material shows the best results obtained (Table S4 and S5).

The reagents were Polyamine: $2.67 \text{ kg}^{-1}$, Polyacrylamide $6.03 \text{ kg}^{-1}$, H2SO4: $12.41 \text{ L}^{-1}$, FeCl3: $30.12 \text{ kg}^{-1}$, SB: $2.73 \text{ kg}^{-1}$, NaOH: $3.08 \text{ L}^{-1}$, OFC: $0.05 \text{ kg}^{-1}$, LP Gas: $0.28 \text{ m}^{-3}$, CH3OH: $1.00 \text{ L}^{-1}$. A cost for disposal of generated sludge of $1.30 \text{ kg}^{-1}$ was considered. Evaluating the economic feasibility of four best-evaluated alternatives, three of them were using OFM. The criteria that favored the OFM options were the low consumption of products and the lower cost for sludge handling. Concerning technical feasibility, the same situation was presented: of the four best-evaluated alternatives, three of them were using OFM. The criteria that favored the OFM options were the final pH value and COD removal. It should be noted that of the six best-evaluated alternatives, both in technical feasibility and in economic feasibility, no alternative used FeCl3. On the other hand, the criteria that most devalued the use of FeCl3 as a coagulant were its high cost — compared to organic coagulants —, use of compounds for pH conditioning, a large amount of sludge generated — compared to organic coagulant options —, as well as the cost of handling the sludge generated.

Table 8 shows six best-evaluated alternatives MCM (Stage 1 and 2); and the three best-evaluated ones of Stage 3. Although the use of polyamine was a better-evaluated alternative than the FeCl3 option, the use of OFM was the option that achieved the greatest COD removal. From the three best treatment alternatives, the first two were using OFM; while the use of Polyamine obtained its best evaluation being the third, fifth, and sixth-best evaluated alternatives. MCM is a tool used to evaluate different options by scoring them against criteria of interest so that an attempt is made to objectify the choice. It was possible to propose the use of MMC as an alternative for PIC evaluation, by integrating technical and economic factors. While it is true that the jar test and the use of MSR allow determining optimal process conditions concerning a target variable (usually the removal of COD), the use of MMC permits to emphasize economic factors, as well as additional technical factors.

### Table 7. Characterization of the *Opuntia ficus* mucilage.

| Sample | Parameter (%) | Moisture | Crude protein | Ash | Raw fiber | Carbohydrates |
|--------|---------------|----------|---------------|-----|-----------|---------------|
| 1      |               | 52.90    | 5.30          | 7.55| 0.00      | 34.25         |
| 2      |               | 53.27    | 4.70          | 10.79| 0.00      | 31.24         |
| 3      |               | 52.53    | 4.10          | 9.17 | 0.00      | 34.20         |
| Mean   |               | 52.90    | 4.70          | 9.17 | 0.00      | 33.23         |
| SD     |               | 0.37     | 0.60          | 1.62| 0.00      | 1.72          |

SD: Standard deviation, n = 3. n: Number of repetitions.

### Table 8. Multi-Criteria matrix: Six best-evaluated alternatives in Stage 2 and 3; and three best-evaluated alternatives in Stage 1.

| Experiment/Stage | Dose (g L⁻¹) | Coagulant | Flocculant | Evaluation |
|------------------|--------------|-----------|------------|------------|
|                  |              |           |            | Technical | Economical | Total |
| 13/3             | OFM          | SB        |            | 37.50     | 44.00      | 81.50 |
|                  | 0.50         |           |            |           |            |       |
| 14/3             | OFM          | SB        |            | 37.50     | 42.00      | 79.50 |
|                  | 0.75         |           |            |           |            |       |
| 13/2             | Polyamine    | Polyacrylamide | 0.50 | 0.025 | 35.00     | 44.00  | 79.00 |
| 16/3             | OFM          | SB        |            | 38.75     | 40.00      | 78.75 |
|                  | 0.50         |           |            |           |            |       |
| 10/2             | Polyamine    | Polyacrylamide | 0.50 | 0.015 | 32.50     | 46.00  | 78.50 |
| 16/2             | Polyamine    | Polyacrylamide | 0.50 | 0.035 | 33.75     | 44.00  | 77.75 |
| 4/1              | FeCl₃        | Polyacrylamide | 1.40 | 0.150 | 33.75     | 16.00  | 49.75 |
| 1/1              | FeCl₃        | Polyacrylamide | 1.40 | 0.100 | 32.50     | 16.00  | 48.50 |
| 7/1              | FeCl₃        | Polyacrylamide | 1.40 | 0.200 | 31.25     | 14.00  | 45.25 |

pH: OFM 6.0, Polyamine 7.0, FeCl₃ 6.0.
3.4. Coagulation-flocculation processes

Results obtained from CFP experiments are shown in Supplementary materials (Table S1, S2, and S3). Using RSM with the data generated experimentally at each experimental stage the statistically significant variables that fit the model outlined in Eq. (4) were calculated. Figure 3 shows the contour plots in the stages of experimentation. Table 9 shows the values of these variables — values are specified in their original units. All models were statistically significant (p < 0.005) for the response variable (COD removal). Considering the value close to 1.0 obtained by the correlation coefficient, it can be stated that the models were statistically significant.

