

1 Use of vinasse and coffee waste as chelating agent of photo-Fenton landfill  
2 leachate treatment

3 Rodrigo Poblete<sup>a</sup>, Ernesto Cortes<sup>a</sup>, Norma Pérez<sup>a</sup>, Manuel I. Maldonado<sup>b,c</sup>.

4 <sup>a</sup> Universidad Católica del Norte, Facultad de Ciencias del Mar, Escuela de  
5 Prevención de Riesgos y Medioambiente, 1780000 Coquimbo, Chile.

6 <sup>b</sup> Plataforma Solar de Almería (CIEMAT), 04200 Tabernas, Almería, Spain.

7 <sup>c</sup> CIESOL, Joint Centre University of Almería-CIEMAT, 04120 Almería, Spain.

8 Abstract

9 One of the most interesting methods to treat landfill leachate (LL) is the photo-Fenton  
10 process; however, a disadvantage is that it is necessary that this is carried out with  
11 a solution close to 2.9, being necessary to adjust the pH of the LL, increasing the  
12 operational costs of the process. In this research, the use of different concentrations  
13 of vinasse (VS) coming from pisco and caffeic acid (Caa) from solid coffee waste as  
14 chelating agents of this process, carried out at the natural pH of the landfill leachate  
15 (8.9) was studied. As control, photo-Fenton runs at pH 3, 6 and 8.9 were carried out,  
16 without the adding of the studied chelate.

17 Without the chelating agent, there was a removal of humic acid and COD of 54.2%  
18 and 54.7%, respectively, when the photo-Fenton reaction was carried out at pH 3,  
19 at pH 6 the removal was 13.1% and 39.2% of humic acid and COD, respectively,  
20 and at pH 8.9, the elimination was 10.8% and 16.1% of humic acid and COD,  
21 respectively. When caffeic acid (Caa) was used in the LL in the photocatalytic  
22 processes carried out at pH 8.9, a removal of 24.1%, 43.0% and 47.4% of humic  
23 acid was obtained using 5 mg/L, 50 mg/L and 100 mg/L of Caa.

24 Photo-Fenton process at pH 8.9 using VS, was higher than the obtained at this pH  
25 without using VS but a bit lower than the obtained using Caa. The removal of humic  
26 acid was 27.3%, 30.7% and 36.3% using 5 mg/L, 50 mg/L and 100 mg/L of VS  
27 respectively, and the removal of COD was 32.2%, 35.4% and 39.2% using 5 mg/L,  
28 50 mg/L and 100 mg/L of VS, respectively.

29 Without the chelating agent, the concentration of total Fe in photo-Fenton process  
30 was higher than when it was carried out at pH 3, going from 55.2 mg/L to 49.8 mg/L  
31 after 60 minutes of treatment. In the case of the reaction realized at pH 6 and 8.9, it  
32 changed from 30.4 mg/L to 30.1 mg/L and from 33.8 mg/L to 31.0 mg/L, respectively,  
33 being lower than the get at pH 3, due at the low solubility of Fe at higher pH. When  
34 Caa was used in the LL at pH 8.9 the concentration of total Fe went from 37.5 to  
35 33.2, from 40.2 to 36.8 and from 45.2 to 42.1, using 5 mg/L, 50 mg/L and 100 mg/L  
36 of caffeic acid, respectively. Using VS in the LL at pH 8.9 the concentration of total  
37 Fe along the run went from 35.1 to 32.2, from 39.4 to 34.8 and from 42.1 to 40.2,

38 using 5 mg/L, 50 mg/L and 100 mg/L of VS. Therefore the use of Caa and VS  
39 increase the solubility of Fe at higher pH.

40 The specific energy consumption (SEC) of the photocatalytic processes, considering  
41 the removal of COD, carried out at pH 3 was lower (0.0052 Wh/mg), being higher at  
42 the process carried out at pH 8.9 that used VS in a concentration of 50 mg/L (0.0061  
43 Wh/mg) and being highest at the process carried out at pH 8.9 when Caa was used  
44 at 5 mg/L (0.0064 Wh/mg).

45

46

47 Keywords: Leachate; Chelating agents; Vinasse; Caffeic acid; Wastes; Photo-  
48 Fenton.

49

## 50 Highlights

51 -Vinasse and solid coffee waste have shown high capacity to be used as chelating  
52 agents in photo-Fenton process.

53 -Chelating agents reduce the operational cost of the treatment of the landfill  
54 leachate with photo-Fenton.

55 -There was a relation between the concentration of iron and the removal of organic  
56 matter.

57

## 58 1. Introduction

59 Landfill is the most common method to dispose municipal solid waste, and allows  
60 waste to decompose and degrade until transformation into stabilized material (Gupta  
61 et al. 2014). The percolation of water through the landfill layers and waste  
62 decomposition produces landfill leachate (Puig et al. 2011). The oldest landfill  
63 leachate (LL) effluents were characterized by high toxicity, low biodegradability and  
64 elevated concentrations of organic matter, such as humic and fulvic acids (Silva et  
65 al. 2016). Under this condition of complexity, the biological treatment is not  
66 completely efficient applied in LL (Havukainen et al. 2017), requiring a process that  
67 allows the oxidation of this kind of wastewater.

68 The advanced oxidation processes (AOPs) are considered a promising treatment to  
69 apply to LL because they were capable to transform recalcitrant and complex  
70 compounds present in the wastewater into more biodegradable substance (Jung et  
71 al. 2017). Photo-Fenton process is an AOP and also one of the most interesting  
72 alternative process for the treatment of complex wastewater, due to its feasible and  
73 simple application (Arzate et al. 2017; Giannakis et al. 2016).

74 The classical reaction is very effective in degrading complex organic pollutants into  
75 harmless compounds, low molecular weight organic acids and even CO<sub>2</sub> and water,  
76 reducing the effluent toxicity of the wastewater (ElShafei et al. 2010).

