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Opuntia ficus indica as a polyelectrolyte source for the treatment of tannery wastewater

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ABSTRACT

This work presents the utilization of a natural polyelectrolyte, extracted from the cactus *Opuntia ficus indica*, as an auxiliary coagulant. The polyelectrolyte was employed together with either aluminum sulfate or ferric chloride in the treatment of real tannery wastewater. The parameters analyzed were turbidity, chemical oxygen demand, and total chromium concentration. The removal efficiency of chemical oxygen demand increased from an average of 77% using only aluminum sulfate to 90% in the presence of the natural polyelectrolyte. For ferric chloride, the efficiency increased from 91 to 98% when the natural polyelectrolyte was also used. Under all conditions employed, the level of total Cr is reduced below that permitted by the Brazilian legislation.

Keywords: Tannery waste; Coagulation; Flocculation; Natural polyelectrolyte

1. Introduction

The tannery industry uses large volumes of water and as a result considerable quantities of liquid and solid wastes are produced during leather production. The discharge of these wastewaters without appropriate treatment can cause both extensive environmental pollution and health risks [1].

Brazil is responsible for approximately 10% of the total world production of leather and the southern states of Brazil (Rio Grande do Sul, Parana, and Santa Catarina) concentrate 60% of the total 600 tanneries nationwide [2]. In this light, the scale of the problem is easy to see when it is taken into account that for every kilogram of processed skin produced 30–35 L of effluent result [3,4]. It should also be noted that effluent streams can present high salt concentrations with effluents containing up to 80 g dm^{-3} of sodium chloride [5].

The chrome tanning method, as it is commonly called in the leather trade [6], is by far the most widely used process for leather production, being applied in 90% of the leather produced worldwide [3,7–9]. Often chromium(Cr) is used in excess to improve tanning quality [9]. However, the leather production itself takes up only 60–80% of the applied

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Cr and the remainder is usually discharged into the sewage system [10]. The toxicity of chromium is dependent on its oxidation state: Chromium(VI) compounds (e.g. CrO_4^{2-} and $Cr_2O_7^{2-}$) are highly toxic and carcinogenic [7,11,12]. On the other hand, Chromium (III) compounds at low concentrations do not present toxic effects. In fact, chromium(III) is considered to be a human nutrient and a component of glucose metabolism [13]. Chromium(III) is also more stable and it tends to form inert complexes [7,11]. The hexavalent form is 500 times more toxic than the trivalent form [10].

Tannery effluent also contains high quantities of putrefaction products (proteins, blood, muscular fibers, etc.) and toxic substances such as sulfide, which is used to loosen wool and hair [6,7], dyes, fat, inorganic matter and dissolved and suspended solids. In tannery effluents, wool and hair are responsible for the majority of the biochemical oxygen demand (BOD_5) and chemical oxygen demand (COD) [14].

The characteristics of tannery wastewater can vary widely depending on the day, amount of water used, the process of hide conservation, and the processing capacity [15]. Depending on the tannery plant, the Cr and sulfide stream can be separated and pretreated by coagulation/flocculation and catalytic oxidation processes, respectively, then mixed and treated by biological methods. However, some chemicals are applied such as fungicides, synthetic tannins, and dyes that inhibit the nitrification process [16]. Recalcitrant organic compounds are difficult to degrade by anaerobic and aerobic processes and COD removal is very slow, requiring long hydraulic retention times to complete pollutant removal [17]. As a result, the removal of these compounds by coagulation and flocculation, before biological treatment, is an option that can increase the overall processing speed [17].

The most widely used coagulants are aluminum (Al^{3+}) and iron(Fe^{3+}) salts, which are both easy to handle, apply, and produce less sludge than lime [18]. Aluminum compounds are widely employed in wastewater and water treatment, North American demand for alum in water and wastewater plants being between 450,000 and 500,000 tons in 1993, which is about 50% of total US production [8].

Coagulation followed by flocculation is an effective way to remove high concentrations of organic pollutants [19]; however, the use of coagulant aids (polyelectrolytes) may become necessary in order to improve the efficiency of the treatment [20]. Polyelectrolytes can be classified as natural or synthetic and have been used since 2000 BC when the polyelectrolyte *Strychnos potatorum Linn* was extracted from seeds and utilized as a water clarifier [19].