\[
\text{COD Removal} = a + b \text{pH} + c \text{Coagulant} + d \text{Flocculant} + e \text{pH Coagulant} + f \text{pH Flocculant} + g \text{Coagulant Flocculant} + h \text{Coagulant}^2 + i \text{Flocculant}^2
\] (4)

Table 10 shows a summary of the optimal conditions for maximum COD removal using experimental data (jar test) and MRS. Also, the alternative with the highest score MCDA was included. Comparing the values obtained, different results were observed. The reason for these differences was that the use of MCM allows a more comprehensive evaluation of the CFP. The rating assigned in MCM includes, in addition to COD removal, the weighing of additional criteria, which form the economic and technical feasibility of the process.

3.4.1. Stage 1: FeCl₃-Polyacrylamide

The addition of coagulants to leachates leads to the interaction of cations and their hydrolyzed products with negative colloids, neutralizing their charges, destabilizing them (Amor et al., 2015). Because it neutralizes negatively charged matter in suspension and binds destabilized particles together, CFP generates heavier and larger flocules (Lee et al., 2014; Yusoff et al., 2018). It should be noted that the best COD removal in Stage 1 was in all cases at pH 6.0. These COD removal in pH 6.0 can be explained by the hydrolyzed ferric species, ferric (Fe³⁺) can react with hydroxyl (OH⁻) and form Fe(OH)₃ or Fe(OH)₄, as shown in Eqs. (5) and (6) (Ching et al., 1994).

\[
\text{Fe}^{3+} + 3\text{OH}^- \rightarrow \text{Fe(OH)}_3
\] (5)

\[
\text{Fe}^{3+} + 4\text{OH}^- \rightarrow \text{Fe(OH)}_4
\] (6)

Previous researchers had reported that pH significantly influenced removal efficiencies in the CFP (Amokrane et al., 1997; Liu et al., 2012; Marañón et al., 2008). Compared to other studies that have been implemented in the treatment of stabilized leachates using FeCl₃ as a coagulant, in this investigation a maximum COD removal of 69.2% at pH 6.0 was achieved using 1.4 g L⁻¹; while Tripathy & Kumar (2019), Liu et al. (2012), Moradi and Ghanbari (2014), and Amor et al. (2015) obtained COD removal 73.5, 68.6, 65.0, 63.0% at pH 5.5, 8.0, 7.0, and 5.0; using 1.2, 1.0, 1.5, and 2.0 g L⁻¹ FeCl₃, respectively. The reason for these different results can be attributed to the variability in the composition of the leachates. COD removal can be explained by the elimination of recalcitrant compounds from stabilized leachates (Liu et al., 2012). An increase in the dose of coagulant and a decrease in pH would probably achieve an increase in COD removal, as an adverse consequence the economic factor of the process would increase due to the consumption of more coagulant and the reagent to lower the pH (H₂SO₄), added to the problem of handling the sludge produced at a lower pH. Since in the CFP the economic factor was evaluated within the MCM, it was decided to use pH values close to neutrality and to use the minimum dose of coagulant. The inorganic salts Fe (III) have usually been used as a coagulant to reduce high molecular weight organic matter from various categories of water: surface water, brackish water, and landfill leachate (Singh et al., 2012). The theoretical analysis of mechanism, using FeCl₃ as a coagulant, can be explained as follows: as the pH of supernatant in the coagulation process reduces, the charge densities of the organic matter also decrease, which necessitates lower coagulant doses to initiate charge neutralization and precipitation (Shin et al., 2008). The coagulation efficiency is dominated by the solution pH (Singh et al., 2012).
The high performance of FeCl₃ as a coagulant is evident compared to the use of polyamine, there was a great difference in the maximum COD removal compared to the experiment equivalent to pH 7.0 (p < 0.05 in all cases). The above result seems to contradict the statement made by Hendricks (2006), who established that organic polymeric coagulants have little dependence on pH since the polymer chains will be positively charged to perform the coagulation process, regardless of the pH value. One possible reason for this contradiction may be related to variability in the composition of leachates, variability that affects the effectiveness of the polyamine used at different pH values.

It is important to highlight that pH 7.0 favored the CFP since all the experiments accomplish at pH 8 obtained lower values of COD removal than the experiment equivalent to pH 7.0 (p < 0.05 in all cases). The above result seems to contradict the statement made by Hendricks (2006), who established that organic polymeric coagulants have little dependence on pH since the polymer chains will be positively charged to perform the coagulation process, regardless of the pH value. One possible reason for this contradiction may be related to variability in the composition of leachates, variability that affects the effectiveness of the polyamine used at different pH values.

