Prickly pear, potential adsorbent of copper (Cu^{2+}), iron (Fe^{3+}) and chromium (Cr^{3+}) from contaminated waters

Tuna, potencial adsorbente de cobre (Cu^{2+}), hierro (Fe^{3+}) y cromo (Cr^{3+}) de aguas contaminadas

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Abstract– The aim of the study was to evaluate the potential of prickly pear cactus cladode (Opuntia ficus) to remove copper (Cu^{2+}), iron (Fe^{3+}) and chromium (Cr^{3+}) from aqueous solutions. Distilled water mixed with Cu^{2+}, Fe^{3+} or Cr^{3+} at initial concentrations of 19.60, 16.60 and 17.85 ppm, respectively, were used as media for testing. The aqueous media were treated with two adsorbents: i) a naturally collected cladode (C$_T$), and ii) a cladode chemically modified with calcium (C$_T$Ca). The results indicate that a greater metal adsorption is obtained with the C$_T$Ca adsorbent. Moreover, 2 hours of contact is enough to remove up to 82.75, 78.36 and 87.84% of Cu^{2+}, Fe^{3+} and Cr^{3+}, respectively, with respect to their initial concentrations. Our results suggest that the prickly pear cactus cladode might be potentially effective as an eco-friendly adsorbent for removing heavy metals from contaminated waters.

Keywords: Heavy metals, contaminated water, adsorption, prickly pear cactus cladode.

Resumen– El objetivo del estudio fue evaluar la capacidad del cladodio de tuna (Opuntia ficus) para la remoción de cobre (Cu^{2+}), hierro (Fe^{3+}) y cromo (Cr^{3+}) de soluciones acuosas. Se utilizaron medios modelo a base de agua destilada, y Cu^{2+}, Fe^{3+} o Cr^{3+} a concentraciones iniciales de 19.60, 16.60 y 17.85 ppm, respectivamente. Los medios se trataron con dos tipos de adsorbentes a base de cladodio de tuna: cladodio natural (C$_T$), y cladodio modificado químicamente con calcio (C$_T$Ca). La mayor adsorción de los metales se obtuvo con el adsorbente C$_T$Ca, indicando los resultados que un tiempo de contacto de 2 horas sería suficiente para remover hasta el 82.75, 78.36 y 87.84% de Cu^{2+}, Fe^{3+} y Cr^{3+}, respectivamente, con respecto a sus concentraciones iniciales. Nuestros resultados sugieren que el cladodio de tuna podría considerarse como un potencial adsorbente para la remoción eco-amigable de estos metales de aguas contaminadas.

Palabras clave: Metales pesados, aguas contaminadas, adsorción, cladodio de tuna.

I. Introduction

Current environmental legislation establishes that industrial effluents must be treated before being released into the water, soil and/or air, since of them contain toxic substances that adversely affect the functioning of ecosystems. Heavy metals are some of the most toxic pollutants present in industrial effluents [1].

Resolution 023-2016-OEFA/TFA-SEM of the Peruvian Ministry of the Environment (MINAM, for its acronym in Spanish) refers to heavy metals as dangerous environmental pollutants due to their non-biodegradability and accumulation risk [1]. Since most heavy metals have no known metabolic functions in living organisms, they cannot be degraded or removed easily, affecting the biodiversity of soils, rivers and lakes, and in many cases, killing living organisms present in those ecosystems [2,3].

Heavy metals can be transported into bodies of water, filtered through the soil, reach drinking water sources or crops, and ultimately be incorporated into the food chain and affect human beings with severe health consequences. In fact, high concentrations of heavy metals cause diseases such as skin rashes, nose bleeds, respiratory problems, suppressed immune systems, liver diseases, asthma, anemia, skin lesions, diabetes, neurotoxicity, nephrotoxicity, cardiovascular diseases, osteoporosis, and cancer, among others [2,3,4].

A. Metal contamination in Peru

Several Peruvian industries including mining, textile, paint and electroplating are prone to dumping effluents with high concentrations of metals such as copper (Cu), iron (Fe), chromium (Cr), lead (Pb) and arsenic (As) into sewerage systems and water basins [5], in many cases surpassing the maximum limits permitted by current legislation [6].