Various natural and synthetic polyelectrolytes have been used in coagulation and flocculation processes. Polyelectrolytes can be classified in various manners [21,22]. However, the IUPAC Gold Book describes polyelectrolytes as *polymers composed of macromolecules in which a substantial portion of the constitutional units contains ionic or ionizable groups, or both* [23]. The literature demonstrates that polyelectrolytes have been used as flocculants in wastewater treatment from textile plants [24], tanneries [6,15,25], and landfill sites [26].

Natural polyelectrolyte can be extracted from various sources. Chitin, extracted from silkworm chrysalides, was employed for the production of chitosan, which is an alternative to the natural polyelectrolyte [27,28]. It can also be extracted from *Moringa oleifera Lam* (*M. oleifera*) (a tree native to Northern India [29]) and the cactus species *Cereus peruvianus* and *Opuntia ficus indica* [17].

The cactus *Opuntia ficus indica* [17,30–33] is native to North and South America and has been used for analgesic and anti-inflammatory purposes [33]. In addition, the cactus is a source of a negatively charged natural polyelectrolyte [17,33].

The aim of the current study is to investigate the effect of using a natural polyelectrolyte, obtained from the cactus *Opuntia ficus indica*, in tandem with the commonly used coagulating agents, aluminum sulfate and iron chloride, for the removal of organic load and total chromium from real wastewater, obtained from a tannery in the city of Maringa, Parana state, Brazil.

2. Methods

2.1. Extraction of polyelectrolyte

The preparation of the natural polyelectrolyte was performed in the following way: the cactus *Opuntia ficus indica* (Fig. 1) was cut into small pieces and transferred to a 1-L flask and distilled water (0.5 dm^3) was added. The flask was maintained at 10°C for 12 h; and after this period, the solution was filtered using a nylon bolter. This solution was maintained at 4°C. An aliquot of the sample was lyophilized and the concentration of the polyelectrolyte was determined by the difference between dry and wet masses. An average of 300 g of raw cactus pulp supplied 3.8 g of polyelectrolyte.

2.2. Sample collection and treatment

Wastewater samples were collected from the wastewater discharge of a tannery located in the district of Maringa, Parana State, Brazil. The pH and

Fig. 1. Cactus *Opuntia ficus indica*.

dissolved oxygen of the collected samples were measured and the samples were kept under refrigeration until use.

The coagulants used were $Al_2(SO_4)_3 \cdots 18H_2O$ and $FeCl_3$.The natural polyelectrolyte extracted from the cactus *Opuntia ficus indica* was used as a coagulation aid. The best pH range for flocculation and optimum concentration range for the natural polyelectrolyte and coagulant dose were determined using jar test experiments. A jar test (Milan-JT 101) with $6 \times 1.0\text{-dm}^3$ flasks was employed for coagulation and flocculation studies. To determine the efficiency of coagulation, COD and turbidity were determined before and after the jar test.

2.3. Chemical analysis

Dissolved oxygen and pH were measured with an oximeter (YSI model 52) and a pH meter (Marte MB-10), respectively. Absorbance measurements were carried out using an ultraviolet–visible (UV–Vis) spectrophotometer (Shimadzu UV mini 1240).

All chemical analyses were carried out according to the *Standard Methods for the examination of water and wastewater* [34]. Chemical oxygen demand determinations were carried out using the closed reflux with colorimetric method. Turbidity was measured using a turbidimeter (Hach, model 2100A), calibrated with turbidity standards. Total chromium was determined using an atomic absorption spectrophotometer model VARIAN 10 plus ($\lambda = 357.5$ nm, with a reducing air–acetylene flame). The samples were digested in a mixture of HNO_3 and $HClO_4$.

3. Results and discussion

3.1. Coagulation with aluminum sulfate

According to the literature, Al salts present two distinct mechanisms for impurity removal: charge neutralization and incorporation of impurities in an amorphous hydroxide precipitate and other Al hydrolysis products [6,35].

It is well known that the pH of the coagulation process is an important factor in determining the efficiency [36]. In the present study, an initial test to establish the optimum pH for the coagulation process was performed using the *jar test* method. The jar test was conducted over a pH range of 4.0–8.0, with the degree of turbidity removal used as the parameter of interest. Fig. 2 presents the extent of turbidity removal as a function of pH.

It can be seen from Fig. 2 that the greatest reduction in turbidity is in the pH range 5.0–6.0 and that the best value obtained is at pH 6, where 87% of the original turbidity is removed. At pH values below 5 and above 6, the removal of turbidity is between 60 and 65% in all cases. These results can be easily understood by considering the behavior of Al salts when they are added to aqueous solutions, where they dissociate to give both bivalent (Al^{2+}) or trivalent (Al^{3+}) species. In the case of the Al^{3+} ion, with its high charge, it can neutralize the surface electrostatic charges and after successive collisions, colloid agglomeration and settlement occur [36].