77 This photocatalytic process based on the photo activity of the ferric species that  
78 enhanced the Fenton reaction, lead to the formation of hydroxyl radicals when iron  
79 ions react with H<sub>2</sub>O<sub>2</sub> (Eqs. 1 and 2).



82 However, one of the disadvantages of this process is the low solubility of the ferric  
83 species at neutral or high pH, requiring the adjustment of the pH of the solution to  
84 near 3, and subsequently, the neutralization after treatment, increasing the  
85 operational cost (Pignatello et al. 2006), salinity of the solution, and sludge  
86 generation (Lipczynska-Kochany and Kochany 2008), limiting the full scale  
87 application in industrial wastewater process (Giannakis et al. 2016). Additionally, the  
88 acidification process might produce the emissions of some gases into the  
89 atmosphere containing cyanides or sulphides (Lipczynska-Kochany and Kochany  
90 2008).

91 At high pH, Fe(III) would precipitate into the reactor and exist as insoluble  
92 complexes, hydrous oxyhydroxides (Fe<sub>2</sub>O<sub>3</sub>·nH<sub>2</sub>O), which cannot be reduced to  
93 dissolved Fe(II), ceasing the Fenton reactions (Zhang and Zhou 2019). This  
94 behaviour strongly reduces the efficiency of photo-Fenton at neutral or high pH  
95 (Nahim-Granados et al. 2019).

96  
97 Chelating agents are substances with numerous coordinating sites that have the  
98 capacity to form bonds with metal ions, being possible to be used at high pH to form  
99 soluble complexes with Fe(II)/Fe(III), allowing the production of oxidative species by  
100 the reaction of Fe(II)/Fe(III) and H<sub>2</sub>O<sub>2</sub> (Lipczynska-Kochany and Kochany 2008).  
101 This behaviour also may promote steric effect on iron, enhancing the efficiency of  
102 binding to target molecules and hydroperoxide (Chevion 1988).

103 Chelating agents, **even when commonly used, must have** suitable functional groups,  
104 from which atoms can donate a pair of electrons to a metal atom to produce the  
105 formation of a ring with the metal atom and the functional groups (Ruíz-Delgado et  
106 al. 2019).

107 The stability of a complex, that depends on the equilibrium for its formation in the  
108 solution, is related with the strength of the interaction between chelating agents and  
109 metal ions along the reaction time. The stability of the complex depends on the acid  
110 ionization constant (pKa) of the ligand, the substituents, the characteristics of the  
111 donor atoms, the central metal atom, and the number and ring size of the complex  
112 (Somasundaran and Nagaraj 1984). Based on previous reports, the pH dependence

113 can be minimized by the formation of ferric organocomplexes (Miralles-Cuevas et al.  
114 2014).

115

116 Several organic compounds have been tested as ligands for ferric complexes, to be  
117 used in the photo-Fenton process. For instance, ions of  $Fe^{3+}$  form stable complexes  
118 with ligands such as carboxylic acids and amino-polycarboxylic acids, in a wide  
119 range of pH (Zhang and Zhou 2019). Depending on the ligand, the complex has  
120 different light absorption properties, for instance carboxylic acids and iron complexed  
121 present high quantum yield (Miralles-Cuevas et al. 2014).

122 Also, the use of photo-Fenton applied in the treatment of wastewater was enhanced  
123 by the addition of organic acids such as tartaric, ascorbic, citric and caffeic acid  
124 (Villegas-Guzman et al. 2017). The increase of iron in solution in the presence of  
125 organic acids can be due to factors such as the chemical and structural properties  
126 of acids. Caffeic acid is a carboxylic acid usually found in coffee beans (Scholz et al.  
127 2016) that can be used as additive in photo-Fenton application and has chelating  
128 activity leading to photo-active complexes (Villegas-Guzman et al. 2017) and  
129 enhancing the production of  $\cdot HO$  (Iwahashi et al. 1990; Iwahashi et al. 1989).

130 Also, phenols have shown a notable chelating activity to transition metallic ions  
131 leading to photo-active complexes and the production of hydroxyl radicals (Villegas-  
132 Guzman et al. 2017). Phenolic and polyphenolic compounds have the capacity to  
133 form very stable complexes with iron at a wide pH range (Masoud et al. 2014),  
134 allowing its availability for photo-Fenton processes. Gallic acid, as polyphenol, is  
135 capable to form complexes with  $Fe^{3+}$  that are capable of participating in its reduction  
136 (Hynes and Coinceanainn 2001).

137 Polyphenolic compounds are present in industrial wastewaters produced from the  
138 processing of natural products, such as olive mills, distillery and wineries among  
139 others (Papoutsakis et al. 2016; Lucas et al. 2009). Polyphenols are also present in  
140 the distillation of pisco, an emblematic alcohol beverage produced in Chile and Perú  
141 (Vázquez-Rowe et al. 2017). In this process, the wastewater generated is called  
142 vinasse and represents the 70% of the distillate liquid (Poblete et al. 2020). [Authors](#)  
143 [considered that vinasse are toxic and which may affect to sensitive organisms such](#)  
144 [as plants, bacteria and animals \(Sousa et al. 2019\), delaying germination or](#)  
145 [inhibiting the vegetative growth of studied plants due the presence of polyphenols](#)  
146 [\(Mosse et al. 2010\) and considered as phytotoxic and antimicrobial \(Moran-Salazar](#)  
147 [et al. 2016\). However also has been used as fertilizer due it is rich in potassium,](#)  
148 [carbon and nitrogen \(Fuess et al. 2017\) can be used in yeast production \(Arslanoğlu](#)  
149 [and Tümen 2021\) and its use stimulates the increase in P of higher soil lability](#)  
150 [\(Oliveira Filho et al. 2021\).](#)

151 [The use of polyphenols coming from vinasse of pisco or caffeic acid obtained from](#)  
152 [solid waste of coffee, in an adequate concentration, could be useful as an additive](#)  
153 [in photo-Fenton process in the treatment of LL, allowing to keep iron in solution at](#)

154 the natural or higher pH of this wastewater, avoiding its acidification. If this  
155 hypothesis works, it would be an interesting alternative to the use of expensive  
156 commercial chelating agents, such as oxalic acid, ethylenediaminetetraacetic acid  
157 and ethylenediamine-N,N'-disuccinic acid, being able to save this cost and promote  
158 circular economy.