In fact, one case of heavy metal pollution is taking place in the La Libertad region in northern Peru, in which the mining and leather tanning industries are dumping wastewater that was not previously treated. In addition, high levels of metal pollution have been reported in the Moche river, which is Trujillo's (capital city of La Libertad) most important and closest river. As a consequence, the surrounding populations that use the water to irrigate their crops or raise animals for meat and milk, have been seriously affected [5].

B. Treatment of heavy metal contaminated water

Traditional treatments of industrial effluents are based on physical processes, ion exchange chemical treatments, precipitation and coagulation, among others [7]. However, these processes require technological investment that, in many cases, make them economically unfeasible [2].

Within the ion exchange process, a dissolved metal (adsorbate) is retained in a solid support (adsorbent), typically resin, which establishes the adsorbate-adsorbent balance, that ultimately allows for the removal of metal ions from the polluted medium. For instance, the application of sulfonated polystyrene-based resins to remove Cr^{6+} at rates of up to 98% [8]. However, one of its disadvantages is related to the use of potentially polluting materials such as polystyrene for the synthesis of sulfonated resins. Polystyrene generates environmental problems related to its high persistence in the environment due to its resistance to biodegradation [9].

Another treatment, commonly used for tannery effluents, is chemical precipitation with NaOH or $Ca(OH)_2$, which can remove up to 82% of metals [10]. Despite its effectiveness, the process produces huge amounts of sludge that must also be treated before final disposal. For example, after calcination at 250 °C, and subsequent H_2SO_4 leaching, the process becomes costly due to its high energy consumption [11].

C. Agro-industrial waste for metal removal

Peru generates considerable amounts of agro-residues that are not properly utilized, including fruit and vegetable skins, cereal residues and agricultural biomass, among others. In this regard, several studies have proposed the use of agricultural waste products as adsorbents to remove metals from polluted water [2,12-15]. These proposals rely on the chemical adsorption phenomenon, taking advantage of the interaction between the metal ions and the polymers constituting these wastes.

Among the polymers that have the ability to adsorb metal ions are pectin and lignin, present in a wide variety of plant biomasses. Both polymers contain hydroxyl (OH), carbonyl (CO), and carboxyl (COOH) groups, which are able to fix metal ions [15,16].

In addition, the insulation of pectin has been demonstrated to be an interesting alternative for removing metals. For instance, pectin from orange peel has been used to remove effluents containing Fe in Peruvian mines, removing up to 54% of metals [17], in a process that is directly related with -COOH groups of pectin, such as metal chelators. Nevertheless, this procedure is costly as it involves the extraction and purification of pectin.

D. Prickly pear or tuna (Opuntia ficus): potential adsorbent of heavy metals

The prickly pear or nopal cactus (*Opuntia ficus*) is a vegetal biomass with high polymer content and the potential to remove metals from polluted waters [18,19]. In Peru, it is mainly used to produce the fruit that grows on the cladodes and as a host for the breeding of cochineal (*Dactylopius coccus*), and to a lesser extent as fodder for livestock [19]. This plant grows wild in different areas of the coast and the Andes and has not yet been massively exploited for industrial purposes.

In this regard, some studies have reported the usefulness of prickly pear cactus cladode extracts as flocculants during water clarification, and as adsorbents of metals in contaminated waters [19,20]. Its adsorption mechanism is related to the presence of polymers in the cladode mucilage, whose main components are arabinose, galactose, rhamnose, xylose, galacturonic acid, and specially, pectin [21]. However, as in other cases, the main disadvantage of this alternative is the high cost involved in obtaining and purifying the extracts, which contain high concentrations of polymers, in particular, pectin [18,19].

On the other hand, previous studies have reported that it is possible to improve the adsorption capacity of biomasses used as metal adsorbents by applying chemical treatments, such as the incorporation of calcium ions (Ca^{2+}) [22]. The improvement in adsorption capacity might be related to the ion exchange between the incorporated Ca^{2+} ions and the dissolved metals in the contaminated water.

In this context, the aim of the study was to evaluate the ability of prickly pear cactus cladode to remove copper (Cr^{2+}), iron (Fe^{3+}) and chromium (Cr^{3+}) from polluted waters, considering its low cost and high availability in Peru, as well as to evaluate whether Ca^{2+} chemically modified cladodes (C_TCa) improve metal adsorption capacity when compared to naturally collected cladodes (C_T).