The Al^{3+} ions in water are hydrated and hydrolysis of these ions replaces the water molecules by hydroxyl

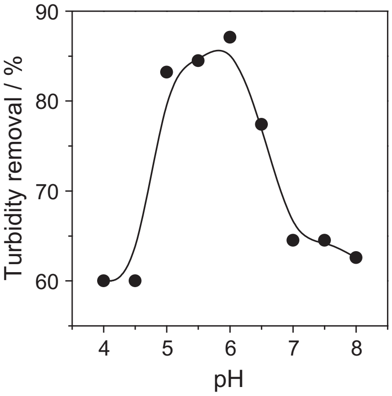

Fig. 2. Turbidity removal from tannery wastewater samples using $Al_2(SO_4)_3$ at different pH values.

ions. This can also be thought of as a progressive deprotonation of water molecules in the primary hydration shell. Omitting the hydration shell, the deprotonation of aluminum is represented by expression 1 [36].

$$Al^{3+} \rightarrow Al(OH)^{2+} \rightarrow Al(OH)_2^{+} \rightarrow Al(OH)_3 \rightarrow Al(OH)_4^{-} \quad (1)$$

Since each step involves the loss of a proton, increasing the pH will shift the equilibrium to the right of expression 1. The solubility of aluminum hydroxide is high at pH values < 6.0; at pH 4.0, the concentration range of soluble Al ions is 25,000–30,000 mg dm^{-3} Al^{3+}. However, when the pH is in the region of 6.0, the minimal solubility is approximately 5.4 × 10^{-2} mg dm^{-3} of Al^{3+} [36,37]. Thus, considering these points, the higher turbidity removal at pH 6.0 (Fig. 2) can be attributed to the greater formation of $Al(OH)_3$ at this pH value. As the $Al(OH)_3$ species is a gelatinous flock, it will drag suspended materials to the bottom of the jar [18,38].

Above pH 6.0, turbidity removal decreases due to the formation of soluble Al complexes at this pH, especially the aluminate ion, which is more soluble than $Al(OH)_3$. In the case of Al, the dominant species in solution changes from Al^{3+} to $Al(OH)_4^{-}$ over little more than one pH unit [36].

To optimize the coagulant dosage, the pH value of the wastewater was maintained at the optimum pH value, determined previously in the jar test (pH 6) and coagulant doses ranging from 60 to 85 mg dm^{-3} at 5 mg dm^{-3} concentration increments were applied, using the same conditions for the optimization of the pH. The effect of the coagulant dosage on COD removal is shown in Fig. 3. The turbidity removal is also shown in Fig. 3 and it can be observed that it does not vary greatly from that seen in Fig. 2 over the dosage range studied.

It can be seen from Fig. 3 that COD removal is most effective at 75 mg dm^{-3} of the coagulant. If we consider that the COD of the raw sample was 614.4 mg dm^{-3}, and when the coagulant was added at optimum concentration, the residual COD decreased to 141.8 mg dm^{-3}, a removal efficiency of approximately 77%. Concentrations above this value did not result in increased COD removal; probably because particle restabilization occurs, as demonstrated in the relevant literature [36,38].

In Fig. 4, the extent of removal of the total Cr is presented. It can be seen that the raw effluent contains a total content of Cr at approximately 1.27 mg dm^{-3}, which is well above that established by the Brazilian legislation for discharge of effluents into receiving waters (0.5 mg dm^{-3} Cr) [37]. However, the addition of Al salts is sufficient to make Cr concentration compliant with the legislation [37], with at least 72% removed at all the studied concentrations. The maximum removal of Cr is at 75 mg dm^{-3}, as seen for the removal of COD, with up to 83% Cr removed. From a commercial point of view, Cr that settles as $Cr(OH)_3$ can be converted into a Cr^{3+} aqueous solution by the addition of sulfuric acid, and this solution supplied with additional amounts of Cr salts can be reused in the tanning process [39].

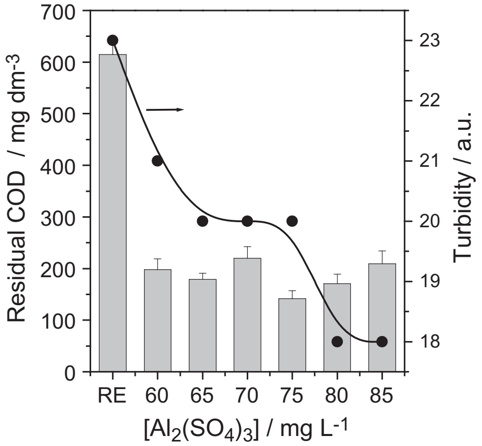

Fig. 3. Effect of $Al_2(SO_4)_3$ concentration on COD and turbidity removal of tannery wastewater samples.