The high performance of FeCl₃ as a coagulant is evident compared to the use of polyamine, there was a great difference in the maximum COD removal compared to the experiment equivalent to pH 7.0 (p < 0.05 in all cases). The above result seems to contradict the statement made by Hendricks (2006), who established that organic polymeric coagulants have little dependence on pH since the polymer chains will be positively charged to perform the coagulation process, regardless of the pH value. One possible reason for this contradiction may be related to variability in the composition of leachates, variability that affects the effectiveness of the polyamine used at different pH values.

3.4.3. Stage 3: Opuntia ficus-mucilage-sodium bentonite

Regarding the decision to use bentonite as an aid to the Coagulation-Flocculation process achieve by OFM, the results obtained indicate that it was a wise choice. It was possible to confirm the statement of Miller et al. (2008) that the addition of sodium bentonite favors the CFP. Contrasting the best COD removal in the different stages of experimentation (using jar test) was observed that the use of OFM (Stage 3) achieved the best result (71.1 ± 1.7%), compared to Stages 1 and 2 (69.2 ± 0.85% and 37.8 ± 1.1%, respectively); although there was no statistically significant difference in the values of Stage 1 and 3 (Student t-test t = 1.73, p = 0.15). It should be noted that by consuming OFM as a coagulant, an additional benefit is obtained: the use of a product that producers consider a residue, due to its great thickness. The concept that a residue (OFM) is used to treat another residue (leachates) was applied.

The predominant CFP mechanism for OFM was adsorption and bridging, whereby clay particles do not directly contact one another but were bound to a polymer-like material from Opuntia spp (Miller et al., 2008; Yin, 2010). On the basis that CF occurs through a polymer bridge, polymers naturally present in OFM were considered as the active coagulating ingredients: the carbohydrates (Oladoja, 2015; Yin, 2010). The bridging mechanism consists of polymer chains that destabilize stable particles by forming a bridge between them to give rise to so-called flocs (Bolto and Gregory, 2007; Yin, 2010). Positively charged polymer chains neutralize the negative charge of organic matter allowing the precipitation of flocs produced by bridges between polymer-organic matter complexes. Williams (2007) proposes the mechanism of interaction between colloids and soluble natural organic polymers, including the dispersion and adsorption of the coagulant, as well as the formation of bridges and their multiplication (Figure 4).

### Table 9. Variables of the response surface model in the stages of experimentation.

| Variable | Stage 1 | Stage 2 | Stage 3 |
|----------|---------|---------|---------|
| a        | 311.5000| 57.8074 | -232.6820|
| b        | -96.0200| -11.5704| 42.3389 |
| c        | 2.7430  | -13.6444| 206.1330|
| d        | 1344.0000| 5512.2200| 49.4333 |
| e        | 4.7111  | -24.1111| -26.8889|
| f        | 143.4000| -45.5556| -9.0833 |
| g        | -200.0000| -2.5333 | -26.8889|
| h        | -15.9111| -26.8889| 4.3028 |
| i        | 1470.0000| -125444.4000| 4.3028 |
| R²       | 0.8440  | 0.847   | 0.9590 |
| LF       | 0.0000  | 0.0000  | 0.0000 |

R²: correlation coefficient. LF: Lack of fit.

### Table 10. Summary of optimal conditions and highest score Multi-Criteria Matrix.

| Stage | Parameters | Jar Test | RSM | MCM |
|-------|------------|----------|-----|-----|
| 1     | pH         | 6.00     | 6.00| 6.00|
|       | FeCl₃ (g L⁻¹) | 1.40     | 3.00| 1.40|
|       | Polyacrylamide (g L⁻¹) | 0.10     | 0.10| 0.15|
|       | COD Removal (%) | 69.20 ± 0.90| 70.50| 55.70 ± 2.40|
|       | Experiment | 1        | 3   | 4   |
| 2     | pH         | 7.00     | 7.00| 7.00|
|       | Polyamine (g L⁻¹) | 0.75     | 0.50| 0.50|
|       | Polyacrylamide (g L⁻¹) | 0.025   | 0.02| 0.025|
|       | COD Removal (%) | 37.80 ± 1.10| 34.20| 33.60 ± 2.40|
|       | Experiment | 14       | 10  | 13  |
| 3     | pH         | 6.00     | 6.00| 6.00|
|       | OFM (g L⁻¹) | 0.75     | 1.00| 0.50|
|       | Sodium bentonite (g L⁻¹) | 3.00     | 3.00| 1.00|
|       | COD Removal (%) | 71.10 ± 1.70| 71.90| 53.20 ± 1.70|
|       | Experiment | 17       | 18  | 13  |