II. MATERIALS Y METHODS

The adopted methodology for the experimental tests is based on the procedures of the references presented in the corresponding sections. The study was carried out in the Laboratory of Instrumental Analysis of the Engineering Faculty of *Universidad Privada del Norte* (Trujillo city).

A. Preparation of adsorbents based on prickly pear cactus cladode

First, the cladodes were washed in order to remove impurities, and cut into 1 cm x 1 cm pieces, to be subsequently dried at 60°C for 48 hours. The dried biomass was divided into two portions and treated following the methodology shown in Figure 1. This was done to obtain two types of adsorbents:
- **C_T**: Cladode without chemical treatment.
- **C_TCa**: Ca^{2+} chemically modified cladode.

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Biomass
(1 cm x 1 cm)

↓

Drying
(60 °C / 48 hours)

↓

Milling and sieving
(300 μm) → Demethoxylation
Biomass : NaOH 0.2M

↓

Ca²⁺ cross-linking
Biomass : CaCl₂ 0.2M

↓

Drying
60 °C / 48 hours

↓

Milling and sieving
(300 μm)

Cladode without
chemical treatment

C_T

Ca²⁺ chemically
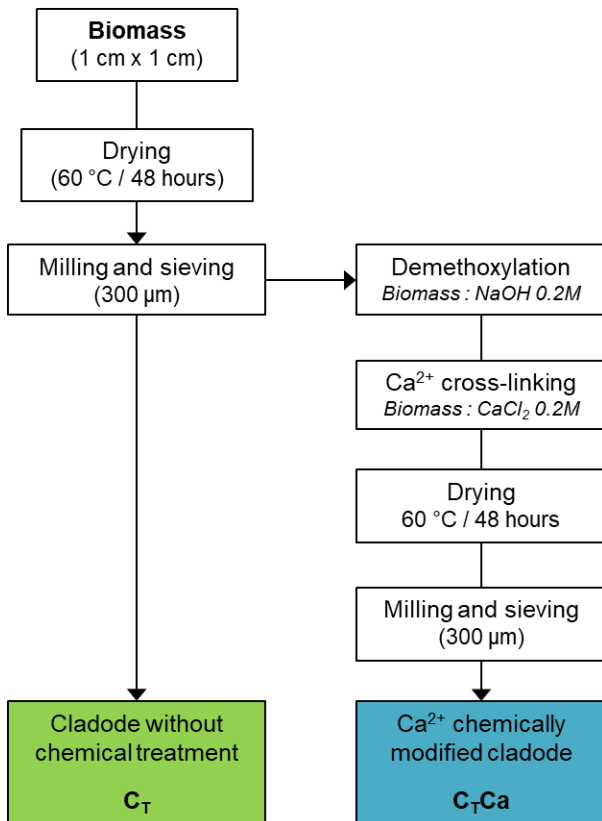modified cladode

C_TCa

Fig. 1 Applied treatments to get two different adsorbents: i) natural collected cladode (C_T) and chemically modified cladode incorporating Ca^{2+} (C_TCa).

A factorial design was applied (Table 1), in which the residual concentration of Cu^{2+}, Fe^{3+} or Cr^{3+} (or its equivalent in removal percentage) is the dependent variable, while the type of biomass and the contact time were treated as independent variables, working in triplicate in each trial. Figure 1 summarizes the experimental procedure.

TABLE 1
EXPERIMENTAL DESIGN APPLIED FOR EACH METAL

Treatment time	Adsorbent	
(hours)	C_T	C_TCa
	Y_{111}	Y_{211}
2	Y_{112}	Y_{212}
	Y_{113}	Y_{213}
	Y_{121}	Y_{221}
4	Y_{122}	Y_{222}
	Y_{123}	Y_{223}