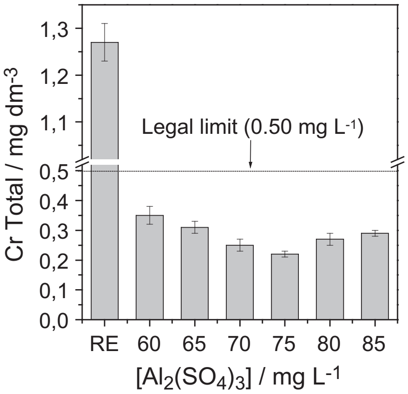

Fig. 4. Cr removal from tannery wastewater samples at different $Al_2(SO_4)_3$ concentrations.

In the next step, the optimization of the natural polyelectrolyte dosage was studied using the optimum pH and optimum coagulant concentration determined previously. The natural polyelectrolyte dosage in the range of 1.0–1.4 mg dm^{-3}, at intervals of 0.1 mg dm^{-3},

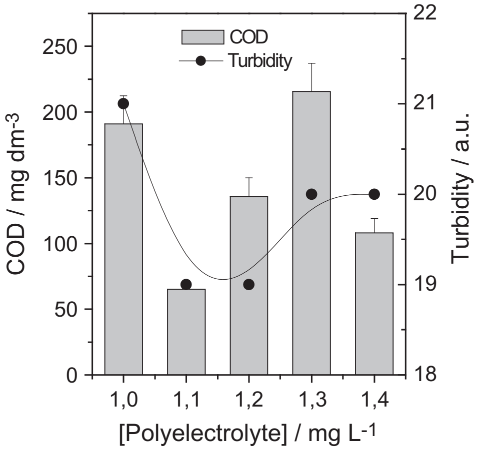

Fig. 5. COD removal and turbidity from tannery wastewater samples after treatment with optimal $Al_2(SO_4)_3$ concentration, with different natural polyelectrolyte concentrations.

was added to the jar tests and the results are shown in Fig. 5.

It can be seen that COD removal is most effective at 1.1 mg dm^{-3} of the natural polyelectrolyte added and higher concentrations did not improve efficiency. From Fig. 5, it can be observed that the residual COD is reduced to approximately 65 mg dm^{-3} giving an overall removal of ~90% compared to the raw effluent, which gives an increase of 13% compared to the use of Al salts by themselves.

The improved results obtained for the polyelectrolyte are due to the fact that the positively charged metal ion forms a bridge between the anionic polyelectrolyte and the negatively charged functional groups on the colloidal particle surface [17] and, due to its long molecular chain, the extremities of the molecule interact with other colloidal particles until neutrality is obtained [21], forming a dense net, which then settles. The addition of the polyelectrolyte at other Al salt concentrations did not result in any great difference to the quantity of Cr removed.

3.2. Coagulation with $FeCl_3$

Ferric salts are widely used as coagulants and phosphate removing agents, being added directly to the effluent. Fe^{3+} ions hydrolyze rapidly, producing a number of Fe^{3+} species [37,38]. However, a major problem is to control the species formed after dissolution in water [40,41].

To optimize the pH of the coagulation process, the jar test was performed over the pH range of 4.0–8.0, as for the use of Al salts, and the degree of turbidity removal was used as the appropriate figure of merit (Fig. 6). It can be seen that turbidity removal is most effective at pH values between 4.5 and 5.0. As a result, all the subsequent investigations were performed at pH 5 because the raw effluent was already slightly alkaline, and therefore the addition of smaller quantities of acid was necessary to reach this pH value. Subsequently, the optimum dosage of ferric chloride was studied with additions of 150–250 mg dm^{-3} $FeCl_3$.

With the variation of the $FeCl_3$ concentration, collision restabilization was not observed (as occurs in the case of aluminum sulfate) and as a result, the removal of COD is proportional to the increase in $FeCl_3$. Using this result, the coagulation study was performed in terms of different $FeCl_3$ concentrations while maintaining the concentration of the polyelectrolyte constant. Figs. 7 and 8 show the removal of COD and the total Cr concentration after treatment with $FeCl_3$, respectively.

