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1 **Enhanced electrokinetic remediation of multi-contaminated dredged sediments and**  
2 **induced effect on their toxicity**

3

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24

25 **Abstract**

26 Electrokinetic (EK) remediation is often developed for metal decontamination but  
27 shows limitations for polycyclic aromatic hydrocarbons (PAHs) and polychlorobiphenyls  
28 (PCBs) which are nonionic and involve low aqueous solubility. This paper reports many  
29 laboratory studies devoted to the investigations of EK efficiency on the mobility and the  
30 removal of metals, PAHs and PCBs from dredged sediments, using a mixture of chelating  
31 agent and surfactants. The results showed that increasing chelating agent concentration was  
32 favorable for both metal and PAH removal. Applying a periodic voltage gradient associated to  
33 a low concentration of additives provided the best removal of Zn, Cd and Pb and also the 16  
34 priority PAHs. The tested fresh harbor sediment was highly resistant to metal and organics  
35 mobilization and transport because of an aged contamination, a high buffering capacity, a  
36 very low hydraulic permeability and a high organic matter content. However, experiments  
37 performed on a former sediment which was deposited many years ago provided better  
38 removal results, involving low organic matter and carbonates content. The efficiency of the  
39 EK process was also assessed by measuring the acute toxicity of the EK-treated sediment on  
40 the copepod *Eurytemora affinis* exposed to sediment elutriates.

41

42 **Key words**

43 Electrokinetics, sediment, remediation, pollutants, toxicity, copepod

44

## 45 **1. Introduction**

46

47         Traditional industrial methods of decontamination (thermal desorption, flushing, etc.)  
48 are not adapted to fine grained and highly hydrated materials (Perrodin et al., 2012). Among  
49 physico-chemical methods which could be developed in the future, one way consists in  
50 immobilizing the contaminants to avoid their spreading in the environment; another way is to  
51 extract a great proportion of them from the sediment. Electrokinetic (EK) remediation has  
52 appeared for many years as a promising technology for treating the organics/inorganics  
53 contaminated materials of low permeability, with a great potential for *in-situ* application (Kim  
54 et al., 2011; Ferrucci et al., 2017). Sediment contamination involves different organic,  
55 inorganic and organo-metallic pollutants but heavy metals and persistent organic pollutants  
56 (such as polycyclic aromatic hydrocarbons, PAHs or polychlorobiphenyls, PCBs) are  
57 particularly of great concern regarding their toxicological hazard. Since electromigration has  
58 generally a higher impact than electroosmosis, EK remediation has focused mainly on  
59 charged species such as heavy metals for many years (Kim et al., 2011; Rozas and Castellote,  
60 2012; Iannelli et al., 2015). However, attention also focused more recently on removing  
61 neutral contaminants such as PAHs or PCBs from contaminated soils (Maturi and Reddy,  
62 2008; Alcantara et al., 2008; Fan et al., 2014), but only few studies dealt with fine-grained  
63 sediments (Colacicco et al., 2010; Hahladakis et al., 2013). For the nonionic organics, the  
64 electroosmosis (migration of the pore aqueous solution through the sediment matrix) is the  
65 main transport mechanism. The main challenge of EK technology is the conversion of all  
66 these low soluble pollutants into mobile forms in order to extract them. So enhancing agents,  
67 added to the processing fluids, turn out necessary to obtain effective removals of each kind of  
68 contaminants. Acidic pH enhances metals solubilization and their transport to the cathode  
69 reservoir, whereas complexing agents convert soil-bound metals into soluble complexes and

70 enhance their removal (Giannis et al., 2010; Song et al., 2016). For PAHs and PCBs,  
71 enhancing additives such as surfactants allow their better desorption from sediment particles  
72 and solubilization in the aqueous pore fluid. (Maturi and Reddy, 2008; Fan et al., 2014;  
73 Hahladakis et al., 2013). Biosurfactants have been recommended in remediation approaches  
74 for organics, due to their biodegradability and low toxicity (Megharaj et al., 2011), but only  
75 few studies were carried out in EK remediation (Gonzini et al., 2010; Ammami et al., 2015).  
76 The demonstration of the effectiveness of a remediation method is generally based on its  
77 capacity to lowering the level of the target toxic substances. However, chemical  
78 transformations occurring during the treatment could modify the mobility/accessibility of  
79 such substances and possibly make them more hazardous for the living organisms, even if  
80 their levels were reduced. It is why there is an interest for incorporating toxicity tests to  
81 demonstrate the effectiveness of a remediation process (Wang et al., 2009). Among the battery  
82 of tests developed, *in vivo* bioassays using aquatic organisms were recognized suitable for  
83 assessing sediment toxicity and their potential biological effects in the environment  
84 (Mamindy-Pajany et al., 2010). Among aquatic organisms, copepods have been suggested as a  
85 reference species for the bio assessment of freshwater, estuarine, and marine environments  
86 (Kulkarni et al., 2013). The calanoid copepod *Eurytemora affinis* is a dominant inhabitant of  
87 estuaries in the northern hemisphere able to bioaccumulate various contaminants such as  
88 PCBs or PAHs. Given its ecological relevance, this species has become a model for  
89 ecotoxicology studies (Legrand et al., 2016; Lesueur et al., 2015). This paper reports the  
90 results of many studies devoted to evaluate the potential of an electrokinetic remediation  
91 process using mixtures of eco-friendly enhancing additives for the treatment of a multi-  
92 contaminated harbor sediment with regard to environmental regulations. The efficiency of  
93 such process was measured through the pollutants removal combined with the evaluation of

94 the toxicity of the treated sediment, assessed by the mortality of *E. affinis* copepods exposed  
95 to sediment elutriates.

## 96 **2. Materials and methods**

97

### 98 **2.1 Experimental set up and procedures**

99 Samples were collected from fresh dredged sediment upward the Tancarville (Le  
100 Havre, France) channel close to the Seine River, and also from an aged (7 years) sediment in a  
101 deposit land made of materials of the same dredging area. The material is a silty soil  
102 involving 75% of silt particles and 6% of clay particles. The organic matter and carbonates  
103 contents are respectively 11% and 30%.