COD Removal: Mean ± Standard deviation, n = 3.
Fe^{3+} + H_2O → Fe(OH)^{2+} + H^+  

(7)

In the cases of treatments with organic coagulants (Polyamine and OFM), little variations were found in the pH of the effluents. In Stage 2—with an initial pH of 7.0—effluents with pH values of 7.2–7.8 were obtained. Under optimal conditions for maximum COD removal, a pH of 7.5 ± 0.11 was obtained. In experiments with an initial pH of 9.0, the pH variation of the effluent was even lower, with values 8.2–8.3. The increase in pH in Stage 2 would be explained by the addition of the coagulant: Polyamine. Organic polyamine is a class of compounds that contains two or more alkaline amine groups (Yang et al., 2020), which would favor an increase in pH. In Stage 3, with an initial pH of 6.0, the pH values in the effluent were 6.5–6.8. The pH of the effluent at the optimal conditions of maximum COD removal had a pH of 6.6 ± 0.06. The increase in pH adding OFM can be explained by the alkaline character of the polysaccharides (Zheng et al., 2020), facilitating the increase in pH (32.6 ± 1.18% was the carbohydrate content of the OFM in this investigation). Furthermore, the effect of the addition of sodium bentonite must be considered. Bentonites are clays essentially composed of minerals (Hidalgo et al., 2016) that have a buffer effect. Taking as a reference the experimentation conditions for the highest COD removal, the following color removal values were obtained: Stage 1 95.5 ± 2.9%, Stage 2 48.8 ± 3.6%, and Stage 3 33.48 ± 0.82%. The high value of color removal using FeCl3 (Stage 1) must be related to the high values of COD removal (>60%). A lower presence of humic substances in the effluent would cause a decrease in color. The lower color removal in the use of OFM, compared to the other coagulants evaluated, has to do with its plant origin. de Oliveira et al. (2007) state that the concentration of coagulants of plant origin is proportional to the increase in polymerization, which causes the color to become browner, contributing to a higher color value in the effluent.

Concerning the amount of sludge generated it was observed that the use of FeCl3 generated a greater amount compared to the use of organic coagulants, with values that fluctuated 12.1–48.9 kg m⁻³. In the optimal conditions of greater COD removal in Stage 1 amount of sludge generated was 35.3 ± 4.2 kg m⁻³. In Stage 2 amount of sludge generated varied 3.9–7.1 kg m⁻³, and in optimal conditions for maximum COD removal amount of sludge generated was 4.6 ± 0.40 kg m⁻³. Finally, in Stage 3, the amount of sludge generated wide-ranging 5.5–16.3 kg m⁻³, and in optimal conditions (best COD removal) amount of sludge generated was 16.3 ± 0.31 kg m⁻³. The results obtained confirm what was stated by Bolto and Gregory (2007) and Hendricks (2006) who mentioned that the use of organic coagulants produces less sludge compared to the use of inorganic coagulants.

4. Conclusions

The leachate used in the investigation was stabilized type with BI 0.02. The use of OFM as a coagulant was evaluated, obtaining optimal conditions for maximum COD removal (71.1 ± 1.7%) results that were not statistically different from the alternative of using FeCl3 (69.2 ± 0.85%). The use of polyamine as a coagulant did not favor the COD removal, obtaining results below 40%. Concerning the OFM extraction process, it was possible to achieve an average yield after drying was 0.70 ± 1.17%, based on fresh weight, with a carbohydrate content of 32.6 ± 1.18%.

MCM allowed weighing economic criteria that the jar test and RSM do not consider at all (technical and economic aspects). In this way, it was possible to develop a more comprehensive process evaluation considering additional aspects to COD removal. MCDA approaches the evaluation of the CFP differently from traditional methods (jar test and RSM), allowing a broader vision, which includes a greater number of criteria so that it was possible to assign different weighted weights to the criteria considered based on their technical or economic importance. According to MCM, of the three best alternatives, the first two used OFM, while the third-best alternative used Polyamine.

The alternative for the use of OFC developed in this research was an option for the OFC valorization that, in most cases, producers consider them a residue, due to their great thickness, which makes them little commercial. In this way, a residue (OFC) was used to treat another residue (leachates).

Declarations

Author contribution statement

Alfredo Martínez-Cruz: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

María Neftali Rojas Valencia: Conceived and designed the experiments; Wrote the paper.

Juan Antonio Araiza-Aguilar: Analyzed and interpreted the data. Hugo Alejandro Nájera-Aguilar & Rubén Fernando Gutiérrez-Hernández: Contributed reagents, materials, analysis tools or data.

Funding statement

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Data availability statement

No data was used for the research described in the article.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

Supplementary content related to this article has been published online at https://doi.org/10.1016/j.heliyon.2021.e07510.