159 At our best knowledge, an evaluation of the capacity of caffeic acid and  
160 polyphenols, coming from industrial waste, as chelating agent in the photo-Fenton  
161 processes in order to reduce the toxicity of landfill leachate has not been carried out,  
162 therefore the main goal of this investigation is the evaluation of caffeic acid (Caa)  
163 coming from solid waste of coffee and also polyphenols coming from vinasse (VS)  
164 obtained from the production of Chilean pisco, used as chelating agent in photo-  
165 Fenton process in the treatment of landfill leachate at this natural pH.

## 166 2. Materials and methods

167 Runs of photo-Fenton process were carried out using Caa or VS to evaluate these  
168 [substances](#) as chelating agents in the treatment of an old and toxic LL, at pH 6 and  
169 the natural pH of the LL (8.9). Considering that a high load of chelate should be  
170 avoided since the organic content of the solution would dramatically increase, it is  
171 important to restrict the addition of the chelating agent in an adequate concentration  
172 (Ruíz-Delgado et al. 2019), so different concentrations of Caa and VS as a chelating  
173 were tested to determine the adequate amount of that.

### 174 2.1. Experimental design

175 The LL was obtained from 3 different places of a landfill (16.7 ha total area) located  
176 in Coquimbo, Chile, that manages domestic waste. The main characteristics of the  
177 raw LL samples are shown in Table 1. After collection, LL samples were submitted  
178 to a coagulation/flocculation process, stirring for 2 h at 150 rpm, in order to reduce  
179 total solids in the water, through the addition of 1 g/L FeCl<sub>3</sub> (Merck), after which the  
180 supernatant of the coagulated/flocculated was taken. This reagent concentration  
181 was chosen considering prior results from our investigation (Poblete and Painemal  
182 2018). After that, LL samples were filtered using a 5 µm filter and stored in the dark,  
183 at 4 °C to maintain inherent characteristics.

184 The VS was used as source of polyphenols and was obtained from a wastewater  
185 generated in Pisco Capel Company, Coquimbo, Chile. This company produces pisco  
186 through distillation process. The main characteristics of the VS samples are shown  
187 in Table 1.

188 The coffee waste, as source of caffeic acid, was collected from coffee machine  
189 shops in Coquimbo, Chile, which is an abundant and free by-product of food industry  
190 still rich in molecules that could be exploited (Kang et al. 2002)(Kang et al.  
191 2002)(Kang et al. 2002)(Kang et al. 2002)(Kang et al. 2002)(Kang  
192 et al. 2002; Jeszka-Skowron et al. 2016).

193 An ultrasonic method was used to extract the caffeic acid present in solid coffee  
 194 waste (Oniszczyk et al. 2014) using an ultrasound Elmasonic E60 H equipment  
 195 (Germany, 500 W, 37 kHz frequency). 500 g of **dried** coffee waste and 1 L of distilled  
 196 water were placed into the ultrasound reactor that worked during 1 h. After that, the  
 197 supernatant was taken and filtered, using a 5 µm filter and stored in the dark, at 4  
 198 °C. The main characteristics of the Caa samples are shown in Table 1.

199 Table 1. Landfill leachate, caffeic acid and vinasse characteristics

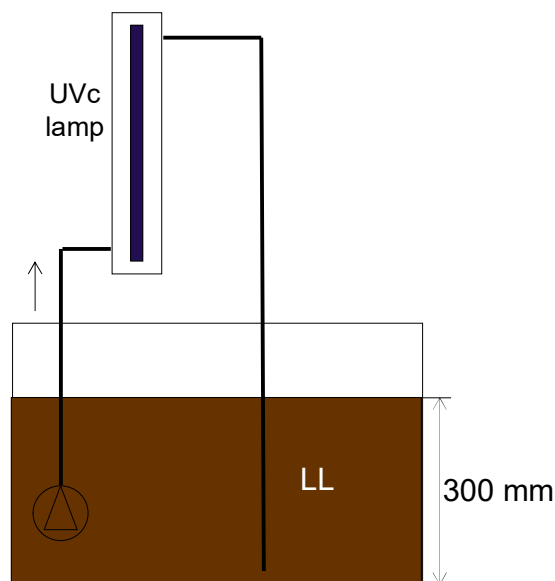
Parameter		LL	Caa	VS
			Value	
COD	mg/L	5,120-5,300	2,800	5,100
pH		8-85-8.96	4.7	3.6
Total solid	mg/L	21,800-22,300	380	940
Conductivity	mS/cm	40.3-42.8	12.5	14.7
Polyphenols	mg/L	-	-	270
<b>Humic acid</b> (ABS <sub>254</sub> )		13.8-15.8	-	-

200

201 The alkaline pH of the **LL** is related with the presence of inorganic pollutant fractions  
 202 such as iron and also with presence of solids that attenuate the light transfer  
 203 capacity, producing a high turbidity of the **solution** (Seibert et al. 2017).

204 The LL was placed in a 5 L useful capacity tank, pumped into the UVc photoreactor  
 205 using a centrifugal submerged pump (30 W of power) and then returned to the tank  
 206 (Fig. 1), producing a recirculation flow rate of approximately 10 L/min. The UV lamp  
 207 (Atman unit) has a power of 36 W with 254 nm wavelength.

208 The initial concentration of Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub> used in the reaction was of 56 ppm and  
 209 1000 ppm, respectively (Poblete et al. 2012), according to the results of our  
 210 investigation group.