104 The experimental EK remediation setup (Figure 1) was described in previous papers  
105 (Ammami et al., 2014; Song et al., 2016). The main device, made of Teflon  
106 polytetrafluoroethylene (PTFE) material, includes a sediment chamber (cylinder of 4.9-cm  
107 inner diameter and 14-cm length) and two electrode compartments. These three elements are  
108 assembled with four clamping rods and sealed by two O-rings. The dredged sediment sample  
109 was packed into the chamber by compacting approximately 380 g of wet dredged sediment in  
110 a manner to obtain a homogeneous specimen. The specimen was introduced in the cell at a  
111 water content close to 115%, reaching a complete water saturation of the material (103%).  
112 Graphite electrode plates were placed in each electrode compartment, separated from the  
113 sediment by porous (0.45  $\mu\text{m}$ ) fiberglass filter paper (Millipore) and a perforated grid made of  
114 Teflon. A processing fluid was used in both electrode compartments in order to enhance the  
115 remediation process. Two pumps (from KNF) filled the electrode reservoirs with aqueous  
116 processing fluids (10 mL h<sup>-1</sup>). All the tests were performed under an electrical field of 1.0 V  
117 cm<sup>-1</sup> for a duration of 21-28 days with a continuous or an intermittent (5 days on; 2 days off)  
118 procedure. During tests, effluents were collected by two overflow pipes from both electrodes

119 and then stored in glass flasks. Different processing electrolytes were prepared (Table 1) and  
120 used to feed both electrode compartments. As a control test, pure water was previously used  
121 as electrolyte. During the test, the volume of outlet effluent was monitored for accumulated  
122 electroosmotic flow (EOF) calculation. At the end of each test, the sediment was recovered  
123 and cut into four slices (S1 to S4, from anode to cathode) which were lyophilized and  
124 submitted to physicochemical analysis (pH, metal concentration, organic contaminant  
125 concentration, etc.).

126

## 127 **2.2 Analytical methods**

128 The pH and the electrical conductivity (EC) in the sediment and in the effluents were  
129 measured according to NF ISO 11265 and NF ISO 10390 standards, respectively, using the  
130 ratio water / sediment close to 10:1.

131 The extraction of PAHs was carried out by means of a microwave assisted extractor  
132 (MAE method: Microwave Assisted Extraction). After lyophilization, 5 g of natural dry  
133 sediment (before or after treatment) was weighed and mixed with a solution of 40 mL of  
134 acetone /toluene (1:1) solvent in a special Teflon tube dedicated for the extractor (MarsX,  
135 CEM corporation). The heating temperature raised to 130 ° C in 5 minutes with the power of  
136 1200 W for 6 extractions at the same time. Then, this temperature was maintained during 25  
137 minutes prior to sample cooling. The liquid phase was then filtered with syringes and PTFE  
138 filters of 0.2 µm opening. A concentration step was required before analysis: a keeping  
139 solvent (60 µL of octanol) was introduced into the recovered eluents which were evaporated  
140 completely by using a miVac system (vacuum concentrator). The keeping solvent was then  
141 re-diluted with 1440 µL of toluene to give a final sample volume of 1.5 mL. Then, 990 µL  
142 were collected from the sample, in which 10 µL of a mixture of two internal standards  
143 (perdeuterated Phenanthrene D10 and Perylene D12 at 100 mg/L) was introduced. By using

144 gas chromatography (GC) coupled with mass spectrometry (MS), samples were analyzed to  
145 determine the quantity of PAH contaminants concerned.

146 The determination of the concentrations of trace metals (TM) in the sediment  
147 consisted of a mineralization prior to the quantitative analysis. During the mineralization,  
148 samples were dissolved and oxidized with strong acids and a heating step in order to  
149 solubilize and stabilize the TM in an aqueous phase (Song et al., 2016). In this study, 0.5 g of  
150 freeze-dried sediment was mixed in a special glass tube of 35 mL with 8 mL of reversed aqua  
151 regia which contains 6 mL of 69% nitric acid and 2 mL of 37% hydrochloric acid. First, this  
152 mixture was reacted for half an hour at ambient temperature for releasing the generated gas  
153 (CO<sub>2</sub>). Then, the heating step was carried out using a pressurized microwave mineralizer  
154 (Discover SP-D, CEM, USA). The mixture was heated up to 200 ° C with an increase of the  
155 pressure up to 300 psi ( $\approx$  2.07 MPa) during 4 min and then these parameters were maintained  
156 during 4 min. After cooling, the mixture was diluted in 25 mL of ultra-pure water and filtered  
157 by 0.45  $\mu$ m opening filter to obtain the leachate which is then stored in a glass vial at 4 °C  
158 before analysis. The leachates were then analyzed by ICP-AES (Inductively coupled plasma  
159 atomic emission spectroscopy) which is a very sensitive and effective method to detect the  
160 TM concentrations. In this study, five heavy metals (Cu, Cr, Cd, Pb and Zn) were targeted to  
161 evaluate their migration and extraction during the electrokinetic treatment.

162

### 163 **2.3 Acute toxicity tests**

164

165 *Eurytemora affinis* copepods were sampled in the Seine estuary (49°28'19N, 0°15'  
166 52''E; Normandy, France). As previously described (Boulangé-Lecomte et al., 2014), they  
167 were collected with aWP2 plankton net (200- $\mu$ m mesh size; 1-m diameter) and were directly  
168 passed through two sieves (500 and 100- $\mu$ m mesh size) to eliminate large particles and



169 predators. They were placed in estuarine water in isothermal containers. After progressive  
170 acclimatization in the laboratory, they were maintained in 40-L aquariums filled with brackish  
171 water (a mixture of UV-treated filtered sea water and deionized water; Aquacaux, Octeville  
172 sur Mer, France) in optimal conditions (aeration, salinity 10, 15 °C, 12-h/12-h photoperiod)  
173 (Devreker et al., 2009). They were fed *ad libitum* with *Isochrysis galbana* algae (15,000 cells  
174 mL<sup>-1</sup>). They were depurated for at least 3 days in brackish water before each experiment  
175 (Cailleaud et al., 2011). Acute toxicity tests were conducted according to the ISO14669  
176 standard. Copepods were not fed and were placed into a climatic chamber (salinity 10, 15 °C,  
177 12 h/12 h photoperiod). They were exposed to sediment elutriates made from raw sediment or  
178 treated (sections S1 to S4) sediments in glass crystallizers. Aqueous extraction (brackish  
179 water, salinity 10) of the sediment (5 g L<sup>-1</sup>) was performed 24 h before the experiment under  
180 shaking. Adult male copepods were isolated from females, copepodites, and nauplii using a  
181 stereomicroscope (EZ4, Leica Microsystems). Ten males per replicate and three replicates per  
182 condition were randomly distributed in glass crystallizers containing 10 mL of elutriate for 96  
183 h. For each experiment, a control water was added and dead copepods were counted daily and  
184 removed.