It can be seen from Fig. 7 that COD removal is most effective at a dosage of 250 mg dm^{-3} reaching at this point a steady state, and thus dosages above this value do not result in any increase in removal of COD . The COD of the raw effluent was 614.4 mg dm^{-3} and when the optimum concentration of $FeCl_3$ was added, COD decreased to 51.82 mg dm^{-3}, so the removal efficiency was approximately 91.5%, which was more efficient than that seen for the use of aluminum salts. These results are comparable with those of Garrote et al. [15], where COD removals in the range of 84–86% were obtained using only $FeCl_3$. Compared with aluminum sulfate, ferric chloride presented a greater velocity of flocculation and settlement.

From Fig. 8, it can be seen that Cr removal is effective in the $FeCl_3$ concentration range of 150–250 mg dm^{-3}

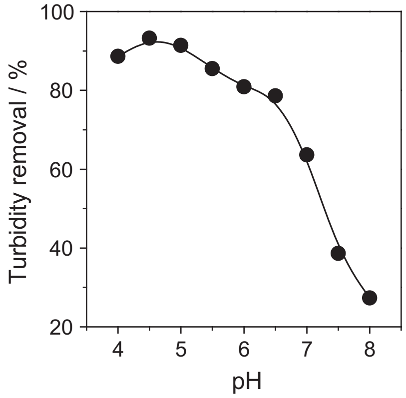

Fig. 6. Turbidity removal from tannery wastewater samples using $FeCl_3$ at different pH.

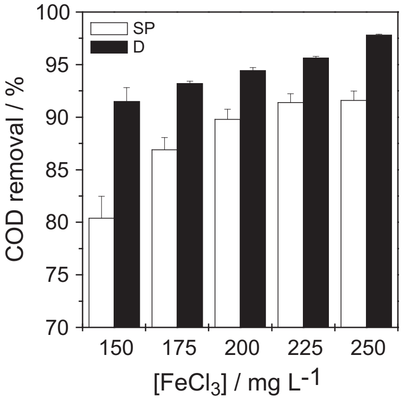

Fig. 7. COD removal from tannery wastewater samples using different concentrations of $FeCl_3$ with and without the addition of the natural polyelectrolyte.

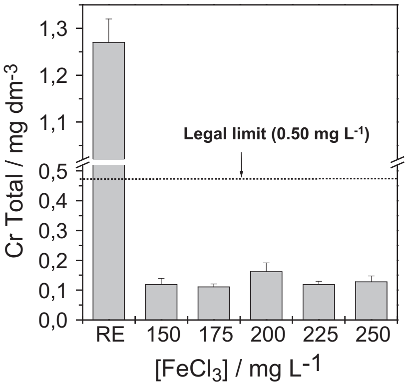

Fig. 8. Total Cr removal of tannery wastewater samples at different $FeCl_3$ concentrations.

and in all cases, the total Cr concentration achieved was below that of the permitted value for effluent discharge (0.50 mg dm^{-3}). The quantity of Cr in the raw effluent was 1.27 mg dm^{-3} and after treatment with $FeCl_3$ in conjunction with the natural polyelectrolyte, the residual Cr was 0.13 mg dm^{-3}, where the Cr removal was 91.2%.

In the coagulation with $FeCl_3$, the analysis was also carried out by the addition of the natural polyelectrolyte. The studies of the optimization of the dosage of the natural polyelectrolyte (as seen previously for Al salts) demonstrated that the optimum dosage was again obtained at 1.1 mg dm^{-3}, and this concentration was subsequently used for the tests. It was observed that with the addition of the natural polyelectrolyte, residual COD decreased to 13.67 mg dm^{-3}, a removal of 97.7% of COD from the raw effluent.

4. Conclusions

The treatment by coagulation/flocculation using $Al_2(SO_4)_3.18H_2O$ and $FeCl_3$ presents promising results for COD and turbidity removal. These results are improved when traditional coagulants are used in conjunction with the natural polyelectrolyte.

Despite the fact that aluminum presents reasonable results, it is a toxic metal and its use as a coagulant can be harmful to the environment. Ferric chloride does not present the same level of toxicity as aluminum sulfate, making it a more attractive coagulant. In all cases, the level of total Cr is reduced below that permitted by the Brazilian legislation.

It should be noted that, during wastewater treatment, pH values and coagulant concentrations need to be monitored, as there exists a strong dependence between these parameters and coagulation efficiency.

The use of this type of treatment is dependent on the characteristics of the industrial activity involved.

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