211

212 Fig. 1. Schematic diagram of the photocatalytic recirculation system.

213 In order to determine an adequate concentration of the proposed chelating agent,  
214 three different molar ratios were tested for total iron: caffeic acid (1:0.01; 1:0.05;  
215 1:0.1), representing 5 mg/L, 50 mg/L and 100 mg/L of caffeic acid, respectively. Also,  
216 three different molar ratios were tested for total iron: polyphenol (1:2.8\*10<sup>-5</sup>; 1:  
217 2.8\*10<sup>-4</sup>; 1:5.6\*10<sup>-4</sup>), representing 5 mg/L, 50 mg/L and 100 mg/L of polyphenols,  
218 respectively. Higher and lower molar mass ratios were selected as an approach to  
219 find the adequate ratio to form the necessary chelate bond with iron and keeping it  
220 in solution at high pH to avoid adding an excess of organic matter.

221 Also, as a control, runs at pH 3, 6 and the pH of the LL without adjustment (8.9),  
222 without the adding of Caa or VS were carried out, to determine the removal of organic  
223 matter under these conditions.

224 With and without chelating agent, the photocatalytic treatment time lasted 1 h,  
225 samples were taken at the beginning and every 10 minutes and COD, humic acid  
226 and the pH were measured. Also, in order to determine the stability of the metal in  
227 solution at these pHs it was measured the concentration of Total Fe during the  
228 experiment. After, the samples were collected and decanted to allow precipitation of  
229 undissolved metal.

## 230 2.2. Analytical determination

231 Caffeic acid concentrations, obtained from the coffee waste, were determined by a  
232 calibration curve using an Optizen Pop spectrophotometer at 280 nm wavelength  
233 (Chuysinuan et al. 2020), and caffeic acid (≥98.0% of purity) from Merck as reference  
234 standard. The polyphenol content present in VS was determined according to the  
235 Folin-Ciocalteau method, using gallic acid from Merck (97.5% of purity) as a  
236 reference standard (Singleton and Rossi 1965). The concentration of humic acid in  
237 LL (Kang et al. 2002) was measured using a spectrophotometer at 254 nm  
238 (Mecasys, Optizen Pop Series UV/VIS, Korea) because high humic acid  
239 concentrations are an indicator of old LL (Kang et al., 2002). COD concentration in  
240 LL was measured according to the colorimetric method (EPA 410.4 protocol) with a  
241 spectrophotometer Hanna HI83099. To evaluate the effect of the used chelating  
242 agents, the concentration of total dissolved iron during the processes was measured,  
243 filtering 50 mL of solution every 10 minutes, using millipore 0.2 μm membrane filters  
244 (Ruíz-Delgado et al. 2019). Iron was measured according to the EPA phenantroline  
245 method 315B.

## 246 2.3. Energy and economic assessment

247 Considering that an important issue in the AOP are the operation costs of the  
248 process, it is important to determine this parameter. Therefore, the specific energy  
249 consumption (SEC) of the photocatalytic treatment carried out was determined using  
250 Eq. 3:

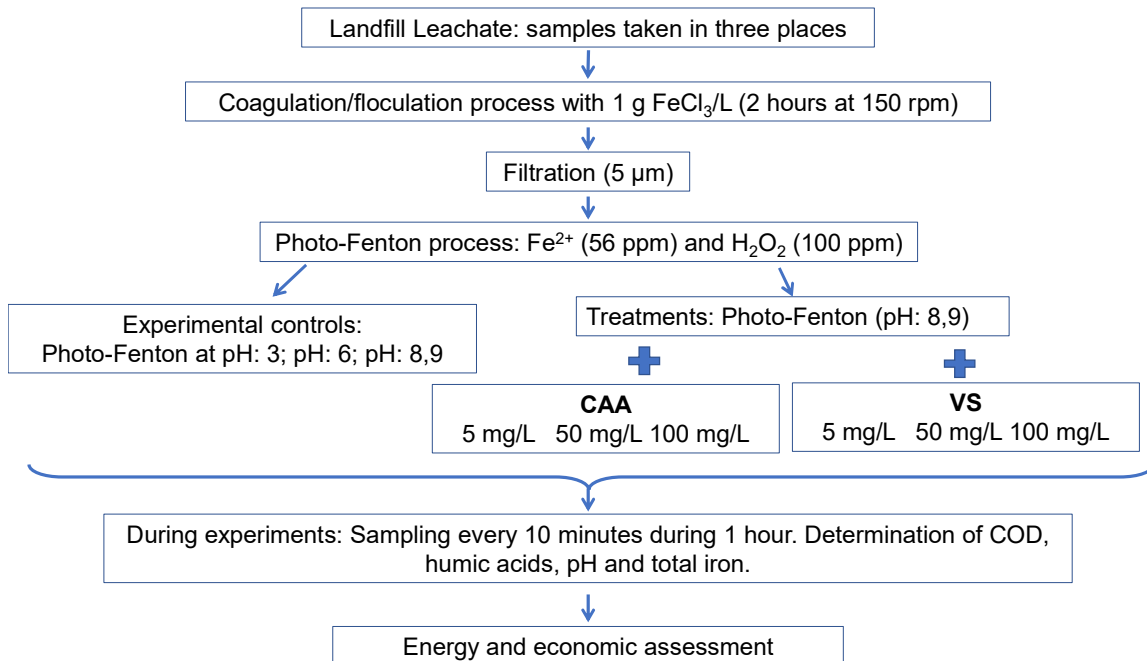
251 
$$SEC = \frac{\sum P*t}{(C_0 - C_f)*V} \quad (3)$$

252 Where P is the electrical power input consumed by the equipment used in the  
 253 photocatalytic process (W), t is the treatment time (h), V is the volume of wastewater  
 254 treated (L) and, C<sub>0</sub> and C<sub>f</sub> are the initial and final concentrations of COD present in  
 255 the LL (mg/L), respectively (Krýsa et al. 2018).

256 A preliminary economic assessment of the evaluated photocatalytic processes was  
 257 realized by determining and comparing the operational costs of the evaluated  
 258 processes, considering energy consumption and reagent costs.