B. Experimental tests

The samples were based on $Fe(NO_3)_3$, $Cu(NO_3)_2$ and $Cr(NO_3)_3$ (Merck Millipore, Germany) in distilled water. Hence, 100 mL of each aqueous medium was taken, and 1.0 g of the corresponding adsorbent was added to each medium. The samples were stirred at 250 rpm, at room temperature, with contact times of 2 and 4 hours, as shown in Table 1.
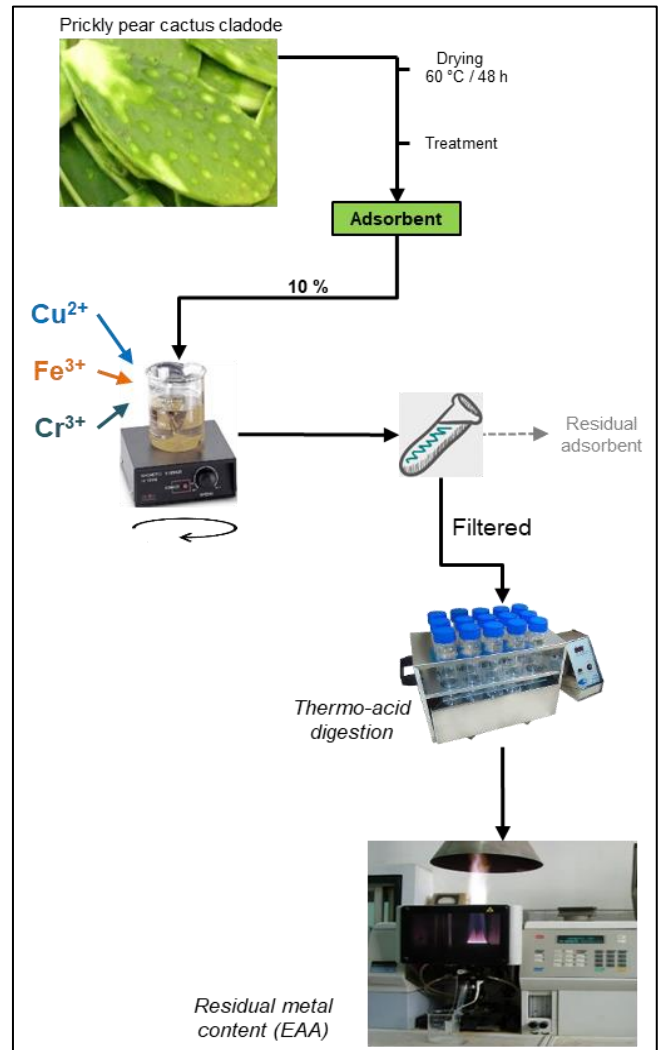

Fig. 2 Experimental procedure for the removal of Cu^{2+}, Fe^{3+} and Cr^{3+} from contaminated waters.

C. Digestion of the samples and analysis of the residual metal content

The samples obtained after treatment were filtered and subjected to thermo-acid digestion, following the procedure proposed by Campos-Flores et al. [14]. To this purpose, 25 mL of each sample were taken, and 2 mL of HNO_3 and 1 mL of HCl were added. Digestion at 120 °C in a digester Digi Prep Jr (SCP Science, Canada) was carried out, evaporating half of the content. Then the temperature was increased to 140 °C to evaporate to final volume of 5 mL. We let the samples cool and added 0.5 mL of HCl to each, diluting them with ultrapure water to 50 mL.

The metal content was analyzed using Atomic Absorption Spectrophotometry (Spectrophotometer Agilent Technologies 200 Series AA, United States), at wavelengths of 248.3, 324.8, and 357.9 nm for Fe, Cu, Cr, respectively.

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D. Removal of Cu^{2+}, Fe^{3+} and Cr^{3+} using biomass of prickly pear cactus cladode

The percentage of each metal adsorbed by the respective adsorbent was determined by [2]:

$$Removal\ (\%) = \frac{(Co-C)}{Co}\ x\ 100 \qquad (1)$$

Where Co is the initial concentration of each metal (mg/L or ppm), and C is the metal residual concentration (mg/L or ppm) after being treated with the respective adsorbent.

E. Statistical analysis

An Analysis of Variance (ANOVA) was employed to identify significant differences, whereas Tukey's HSD test (5% significance) was used to identify treatments with the greatest effect on each type of adsorbent at each contact time. The IBM SPSS Statistics 24.0 (IBM Corp., Armonk, United States) software was used in the statistical analysis.