185

### 186 **3. Results and discussion**

187

#### 188 **3.1 Evolution of physical and chemical parameters**

##### 189 *3.1.1 Sediment pH after EK treatment*

190 Figure 2a shows that without any additive (EK0 test), the water electrolysis generated  
191 H<sup>+</sup> ions in the anode compartment which made the sediment pH decreased to 5.57 near the  
192 anode, and at the same time OH<sup>-</sup> ions generated in the cathode compartment increased  
193 significantly the sediment pH near the cathode up to 10.68. However, the sediment sample in

194 the middle of the experimental cell was not affected compared to the initial pH value of  
195 sediment ( $8.4 \pm 0.2$ ). When adding citric acid (CA) (EK1 to EK3 tests), a pH decrease  
196 affected the whole sample, typically near both sections close to the electrodes (anode and  
197 cathode). However, acidification effect was not so effective in sections 2 and 3 close to the  
198 middle of the sample where pH is higher than 6. This is attributed to the high buffer capacity  
199 of the natural sediment involving a high carbonates content (30%). One purpose of  
200 acidification of the sediment by using processing additives is to enhance the dissolution of  
201 heavy metals. But even with 0.2 mol/L of citric acid, the acidification of the whole sample  
202 was not achieved and the pH value which is around 7 was still too high to solubilize heavy  
203 metals. This will be described in details in the further section. One result which need to be  
204 emphasized is that rhamnolipid biosurfactant made round-trips in sections 1 and 2 because its  
205 pKa is around 4.8 which is located between pH values of sections 1 and 2. Along  
206 electroosmotic flow (EOF), neutral rhamnolipid in section 1 migrates to section 2 where  
207 rhamnolipid becomes negatively charged because of higher pH value. So, under the effect of  
208 applied electric field (electromigration), it moves back to section 1. At high pH reached  
209 conditions (EK4 test with EDDS,  $\text{pH} > 8$  (Fig. 2a), saponin biosurfactant ( $\text{pKa} = 6.8$ ) becomes  
210 also negatively charged and migrates towards the anode in opposite direction to the  
211 electroosmotic flow as rhamnolipid acts. This charge modification of saponin is not  
212 noticeable when saponin is used in combination with citric acid (EK2, EK3 tests), where the  
213 pH is typically lower than 7 (Fig. 2a). In this case, saponin is roughly neutral and migrates  
214 along with EOF towards the cathode.

215

### 216 *3.1.2 Electric current intensity during the EK process*

217 The global trend of electric current intensity displayed a high value before a drastic  
218 decrease, in particular after each restart of on-voltage period in many tests. The current

219 magnitude overall decreased along successive on-voltage cycles before reaching stable values.  
220 Figure 2b displays the evolution of electric current recorded for several tests. One can note  
221 that the average residual value of electric current recorded during EK1 and EK2 tests  
222 (performed with 0.2 mol/L of citric acid) at stable phase was close to 12 mA, twice than the  
223 value obtained with pure water test (6 mA) and slightly higher than that of EK 3 test  
224 performed with 0.1 mol/L of CA. However, the 'flushing' effect involved in tests performed  
225 with the help of citric acid was lower than that obtained in EK0 test. That means that a re-  
226 establishment (restoration) of the ions concentration after two days 'off' is more important for  
227 EK0 test than EK1 and EK2 tests. This could be due to the strong dissociation or dissolution  
228 of the exchangeable salt fractions, weakly associated with the sediment particles in the first 50  
229 hours in the presence of citric acid. This effect reached a stable state at 100 h treatment  
230 duration. Without citric acid, the dissociation of salts occurred gently during 500 h of  
231 treatment, until the last electric cycle. At each voltage restart, the ion concentration was  
232 higher than that of previous stable phase of electric current.

233 Furthermore, the sediment dewatering was much more important when treated with  
234 citric acid compared to the control test (pure water). This result is discussed more far in the  
235 section related to EOF results (next section). As a consequence of dewatering result, the ions  
236 movements in the sample and thus the current slowed down. It inhibited the increase of  
237 electric current at the restart phase for citric acid tests because the electrolyte could hardly or  
238 never reach the initial electrolyte concentration in dried sediment section. Furthermore, a  
239 decrease of ions movement (current) might be due to the formation of non-conducting  
240 gaseous bubbles on the surface of electrodes and in the sediment sample due to water  
241 electrolysis and sediment acidification (Song et al., 2018).

242 For EK4 test using EDDS as a chelating agent, the average current was around 20 mA  
243 which is even higher than that obtained for tests using CA. This high value is due to the

244 alkaline environment (EDDS is not a weak acid unlike CA) overall the sediment sample in the  
245 electrokinetic cell (Fig. 2a) where no dewatering was observed during more than 600 hours  
246 treatment. The ‘flushing’ effect on electric current was important at each restart (Fig. 2b).  
247 This is attributed to the reset of EDDS-Na<sub>3</sub> ions in the sediment sample during the two days’  
248 rest. However, for the third and fourth cycles, the ‘flushing’ effect became shorter. EDDS-Na<sub>3</sub>  
249 ions migrated rapidly towards the two electrodes (EDDS<sup>3-</sup>, Na-EDDS<sup>2-</sup>, Na<sub>2</sub>-EDDS<sup>-</sup> moved to  
250 anode, Na<sup>+</sup> moved to cathode) and thus the current became stable again very quickly.