259 In Fig. 2 are depicted a resume of the methodology carried out in this work research.

260



261

262 Fig. 2. Resume of the methodology carried out.

263 3. Results and discussion

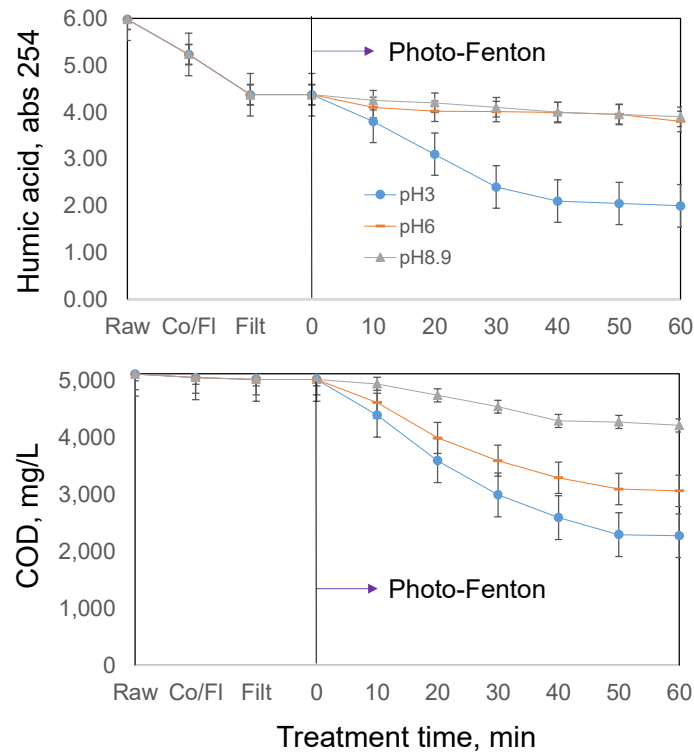
264 3.1. Removal of pollutants and iron concentration

265 In Figure 3, the change in the absorbance of humic acid and in the concentration of  
 266 COD during the pre-treatment and the photocatalytic treatment time, at different pH  
 267 without using chelating agent are depicted. As can be seen, there was a high  
 268 removal of organic matter when the reaction was carried out at pH 3, obtaining a  
 269 removal of humic acid and COD of 54.2% and 54.7%, respectively. When the  
 270 reaction was carried out at pH 6, the removal was 13.1% and 39.2% of humic acid



271 and COD, respectively. In the case of the reaction at pH 8.9, the elimination was  
272 10.8% and 16.1% of humic acid and COD, respectively.

273 Considering the global process that consisted in coagulation/flocculation filtration  
274 and photo-Fenton process at pH 3, the removal of humic acid and COD was 66.6%  
275 and 55.5%, respectively.



276

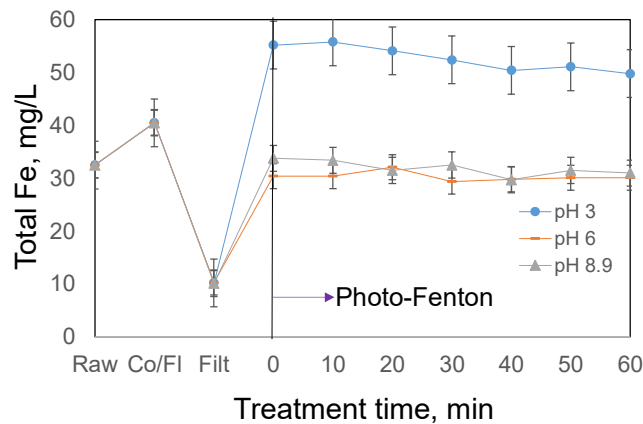
277 Fig 3. Humic acid absorbance and COD concentration at different pH evaluated in  
278 photo-Fenton treatment. Error bars represent the standard deviation of the results  
279 (n=3)

280 The low elimination of humic acid and COD in LL obtained in the photocatalytic  
281 process at pH higher than 3 could be due to the fact that under this condition there  
282 is a reduced amount of iron to react with  $H_2O_2$ , producing less amount of  $\cdot OH$  in the  
283 system (Li et al. 2016) as can be seen in Figure 3.

284 The concentration of total Fe in photo-Fenton process was high when carried out at  
285 pH 3, going from 55.2 mg/L to 49.8 mg/L after 60 minutes of treatment. In the case  
286 of the reaction obtained at pH 6 and 8.9, it changed from 30.4 mg/L to 30.1 mg/L  
287 and from 33.8 mg/L to 31.0 mg/L, respectively (see Fig. 4).

288 As can be seen in Figure 4, the iron concentration, although reduced, is still present  
289 in solution at pH of 6 and 8.9, possibly due the complex matrix of the LL. For  
290 instance, the presence of carboxyl acids that are typically constituent of this kind of  
291 water (Solo-Gabriele et al. 2020; Yu et al. 2020; Hamid et al. 2018) and form ligands

292 with iron (Seibert et al. 2017) could justify the elimination of organic matter at these  
293 pHs.



294

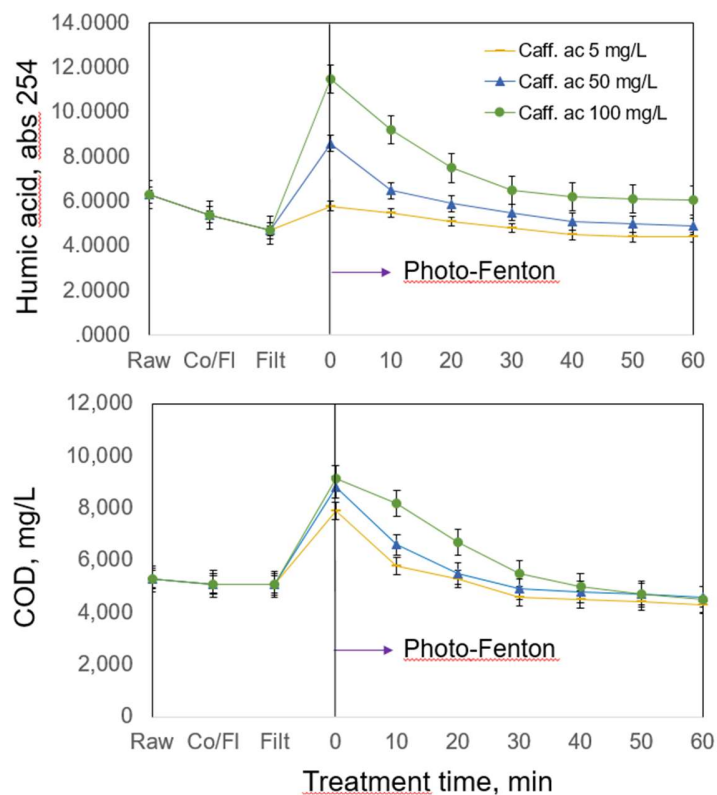
295 Fig 4. Total Fe concentration at different pH evaluated. Error bars represent the  
296 standard deviation of the results (n=3).