III. RESULTS Y DISCUSSION

A. Effect of the biomass on the pH samples

Initially, the solutions presented pH values of around 2.0 (high acidity media), which are lower than 5.5, which is the minimum value required by current legislation in Peru (DS N° 004-2017-MINAM of the Peruvian Ministry of the Environment) [6]. As shown in Table 2, after applying the adsorbents C_T and C_TCa, the acidity of the media decreased, characterized by the increase of pH, with a greater effect in the C_TCa adsorbent.

TABLE 2
MEDIA pH BEFORE AND AFTER APPLYING THE NATURAL CLADODE (C_T) AND Ca^{2+} MODIFIED CLADODE (C_TCA) ADSORBENTS

Metal	Treatment time	C_T	C_TCa
Cu^{2+}	Initial	1.99 ± 0.00 aA	1.99 ± 0.00 aA
	2 hours	2.81 ± 0.01 bA	5.06 ± 0.04 bB
	4 hours	2.79 ± 0.01 bA	5.31 ± 0.03 cB
Fe^{3+}	Initial	2.09 ± 0.00 aA	2.09 ± 0.00 aA
	2 hours	2.85 ± 0.01 bA	5.57 ± 0.01 bB
	4 hours	2.83 ± 0.01 bA	6.01 ± 0.03 cB
Cr^{3+}	Initial	2.03 ± 0.00 aA	2.03 ± 0.00 aA
	2 hours	3.17 ± 0.00 bA	5.64 ± 0.04 bB
	4 hours	3.21 ± 0.01 cA	5.72 ± 0.00 cB

Results represent mean ± SD for three replicates. For each metal, different small letters in the same column indicate significant differences between different treatment times. Different capital letters in the same row indicate significant differences between adsorbents (DSH Tukey's test, p < 0.05).

B. Residual content of Cu^{2+}, Fe^{3+} and Cr^{3+}

Table 3 shows the residual concentrations of Cu^{2+}, Fe^{3+} and Cr^{3+}. The statistical analysis (Tukey's DSH, p<0.05) suggested that there are no significant differences between the treatment times of both adsorbents. This indicates that 2 hours of treatment is enough to reduce the metallic content, since the adsorbent reaches its maximum adsorption capacity due to the saturation of the pectin -COOH groups. The latter act as chelating agents for metal ions [17,21,23,24], leading to the equilibrium of the adsorbent-adsorbate system [25], i.e, from that moment on the adsorbent is no longer able to adsorb more metal ions.

Concerning the type of adsorbent, significant differences were observed between the C_T and C_TCa adsorbents as shown in Table 3. For Cu^{2+} (initial concentration of 19.6 ppm), after 2 hours of treatment, the residual content was 3.38 ppm with the C_TCa adsorbent, while for the C_T adsorbent, the concentration was only reduced to 15.22 ppm. That is, at the same dose, the C_TCa biomass adsorbs a greater amount of metal ions in the same treatment time (2 hours). Note that similar behavior is observed after 4 hours of treatment. Concerning Fe^{3+} (initial concentration of 16.6 ppm), a similar behavior at both treatment times was observed.

TABLE 3
RESIDUAL CONCENTRATION OF METALS (ppm) AFTER TREATMENTS

Metal	Treatment time	Metal residual content (ppm)	
		C_T	C_TCa
Cu^{2+}	Initial	19.60 ± 0.00 aA	19.60 ± 0.00 aA
	2 hours	15.22 ± 0.11 bA	3.38 ± 0.25 bB
	4 hours	15.69 ± 0.25 bA	3.70 ± 0.12 bB
Fe^{3+}	Initial	16.60 ± 0.00 aA	16.60 ± 0.00 aA
	2 hours	12.07 ± 0.15 bA	3.59 ± 0.55 bB
	4 hours	12.38 ± 0.35 bA	3.35 ± 0.36 bB
Cr^{3+}	Initial	17.85 ± 0.00 aA	17.85 ± 0.00 aA
	2 hours	5.05 ± 0.15 bA	2.17 ± 0.12 bB
	4 hours	5.23 ± 0.23 bA	1.71 ± 0.25 bB

Results represent mean ± SD for three replicates. For each metal, different small letters in the same column indicate significant differences between different treatment times. Different capital letters in the same row indicate significant differences between adsorbents (DSH Tukey's test, p < 0.05).