251

### 252 *3.1.3 Cumulative electroosmotic flow*

253 Zeta potential, which determines the direction and velocity of electroosmotic flow  
254 (EOF) is pH dependent. The higher absolute value of zeta potential corresponds to a higher  
255 EOF velocity, and a negative zeta potential leads to an EOF directed from the anode toward  
256 the cathode. For tested sediment, the measured zeta potential (ZetaCompact-CAD Inst.)  
257 before EK treatment was negative (- 32 mV) because of the negative surface charges of  
258 sediment particles. Generally, zeta potential decreases (more negative) with a rise of pH  
259 which gives an increase of EOF velocity. Many researchers (Lambert and Middleton, 1990)  
260 have found that the variation of EOF velocity with pH change is not linear, but rather  
261 represented by a curve which evolves smoothly when pH < 3 and pH > 8, but roughly between  
262 pH values of 5 and 6.

263 For both anode and cathode cumulative EOF curves (Figure 3), an increasing trend  
264 represents a global direction of EOF from anode to cathode, whereas a decreasing trend  
265 means a reverse direction (from cathode to anode). The increasing trend means also that the  
266 reversed EOF is lower than the EOF directed from anode to cathode and its displaced water  
267 volume is lower. Figure 3f displays the evolution of cumulative EOF measured at the cathode  
268 for several tests, and we could note an increase trend over the testing duration, indicating a

269 main direction of EOF toward the cathode. However, this increase was inhibited after an  
270 elapsed time in EK1 and EK2 tests carried out with high concentration (0.2 M) of CA.  
271 This section also details and discusses the effect of CA and EDDS as additives on the EOF.  
272 From Figure 3f we can note that EK 1 and EK 2 tests (performed with 0.2 M CA) had similar  
273 cumulative EOF curves, which means that the effect of biosurfactants (rhamnolipid *vs*  
274 saponin) in used concentrations was negligible on EOF. At the first 200 hours of test, the  
275 cumulative EOF of EK 1 and EK 2 were close to that obtained with pure water (EK 0 test) or  
276 rather quite higher (Fig. 3f). However, after that time the cumulative EOF of EK 1 and EK 2  
277 increased slightly before a very weak decrease, indicating a reverse direction of EOF at the  
278 end of the tests. Ultimately, their cumulative EOF were both lower than that provided by EK  
279 0 (Figs. 3a, 3b, 3c and 3f.) It is interesting to point out that EK 3 test (using 0.1 mol/L of CA)  
280 provided the highest cumulative EOF, compared with other tests (pure water or 0.2 mol/L of  
281 CA) (Fig. 3f). Generally, increasing ionic strength increases the EOF, but if we continue to  
282 raise the ionic strength, the cumulative EOF can be intensively hindered by the too  
283 concentrated charged additive. The overall strong values of EOF recorded at the tests start  
284 were due to sediment water-saturation, which decreased (because of dewatering) as strongly  
285 as the electric current reached high values. At the same time, since electromigration moves H<sup>+</sup>  
286 ions from the anode (where pH=1.98 for 0.2 mol/L of CA) toward the nearby first section of  
287 sediment, the zeta potential becomes close to zero (even-turning positive), leading to a weak  
288 value of EOF and so low dewatering in the S1 section. So, positive values of zeta potential  
289 provided a reversed EOF. This process is indicated by the exponential trend of cumulative  
290 EOF curves recorded at anode side (Figures 3b and 3c, tests EK1 and EK2). But in sections 3  
291 and 4 close to the cathode, owing to high pH value (buffer effect of sediment), EOF was more  
292 important and led to dewatering of these two sections. Rapidly, section 3 and 4 became very  
293 compact and dry, which slowed down the EOF for the next 500 hours of test (Figs. 3 b, 3c and

294 3d), so water could not further get easily into these sections. This is why a weak EOF after  
295 100 h (logarithmic trend of the EOF curve) was recorded for EK1 and EK2 tests. Moreover,  
296 during the dehydration of sections 3 and 4, the electric resistance may raise significantly,  
297 which may lead to the increase of the voltage gradient in these sections. Consequently, for the  
298 sections 1 and 2, the real voltage may be lower than 1 V/cm (Rittirong et al., 2008), which  
299 means that EOF in these sections could be even lower. That is harmful to the remediation of  
300 contaminants (Li et al., 2009; Cameselle and Reddy, 2012). Another reason for the low  
301 cumulative EOF when using 0.2 mol/L of CA as additive was that the electrolyte was more  
302 viscous and so the sediment particles were much closer each to other; so the very high ionic  
303 strength could decrease the electric repulsive force between the particles by compressing the  
304 electrical double layer. This more compact structure could only provide a limited amount of  
305 EOF (Pazos et al., 2011).

306 As mentioned previously, the high value of cumulative EOF in EK 3 test was firstly due to the  
307 dewatering of sediment specimen, as in the two other tests using CA. But in these testing  
308 conditions, the sediment particles were not as compressed (lower ionic strength) as in EK1  
309 and EK2 tests. Consequently, water could be transported freely through the whole sediment  
310 pores.

311 Figures 3b and 3c shows also that after 250 hours test, the variation rate of the cumulative  
312 EOF of EK 1 and EK 2 tests at anode side is greater than that of cathode side. When the curve  
313 slope of cumulative EOF at anode becomes close to that of cumulative EOF curve at cathode,  
314 rehydration of sediment specimen starts from the anode side (section 1). As mentioned,  
315 section 3 was dehydrated (small slope of EOF curve) and became compact, and water from  
316 the anode side could not easily pass through. That was observed when the specimen was cut  
317 into 4 slices after EK1 and EK2 tests, the section 1 being much wet than the other sections. A  
318 slight decrease of EOF on the cathode side is due to the water diffusion (osmosis) from the

319 cathode compartment to section 4 which is wetter than section 3. Differently, for EK 3, the  
320 EOF at cathode side was higher than that at anode side overall the test (figure 3d), indicating  
321 that no rehydration occurred. As the pH of section 1 after EK 3 test was not as low as in EK 1  
322 and EK 2 tests, the dehydration effect through EOF affected also section 1 which involved  
323 a global dehydration of the whole specimen. As a result, even though the section 1 of this test  
324 was slightly acidified, this section was not rehydrated from the anode and remained relatively  
325 dry compared to the sections 1 for tests using 0.2 mol/L of CA (tests EK 1 and EK2). This  
326 helps also to explain that the cumulative EOF at the cathode side (800 mL) in EK 3 test (Fig.  
327 3d) was much higher than in any other tests.