297 Figure 5 shows the evolution of organic matter in the processes carried out at pH  
298 8.9 (the natural pH of the LL) using different concentrations of Caa. As can be seen,  
299 after the addition of Caa there was an increase of the humic acid and COD and the  
300 photocatalytic process had the aim of reduce it. Under these conditions, a removal  
301 of 24.1%, 43.0% and 47.4% of humic acid using 5 mg/L, 50 mg/L and 100 mg/L of  
302 Caa was obtained. As can be seen, the run carried out with a higher concentration  
303 of Caa ended its experiments with a high amount of organic matter, even at a higher  
304 removal of the solution which was due to the higher concentration at the beginning  
305 of the photocatalytic process.

306 These interesting results that show the positive effect of Caa in the removal of  
307 organic matter are due to the fact that this compound is a phenolic structure that can  
308 chelate  $Fe^{+3}$  reducing it to  $Fe^{+2}$  and stimulating the Fenton reaction (Márquez et al.  
309 2019a).

310 Although it is known that phenolic compounds have antioxidant properties (Tomac  
311 et al. 2020), some of these compounds, such as caffeic acid, have proven pro-  
312 oxidant effects and the concentration of this compound was proportionally related to  
313 the production of hydroxyl radicals, enhancing the efficiency of the photocatalytic  
314 reaction (Márquez et al. 2019b) which justifies the a higher removal of humic acid  
315 and COD obtained when using a higher concentration of caffeic acid.

316

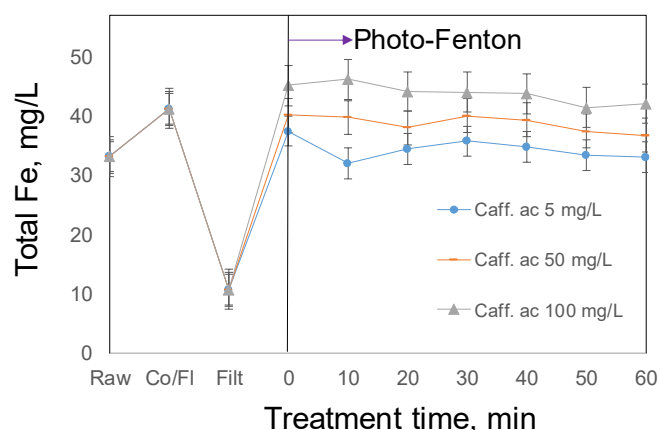


317

318 Fig 5. Humic acid absorbance and COD concentration at pH 8.9 evaluated in  
 319 photo-Fenton treatment. Error bars represent the standard deviation of the results  
 320 (n=3)

321 A high generation of  $\cdot\text{HO}$  in the presence of humic substance and caffeic acid was  
 322 reported, concluding that the addition of caffeic acid increased the oxidation  
 323 efficiency of Fenton-like processes (Lin et al. 2017). It has been observed that caffeic  
 324 acid has a reductive power, allowing the reduction of ferric ion to ferrous ion  
 325 (Chvátalová et al. 2008) in order to enhance the solar photo-Fenton process  
 326 (Iwahashi et al. 1990; Villegas-Guzman et al. 2017).

327

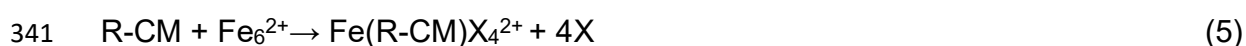


328

329 Fig 6. Total Fe concentration in photo-Fenton treatment using caffeic acid as  
 330 chelating agent at different concentrations at pH 8.9. Error bars represent the  
 331 standard deviation of the results (n=3)

332 As can be seen in Figure 6, there was an enhancement in the concentration of total  
 333 Fe at pH 8.9, when caffeic acid in solution was used and that the higher the  
 334 concentration of caffeic acid, the higher the concentration of Fe was, going from 37.5  
 335 to 33.2, from 40.2 to 36.8 and from 45.2 to 42.1, using 5 mg/L, 50 mg/L and 100  
 336 mg/L of caffeic acid, respectively. **These results are better than the obtained at pH**  
 337 **8.9 without chelating agents, with a, average of 33.8 mg/L (see Fig. 4).**

338 This behaviour could be due to the effect of caffeic acid and Fe, where the chelating  
 339 process occurs due the reaction presented in Eq.(4) and (5) (Holtomo et al. 2015):