The medium containing Cr^{3+} presented higher adsorption of metal ions when compared to the other two metals. The Cr^{3+} residual content was 5.05 and 2.17 ppm for adsorbents C_T and C_TCa, respectively, after 2 hours of treatment (initial concentration of 17.85 ppm). No further removal was found at higher treatment times (4 hours), which is in accordance with the statistical analysis (Tukey's HSD, p < 0.05).

These results indicate that the cladode adsorbent possesses a higher adsorption capacity for Cr^{3+} with respect to Cu^{2+} and Fe^{3+} ions. This rate is even greater for C_TCa, which might be

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related to the incorporation of Ca^{2+}, as found in previous studies [22].

In fact, for C_TCa adorbent, the adsorption process is achieved due to the ion exchange between Ca^{2+} and the Cu^{2+}, Fe^{3+} and Cr^{3+} ions. This mechanism is schematically shown in Figure 3. The process includes two stages: a quick migration from the metal ion (M^+) towards the biomass surface, followed by a slower migration toward the active site of the Ca^{2+} ion, displacing it until it reaches equilibrium in both phases [22]. This provokes the trapping of metal ions in a three-dimensional network formed by the biomass' polymers, and as a consequence the adsorbent is immobilized.
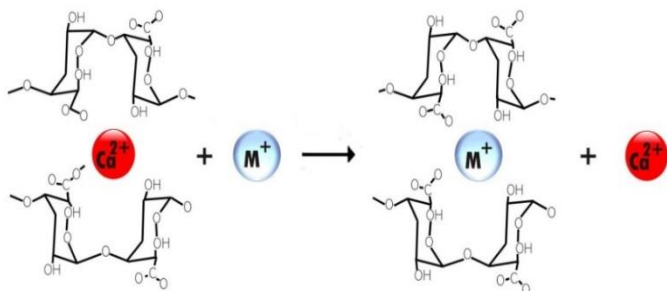

Fig. 3 Ion exchange mechanism between modified Ca^{2+} cladode (C_TCa) and metal ions (M^+) in the medium.

The chemical modification of the prickly pear cactus cladode occurs at the level of the pectin, improving its Cu^{2+}, Fe^{3+} and Cr^{3+} adsorption capacity at rates up to 82.75%, 78.36% and 87.84%, respectively, for 2 hours treatment time, not showing further reduction at greater time (Fig. 4). Regarding Cu^{2+}, a previous study showed similar removal potential after 2 hours of treatment with the cladode modified with Ca^{2+}, reducing the Cu^{2+} content from 19.2 ppm to 3.5 ppm in the medium [26]. However, the aforementioned study used a pH of 4.5 with a treatment time of 24 hours.

Another study has reported successful removal of Cu^{2+}, Cr^{3+} and other metals by isolating pectin from prickly pear cactus cladode [20], which allows for the removal of up to 99 and 98%, respectively. Despite the high efficiency for metal removal, this process is costly, as it requires the use of chemical reagents and heat to achieve the isolation and purification of the pectin.