328 As noted previously, at the same concentration of 0.1 mol/L of chelating agent (EK 3 and EK  
329 4 tests), the weak acid (citric acid) produced a higher cumulative EOF than the weak base  
330 ( $\text{Na}_3\text{EDDS}$ ) (Fig. 3f). At the beginning phase, the sediment was over-saturated, the  
331 cumulative EOF in EK 4 test increased much rapidly than in EK 3 test because of a high pH  
332 environment and a more intensive electric current. It was reported (Pazos et al., 2010) that the  
333 electro-osmotic flow decreased as the concentration of surfactant increased. Moreover, a  
334 larger hydrated ionic radius of cations (such  $\text{Na}^+$  in EK 4) made the zêta potential less  
335 negative, leading to a smaller value of EOF (Kaya and Yeliz, 2005; Song et al., 2016).  
336 Finally, the cumulative EOF in EK 4 test could not be as great as in EK 3 test, but it was still  
337 higher than in EK0 test (water as electrolyte). Furthermore, the phenomena of dehydration  
338 and rehydration described before did not exist for EK4 test using EDDS, because  $\text{EDDSNa}_3$   
339 being a basic solution, the EOF overall the specimen sections was high without any  
340 fluctuation. So the cumulative EOF curves for both anode and cathode involved the same  
341 trend (Fig. 3e), and so the four slices after treatment were as humid as they were before.

342

### 343 **3.2 Organic contaminants in sediment after EK treatment**

### 344 3.2.1 Global removals of organic contaminants

345 The non-enhanced treatment (EK0 test) had no capacity to remediate neither PAHs nor  
346 PCBs because of their high hydrophobicity (Fan et al., 2014), while the highest removals of  
347 PAHs and PCBs were obtained in EK 2 and EK 3 tests, respectively (Table 2). According to  
348 Table 2, the PCBs removals were tightly related with the cumulative EOF at the cathode side  
349 of each EK test. The higher the cumulative EOF was, the higher the removal of PCBs was  
350 obtained. However, the PAHs seemed to be transported by surfactants. EK 4 was not efficient  
351 for PAHs remediation (Fig 4d), owing to the alkaline environment where saponin was  
352 charged negatively and so was unable to desorb the PAHs from a negatively charged sediment  
353 particle surface. The desorption of PCBs in EK 4 test was also less important than in EK 3  
354 test, even though the concentration of saponin in EK 4 was 10 times higher.

355 At the end of EK0 test, concentrations of PAHs and PCBs close to the anode (section 1) were  
356 higher than the initial values. Concentration (measured in mg per kg of solid material) raised  
357 because at anode side the carbonates fraction of sediment was dissolved by generated  $H^+$  ions.  
358 Maini et al. (2000) also reported that the concentration of PAHs at anode side was much  
359 higher than at central and cathode parts after 11 days treatment by applying an electric  
360 current of  $1280 \text{ mA m}^{-2}$ . But if considering organic amounts and not concentrations, we can  
361 note, as shown in Figure 4a and 4b (EK1 and EK2 tests), that they were markedly lower than  
362 the initial values in section 1. This indicates that PAHs and PCBs were not really better  
363 dissolved in the sections 1 and 2; in fact, section 3 contained the largest amount of PAHs (Fig.  
364 4b). This shows that there was actually a transfer of sediment particles (colloids) from the  
365 anode to the cathode during the EK treatment. However, section 2 involved the largest  
366 amount of PCBs instead of section 3 for PAHs and this result could be explained by the  
367 alkaline environment generated by the cathode. In fact, PCBs underwent a reductive  
368 dechlorinating process at cathode side, but as PAHs were not reduced, no obvious elimination



369 of PAHs was obtained at the cathode side unlike PCBs. So, PAHs amount in pore fluid did  
370 not decrease at the cathode side unlike PCBs (Lamichhane et al., 2016).

### 371 *3.2.2 Effect of different biosurfactants on contaminants removals*

372 Biosurfactants and citric acid combinations were effective for the elimination of  
373 neutral contaminants even with low EOF in the first two sections. This was probably due to a  
374 higher desorption of PAHs and PCBs and an increase of their bioavailability/solubility using  
375 these additives (Gill et al., 2014 ; Niqui-Arroyo and Ortega-Calvo, 2010 ; Gonzini et al.,  
376 2010). Furthermore, in EK 1 test, the first two sections involved better removals (in quantity)  
377 than the other sections because rhamnolipid was in its nonionic form (at  $\text{pH} \leq \text{pKa}$ ) and could  
378 desorb organic contaminants more easily and transport them to the cathode side (Fig. 4a). But  
379 PAHs and PCBs tended to accumulate in section 3 because they were transported toward the  
380 anode by the micelles of rhamnolipid, which were in their anionic form ( $\text{pH} > \text{pKa}$ ) (Fan et  
381 al., 2014; Pazos et al., 2011). Unlike EK1 test, the removal efficiency in EK 2 test decreased  
382 from anode to cathode and section 1 involved the most important removal of neutral organic  
383 contaminants than the other sections (Fig. 4b). This can be explained by the presence of the  
384 saponin, which was nonionic in the pH conditions overall the specimen and so, there was no  
385 opposite migration against EOF with the presence of 0.2 mol/L CA.