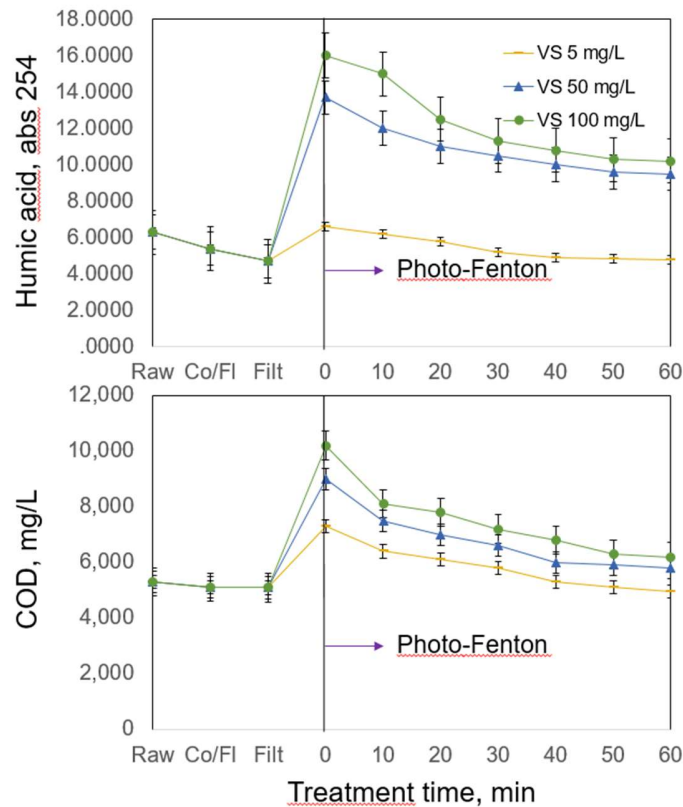


342 Where R-CM represents a phenolic acid, R is the sidechain and X are the ligands.  
 343 Besides, chelation mechanism is spontaneous when the phenolic acids present in  
 344 the site of chelation are in the presence of metallic ion (Fifen et al. 2009).

345 The removal of organic matter in the photo-Fenton process at pH 8.9, using  
 346 polyphenols coming from VS was higher (see Fig.7) than the obtained at that same  
 347 pH without using vinasse (see Fig. 3) but a bit lower than the obtained using Caa  
 348 (see. Fig. 5). **It is possible to observe that the addition of VS get an high increase of**  
 349 **the humic acid and COD and the photocatalytic process partially reduce it.** When  
 350 VS was used, the removal of humic acid was 27.3%, 30.7% and 36.3% using 5 mg/L,  
 351 50 mg/L and 100 mg/L of VS respectively, and 32.2%, 35.4% and 39.2% using 5  
 352 mg/L, 50 mg/L and 100 mg/L of VS, respectively.

353 Ouyang et al. (2019) obtained a high elimination of lincomycin, observing that the  
 354 addition of polyphenols as chelating agent significantly promotes the generation of  
 355 hydroxyl radical and this generation was enhanced when the concentration of

356 polyphenols was increased, results aligned with the ones obtained from this  
357 investigation.



358

359 Fig 7. Humic acid absorbance and COD concentration in photo-Fenton treatment  
360 using vinasse as chelating agent at different concentrations, at pH 8.9. Error bars  
361 represent the standard deviation of the results (n=3)

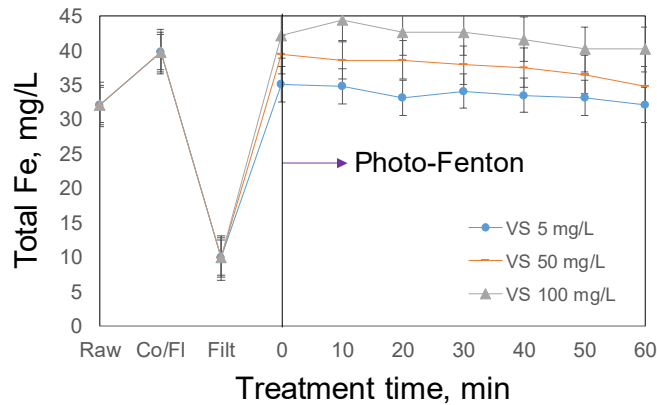
362 As can be seen, a higher concentration of Caa and VS produces an enhancement  
363 in the concentration of organic matter in the LL, promoting the competition of the  
364 contaminants for the oxidant radicals (Ruíz-Delgado et al. 2019) and also a screen  
365 effect of UV photons, that is higher at a raised concentration of chelate, therefore a  
366 large amount of chelate needs to be avoided.

367

368 As can be seen, although at pH 8.9 the concentration of total iron was lower than at  
369 pH 3 without use of chelate, it was higher when vinasse was used than when it was  
370 not used, see Figure 3 and 7. It went from 35.1 to 32.2, from 39.4 to 34.8 and from  
371 42.1 to 40.2, using 5 mg/L, 50 mg/L and 100 mg/L of VS. The reason could be due  
372 to the fact that the chelating agents (polyphenols of VS) form bonds with iron and  
373 allow Fe<sup>3+</sup> to keep soluble at a high pH, due to the formation of complexes (Ruíz-  
374 Delgado et al. 2019).

375

376

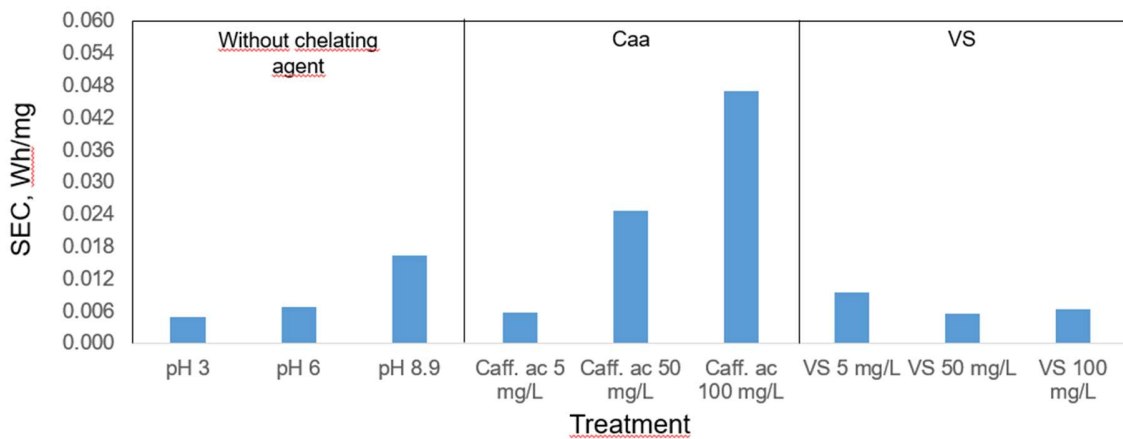


377

378 Fig. 8. Total Fe concentration in photo-Fenton treatment using vinasse as chelating  
 379 agent at different concentrations, at pH 8.9. Error bars represent the standard  
 380 deviation of the results (n=3)