So far, the removal of Cr^{3+} by using adsorbents based on chemically modified cladodes has not been reported, although, the Cr^{6+} removal has been addressed by modifying the prickly pear cactus with H_2SO_4 [27]. This procedure enabled the removal of up to 68 and 40% of Cr^{6+} in solutions at 10 and 30 ppm (pH = 2.0), respectively. Moreover, to the best of our knowledge, adsorbents based on Ca^{2+} chemically modified cladodes for the removal of Fe^{3+} have not been explored.
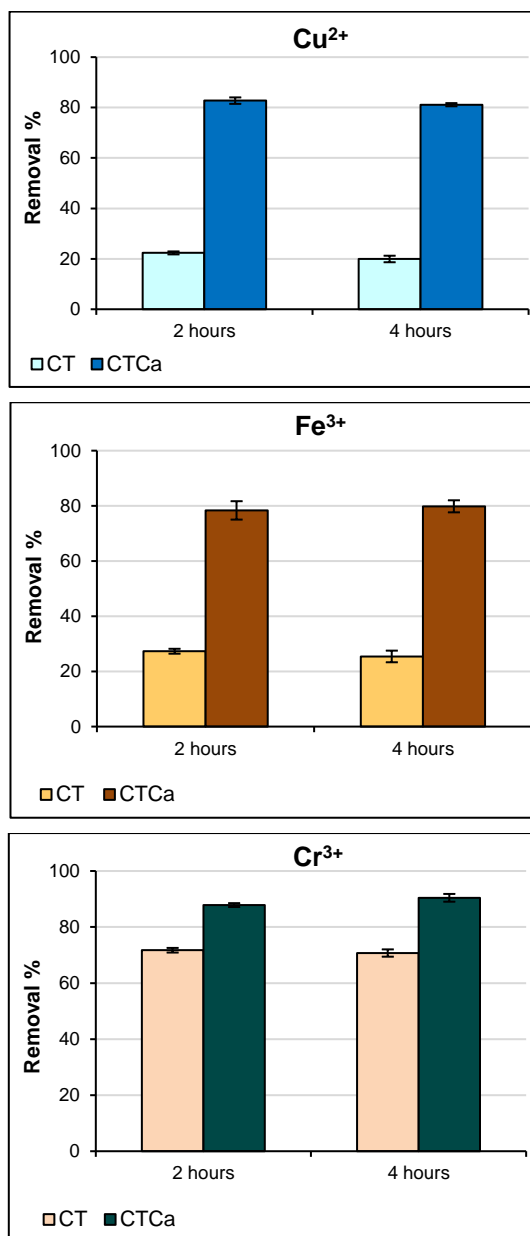

Fig. 4 Removal percentage (%) of Cu^{2+}, Fe^{3+} and Cr^{3+} after treatments with natural cladode (C_T) and Ca^{2+} modified cladode (C_TCa), for times of 2 and 4 hours.

It is worth mentioning that the recurrent problems associated with inadequate control of the dumping of metals in Peruvian river basins is a threat to natural environments. For instance, in the Moche river basin (Region of La Libertad) [5] high levels of metals in various crop fields have been identified. Indeed, the ingestion of agricultural products with high levels of these metals could lead to their accumulation, eventually reaching levels toxic to the body. Furthermore, up to 11.0 ppm of Fe in the Moche river high basin has been found [5], while 9.3 ppm of Cu in the lower basin has been reported [28]. The latter finding is alarming considering that on average 5.0 ppm of Cu is lethal for some fish after only 48 hours of exposure [5]. As a matter of fact, when Cu is combined with other more

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dangerous metals, like arsenic (As) for instance, serious consequences for human health arise [4]. In this sense, the results obtained in this study are interesting alternatives for treating effluents with heavy metals, as metal reductions above 75%, with respect to the initial concentrations, can be achieved (Fig. 4).

Regarding the Cr, levels above 100 ppm have been reported in tannery effluents in several Peruvian cities, in which a significant number of fur tanning companies are concentrated, on many occasions, effluents have been dumped directly into the sewage network [29], which seriously threatens both the environment and human health.

IV. Conclusions

The effectiveness of prickly pear cactus cladode as a potential adsorbent of Cu^{2+}, Fe^{3+} and Cr^{3+} was evaluated. The results indicated that after 2 hours of treatment, the concentration of metals in the tested media can be reduced by more than 75%. The greatest removal potential was reached with the Ca^{2+} modified cladode (C_TCa). Overall, adsorption by prickly pear cactus cladode is a potential alternative to conventional methods of metal removal in contaminated waters. Hence, it can be employed as an effective, easy to use and environmentally friendly technology. Further studies are needed in order to determine optimal adsorption parameters, for instance, the application of Langmuir's models (maximum capacity of adsorption, q_{max}) and the Freundlich model (capacity k and intensity n of adsorption). Moreover, the evaluation of the effectiveness of the prickly pear cactus cladode for the removal of Cu^{2+}, Fe^{3+} and Cr^{3+} in industrial effluents, such as those produced by mining and tanning industries is needed. Lastly, the development of a metal removal procedure with scalable features at the industrial level should be also addressed.

Acknowledgment

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