386 It can be added that the nonionic saponin had a smaller size of micelles than rhamnolipid in a  
387 CA solution. Anionic rhamnolipid molecules can form large micellar aggregates with a  
388 diameter of about 2.5  $\mu\text{m}$  at  $\text{pH} = 3$  (Lebron-Paler, 2008). These large aggregates could not  
389 entirely pass through the filter membrane (0.45  $\mu\text{m}$ ) which was used in this study.  
390 Consequently, there were fewer rhamnolipid micelles entering inside the sediment sample  
391 which so provided a less efficient removal result than using saponin. In addition, saponin is a  
392 nonionic surfactant (in acid condition) that may have more contact with negatively charged

393 sediment particles than anionic rhamnolipids. This means that saponin molecules could  
394 desorb PAHs and PCBs more easily. Consequently, saponin as nonionic biosurfactant  
395 appeared to be more potent than rhamnolipid (rather anionic) for organics decontamination,  
396 which was also proved by other researches (Iglesias et al., 2014).

### 397 *3.2.3 Effect of citric acid concentration on organic contaminants removal*

398 By comparing the two tests (EK 2 and EK 3) using saponin and CA, the best PAH-  
399 decontaminated section was found close to the anode by adding 0.2 mol/L CA (EK 2 test,  
400 section 1) or 0.1 mol/L CA (EK 3 test, section 1). In section 3 after EK3 test (Fig. 4c), there  
401 was a sharp decrease of PAHs and PCBs removals which was attributed to a relatively higher  
402 pH than that involved by 0.2 mol/L CA (EK2 test). More saponin molecules could become  
403 negatively charged in higher pH conditions and could migrate from the cathode toward the  
404 anode, and so had probably less capacity to desorb PAHs from sediment particles. This  
405 explains why the profiles of these two tests are completely different and why the total PAHs  
406 removal is lesser in EK3 test, especially because of the lesser removal of the PAHs in sections  
407 1 and 2.

408 Figure 4c shows that in EK 3 test the negatively charged saponin in sections 3 and 4 impacted  
409 also PCBs' migration (against EOF). However, due to the highest cumulative EOF, 0.1 mol/L  
410 CA as additive was able to remove the PCBs with the same migration profile as the test  
411 carried out with 0.2 mol.L<sup>-1</sup> of CA. When we analyze the cumulated EOF of the three saponin  
412 tests (EK 2, EK 3 and EK 4), the best removal of PCBs is obtained with the test involving the  
413 highest cumulative EOF (EK 3 test), while the lowest elimination of PCBs corresponds to the  
414 lowest cumulative EOF (EK 2 test). It is suggested that after being desorbed by the  
415 surfactants, PCBs, as polarized molecules, were then surrounded and transported by the pore  
416 fluid with EOF. It was also reported that in presence of surfactant, PCBs were transported via

417 EOF (Fan et al., 2014). Compared to PAHs, PCBs' migration depends relatively more on the  
418 pore fluid migration, while PAHs mobilization depends on the surfactant micelles migration.  
419 Accumulation of PCBs in sections close to the cathode was due to the increase of EOF at  
420 anode side and the decrease of EOF at cathode side during the later step of EK treatment (Fan  
421 et al., 2014). This explains why for all the tests PCBs had the tendency to migrate to the  
422 cathode. The case of EK 4 (Fig. 6d) test is singular because its EOF was homogeneous  
423 everywhere which gave a similar removal overall the specimen sections. Figures 6b and 6c  
424 show a similar removal of PAHs and PCBs in section 4 (cathode side) for both EK 2 and EK  
425 3 tests. This result demonstrates that in high pH (neutral) medium, anions such as  $CA^-$  and  
426 [saponin] $^-$  have limited capacity to desorb the hydrophobic organic contaminants.

#### 427 *3.2.4 Effect of chelating agents on organic contaminants removals*

428 In the case of EK 4 test (saponin + EDDS), saponin became negatively charged in the  
429 presence of EDDS in a solution at pH close to 8.9 (Navas-Camacho et al., 2001) and migrated  
430 toward the anode, as it was the case of rhamnolipid in EK 1 test. In addition, the negatively  
431 charged saponin could not efficiently desorb the PAHs from the sediment particles, leading to  
432 the less global removal of PAHs. In this test (EK4), even if the concentration of saponin was  
433 6 times higher than in EK 2 and EK 3 tests, the removal results were not improved but worse,  
434 providing only 11.4% of removal, while a good removal for PCBs (close to 42.7%) was  
435 reached. But compared with EK 2 test, this removal was not significantly improved even with  
436 a higher concentration of saponin and a greater EOF. Since the EOF of EK 4 test was  
437 hindered, compared to EK3 test, probably because of the higher concentration of saponin, the  
438 PCBs removal was lower. The PAHs and PCBs removals (Table 2) provide quite better  
439 results than those reported in literature when using similar additives for EK remediation of  
440 soil or dredged sediment (Gomes et al. 2014; Fan et al. 2014; Colacicco et al. 2010; Li et al.  
441 2009).

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### 443 **3.3 Heavy metals in sediment after the EK treatment**

#### 444 *3.3.1 Effect of citric acid concentration on metals removal*

445         Although CA prevented the apparition of a strong alkaline front in the sediment, its  
446 ability to chelate and solubilize metals was poor and increasing CA concentration in  
447 electrolyte (EK2 and EK3 tests) did not really improve metals removal (Table 2). The  
448 introduction of high amounts of the weak acid in electrolytes did not allow acidifying the  
449 sections near the cathode side, so metals remain probably in their precipitate form  
450 (hydroxides). The use of CA combined with biosurfactants as additives in EK1, EK2 and EK3  
451 tests improved the removal of Cd, Pb and Zn as regard to the reference test (Fig. 5 and Table  
452 2). However, this improvement remained limited and significantly lower than the results  
453 obtained by Ammami et al. (2015) when using as additives CA combined with Tween 20  
454 (EK6 Test, Table 2). It must be noted that even though the experimental conditions were  
455 similar in the two EK remediation experiments, the aged sediment used by Ammami et al.  
456 (2015) involved lower organic matter and carbonates contents and also a high redox (105 mV)  
457 potential (sediment oxidation occurred after the long time land deposit). In our study, the  
458 sediment was directly collected from a harbor channel and had a negative redox potential (-76  
459 mV), and so was a reduced material. In reduced conditions, metals can form complexes with  
460 sulfur, which are known to be immobile in such reduced sediment fractions, even at  $\text{pH} < 3$   
461 (Reddy and Cameselle, 2009; Li et al., 2016). As regards to Cu and Cr removal, CA seemed  
462 to be inefficient for moving Cu and even provided a negative effect on Cr recovery, compared  
463 to the result obtained with pure water (EK0 test). Indeed, under alkaline pH (which was the  
464 case for EK0 test), Cr did not precipitate as a metal hydroxide and formed Cr(VI) which was  
465 soluble and mobile, able to migrate toward the anode. So, the adsorption of Cr(VI) was

466 negligible in an alkaline soil involving a high buffering capacity. But in acid conditions, the  
467 anionic forms of Cr(VI) were reduced as Cr(III) (Reddy, 2013) and could form complexes  
468 with CA which migrate toward the anode. To conclude, CA affected only moderately the  
469 metals removal, leading to overall quite better removal scores than using pure water (excepted  
470 Cr).