381 3.2. Specific energy consumption and economic assessment

382 SEC of the photo-Fenton processes carried out are depicted in Figure 9. As can be  
 383 seen, the processes that use the energy more efficiently, in terms of the energy  
 384 consumed per mass of COD removed, were photo-Fenton process at pH 3 (0.0052  
 385 Wh/mg), followed by the process that used VS as chelating agent in a concentration  
 386 of 50 mg/L (0.0061 Wh/mg) and finally when Caa at 5 mg/L (0.0064 Wh/mg) was  
 387 used. These results showed lower SEC than the obtained in a previous work of our  
 388 investigation group, where the lowest SEC observed was 0.09 Wh/mg of COD  
 389 removed of a LL using activated carbon, ultrasound, ozone and H<sub>2</sub>O<sub>2</sub> (Poblete et al.  
 390 2017).



391

392 Fig. 9. SEC of the photocatalyst process carried out using or without use of  
 393 chelating agent

394 When Caa was used at a higher concentration get a SEC of 0.046 Wh/mg, being the  
 395 processes that consume more energy in relation with the pollutants removed.  
 396 Although under this condition, a high removal of organic pollutants it was obtained.

397 The use of Caa required the utilization of an extra equipment to produce them, the  
 398 ultrasound, that consumes 500 W, which required to take in consideration the energy  
 399 used in this process.

400 Related to the operational costs involved in the photocatalytic processes, where the  
 401 cost of the reagent used and the electric energy consumed in the processes (see  
 402 Table 2) were considered, it was lower for photo-Fenton process carried out at the  
 403 natural pH of LL (8.9) followed by the carried out using vinasse, and higher for the  
 404 treatment carried out using caffeic acid and in the classical photo-Fenton process at  
 405 pH 3. The reason of the higher operational costs is due to the fact that, in this case,  
 406 the use of more electrical energy to extract the caffeic acid from the solid waste (runs  
 407 caffeic acid) and the use a high amount of sulfuric acid to adjust the pH from 8.9 to  
 408 3 (run a pH 3) were required. In the case of the runs using VS were not necessary  
 409 however, with a lower removal of COD, that was higher for classical photo-Fenton  
 410 process and the runs that used caffeic acid.

411 Table 2. Operational costs and organic pollutants removed due the photo-Fenton  
 412 processes carried out

413

		Operational costs (US\$/m <sup>3</sup> )	Pollutants elimination (%)	
			Humic acid	COD
<b>Without chelatings and different pH</b>	pH 3	167.9	52	55
	pH 6	167.9	13	39
	pH 8.9	127.1	11	16
<b>With chelatings and pH 8.9</b>	<b>Caffeic acid</b>			
	Caa 5 mg/L	138.9	24	46
	Caa 50 mg/L	153.0	43	48
	Caa 100 mg/L	168.8	47	51
	<b>Vinasse</b>			
	VS 5 mg/L	137.3	27	32
	VS 50 mg/L	137.3	31	35
	VS 100 mg/L	137.3	36	39

414

415 These operational costs are higher than the obtained by Durán et al. (2012) that  
 416 report 65 US\$/m<sup>3</sup> in the photo-Fenton treatment of the effluent of integrated  
 417 gasification combined cycle power station, possibly due to the fact that this  
 418 wastewater is less contaminated, requiring less reagent to obtain the necessary  
 419 treatment. The operational costs observed in this research work can be reduced  
 420 dramatically if solar energy is used as source of UV radiation instead to used UV  
 421 lamp (Costa et al. 2018; Gil-Pavas et al. 2018).

422

423 4. Conclusions

424 The use of wastes coming from pisco production (VS) and solid coffee (Caa) was  
425 evaluated in order to determine its capacity as a chelating agent in photo-Fenton  
426 process in the treatment on landfill leachate (LL). In the reaction developed without  
427 chelating agent, a higher removal of organic matter was obtained at pH 3 than pH 6  
428 and 8.9. Also, under these conditions the concentration of iron in solution showed  
429 the same trend, higher at pH 3 than in the other pHs.

430 When Caa and VS were used in the photo-Fenton reaction at pH 8.9, a higher  
431 removal of organic matter was obtained than without using them, being better using  
432 Caa. A higher concentration of the chelating agent produced an increase in the  
433 depuration of the LL, in the case of Caa and VS, observing a relation between the  
434 concentration of iron in LL and the removal of organic matter. Although at pH 8.9 the  
435 concentration of iron in solution was lower than at pH 3 without use of chelate, it was  
436 higher when Caa and VS were used than when they were not used.

437 The energy was used more efficiently when VS was applied at medium concentration  
438 and Caa at low concentration, being the SEC a little lower when the photocatalytic  
439 treatment was carried out at pH 3. At pH 8.9 using chelating agents, both Caa and  
440 VS, the removal of organic matter was lower and with a higher SEC that when carried  
441 out at pH 3 and without using chelating agents. The performance of the  
442 photocatalytic treatment carried out using the chelating agent was better than without  
443 using them, at pH 6 and 8.9. Also, the operational costs of the processes were lower  
444 when using a chelating agent and especially lower when VS was used.

445 Considering the removal of organic matter, Caa were the chelating agent that  
446 produced the most interesting results, being useful to be applied in photo-Fenton  
447 process at pH 8.9, without the need to adjust the pH and giving the opportunity to  
448 benefit from a solid waste and promote circular economy. However, it is necessary  
449 to improve the performance of the operational condition to avoid the excessive  
450 discharge of organic matter and the specific energy consumption in the process.

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452

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457

458

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