### 471 *3.3.2 Effect of chelating agents on metals removals*

472 The addition of CA in the cathode compartment (EK7 test) provided much better  
473 metals removal than in the reference test EK0 and EK3 test (Table 2). In this last test, the  
474 presence of saponin seemed to inhibit metals removal. If comparing the removal effect of CA  
475 and EDDS as chelating agents, overall, EDDS did not provide a significant improvement as  
476 shown on Figure 7, which illustrates the distribution of metals along the specimen after tests.  
477 However, the removal efficiency of Pb (14.4%) and Cr (75.8%) was also improved by using  
478 EDDS as electrolyte, indicating that the formation of Pb-EDDS complexes facilitated the  
479 solubilization of Pb (Suzuki et al., 2014) and Cr did not precipitate as a metal hydroxide and  
480 formed Cr(VI) which was soluble and mobile. So, EDDS seemed to be a stronger chelating  
481 agent for Pb, more than CA, in alkaline conditions. Even though Pb removal was improved  
482 through EK 4 test, 85% of this metal remained in the sediment after treatment, indicating that  
483 only exchangeable or mobile fractions of Pb could be removed by chelation with EDDS. In  
484 the case of Zn, it remained in immobile form: its chelation was inefficient by the use of CA or  
485 EDDS. Kim et al. (2011) reported that Cu and Zn complexes in the presence of CA could be  
486 easily substituted by Fe (III) and Ca(II) ions present in large amounts in the sediment. The  
487 competition was not in favor of Cu or Zn, so soluble complexes were not formed and they  
488 remained in their precipitated immobile form. Results (Fig. 5c) showed also that Cd migration  
489 in the specimen during EK 4 test (in presence of EDDS) was opposite to that recorded in EK  
490 3 test (in presence of CA). This was due to the fewer Cd<sup>2+</sup> cations moving toward the cathode.

491 The best removal (75.8%) overall for the metals was obtained for Cr in the EK 4 test (table 2) owing  
492 to the alkaline conditions allowed by EDDS and forming Cr(VI) soluble and mobile. So,  
493 EDDS seems to be a strong chelating agent for Pb and Cr, more than CA. Figure 5c shows also  
494 that Cu accumulates in section 1 (close to the anode) when EDDS is used as additive.

495 Table 2 below summarizes organic and inorganic pollutant removals obtained after all EK  
496 tests carried out in different conditions and also energy consumption during the test. The best  
497 removal of PAHs was obtained from the EK test performed on an aged sediment (collected  
498 after a long time land deposit) using Tween 20 and CA as additives, while the removal of  
499 PCBs was enhanced by the use of saponin and CA. As regards metal removal, each metal  
500 reacted differently to a given combination of additives and the best removals (over 50%) were  
501 obtained for Cr and Zn when enhancing agents were CA and EDDS, respectively. Globally,  
502 the oxidized aged sediment seemed to be more able to release metal pollutants than the fresh  
503 dredged sediment. If comparing these results with those reported in literature, metal  
504 removals are quite similar to those provided by the combination of EDTA and Tween80  
505 (Colacicco et al. 2010; Pazos et al. 2013) where more energy was consumed (electric field  
506 higher than 1 V/cm) and longer treatment. But the metal removals provided by these  
507 experiments are better than that reported by Iannelli et al. (2015) from large scale tests using  
508 strong acids and a longer treatment. In addition, the approach used in this study aims to  
509 perform a sustainable EK treatment by reducing the consumed energy and using friendly  
510 environment additives. The values of energy consumption reported on Table 2 show that  
511 efficient lowering of pollutant concentration and sustainable remediation can be achieved  
512 with a moderate energy cost (200 kWh/Ton), without including additive cost which could  
513 strongly fluctuate. In addition, this amount of energy can be supplied in site by renewable  
514 energy plant and additives may be selected as eco-friendly chelating agents and bio-  
515 surfactants in order to perform a sustainable sediment remediation.

### 516 **3.4 Toxic effect of EK-treated sediment on Eurytemora affinis**

517 The investigation of the impact of EK treatment on toxicity sediment aims to assess if  
518 treated sediments could be used in coastal and marine management without involving more  
519 toxicity. *E. affinis* copepods are suitable organisms for testing ecotoxicity in bio evaluation  
520 because of their short life cycle and their particular sensitivity to chemicals. The bioassay was  
521 conducted by incubating male copepods with aqueous elutriates of sediments for 96h and  
522 monitoring mortality every day. Analysis of variance and Fisher's tests were performed to  
523 determine significant differences between the lethal toxicity of the control medium, the initial  
524 raw sediment elutriate and the treated sediment subsamples obtained from the sections S1, S2,  
525 S3 and S4 after each EK test. The results showed that the longer was the contact time with the  
526 sediment aqueous extract, the more was the lethal effect on copepods. After EK1 test, the S2  
527 section was the most toxic one with significant higher mortality even after the shortest contact  
528 times. However, the toxicity of sediment treated with CA and saponin (EK2 test) was very  
529 different from that treated with CA and rhamnolipid (EK1 test): for EK2, section S1 was the  
530 most lethal. The EK3 run led to a significant increase of the mortality in elutriates from  
531 sections S2 and S4, but only after a long exposure. For EK4 test, all the four sections, S1 to  
532 S4, were lethal whatever the exposure time. It appeared that the mortality of copepods after  
533 EK treatments could depend on various factors: the additives used as enhancing agents, the  
534 pH of the sediment and probably the contaminants levels after each EK test. After compiling  
535 all the results of toxicity tests, and examining various statistical analysis for emerging  
536 statistically significant results, it appeared some interesting conclusions:

537 First, using eco-friendly enhancing additives composed of a mixture of citric acid and  
538 biosurfactants (saponin or rhamnolipids at low concentrations) did not induce an excess  
539 mortality on *E. affinis* copepods, used as a toxicity bioassay, which was a positive criteria.  
540 Test EK4 provided high copepod mortality (after only 48h exposure) and so a great toxicity

541 overall specimen sections. The mortality reached 100% in section 1 after 24 hours of  
542 exposure (Fig. 6). So, the combination of EDDS (0.1 mol/ L) and saponin at high  
543 concentration (5 g/L) was very toxic for all investigated specimen sections. In the case of EK  
544 test using the synthetic surfactant Tween 20 at very low concentration (0.004M) and CA (0.1  
545 M), it involved the lower toxicity among all the EK tests even though many sections  
546 presented a slightly higher mortality (but not significantly) than that recorded for initial  
547 sediment (Fig. 6).

548 Second, the S1 and S2 sections of EK1 and EK2 tests appeared lethal for copepods because of  
549 the significant decrease of the pH in these sections near the anode ( $\text{pH} < 4$ ), which was not  
550 favorable for copepods survival.

#### 551 **4. Conclusions**

552 The electrokinetic remediation studies reported in this paper investigated the  
553 efficiency of different enhancing additives (chelating agents, surfactants and biosurfactants)  
554 on the removal of contaminants (metals, PAHs and PCBs) from fresh and formerly deposited  
555 sediments. The results showed that mixtures of a biodegradable chelating agent (citric acid)  
556 combined with biosurfactants (rhamnolipids, saponin) or the synthetic Tween 20 are  
557 promising candidates for EK multi-decontamination because they did not induce ecotoxicity  
558 after EK treatment. Longer treatment time for clay and carbonate rich sediments seemed  
559 necessary for reaching significant contaminants removal, because of the important buffering  
560 effect of carbonates, which delayed the acidification of the sediment specimen. Saponin was  
561 more efficient than Rhamnolipid because of its nonionic and head/tail ratio (smaller size of  
562 micelles) characteristics. Citric acid combined with nonionic surfactants provided a  
563 significant improvement of pollutants removal. Citric acid may not be the best biocompatible  
564 chelating agent but in moderate concentration, it could provide an interesting efficiency.  
565 However, each additives combination must be adapted to targeted pollutants. The use of



566 environment friendly additives and low voltage led to a sustainable remediation. Indeed, the  
567 association of an aged contamination, a high buffering capacity of the sediment, a very low  
568 hydraulic permeability and a high organic matter content made the citric acid enhancing agent  
569 not achieving sediment acidification and metal chelation. Moreover, even if the nonionic  
570 saponin was better than the anionic rhamnolipid, its concentration was not sufficient, acid  
571 dissolution of organic matter was too poor to allow quantitative PAH, and PCB desorption  
572 and transport.

573         The electrokinetic remediation studies reported in this paper investigated the  
574 efficiency of different enhancing additives (chelating agents and biosurfactants) in the  
575 removal of contaminants (metals, PAHs and PCBs) from fresh and deposited sediments. The  
576 results show that mixtures of biodegradable chelating agents combined with biosurfactants are  
577 promising candidates for EK multi-decontamination. Longer treatment time for clay and  
578 carbonate rich sediments is necessary for reaching significant contaminants removal. Saponin  
579 is more efficient than rhamnolipid because of its nonionic and head/tail ratio (smaller size of  
580 micelles) characteristics. Citric acid combined with nonionic surfactant provides a good  
581 improvement of pollutants removal. Citric Acid may not be the best biocompatible chelating  
582 agent but in moderate concentration it can provide an interesting efficiency. Moreover, even if  
583 the nonionic saponin was better than the anionic rhamnolipid, its concentration was not  
584 sufficient, acid dissolution of organic matter was too poor to allow quantitative PAH, and  
585 PCB desorption and transport.

586         As regards to the toxic effect of EK treatment on copepods, EK treated sediments  
587 appeared statistically more toxic than the raw sediment, because metals probably changed of  
588 mineralogical speciation (particularly Cu and Pb) and became more easily leachable. So it  
589 appears that the bioavailability of contaminants is a better parameter to consider than total  
590 concentration to assess sediment toxicity.

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752 **Table 1.** Summary of performed tests parameters

Test	Voltage (V/cm)	Anolyte	Catholyte	Duration (days)
EK0	1 (5d on / 2d off)	Pure water	Pure water	28
EK1	1 (5d on / 2d off)	Rhamnolipid (1.1 g/L) + Citric	Rhamnolipid (1.1 g/L) + Citric	28



	off)	Acid (0.2M)	Acid (0.2M)	
EK2	1 (5d on / 2d off)	Saponin (0.85 g/L) + Citric Acid (0.2M)	Saponin (0.85 g/L) + Citric Acid (0.2M)	28
EK3	1 (5d on / 2d off)	Saponin (0.85 g/L) + Citric Acid (0.1M)	Saponin (0.85 g/L) + Citric Acid (0.1M)	28
EK4	1 (5d on / 2d off)	Saponin (5 g/L) + EDDS (0.1M)	Saponin (5 g/L) + EDDS (0.1M)	28
EK5 <sup>a</sup>	1 (continuous)	Tween 20 (0.004M) + Citric Acid (1M)	Tween 20 (0.004M) + Citric Acid (1M)	22
EK6 <sup>a</sup>	1 (5d on / 2d off)	Tween 20 (0.004M) + Citric Acid 0.1M)	Tween 20 (0.004M)+ Citric Acid (0.1M)	24
EK7	1 (continuous)	Pure water	Citric Acid (1M)	21

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758 **Table 2.** Summarized removals of organic and inorganic pollutants and average energy consumption

759 from EK tests

Test	Removals (%)							Energy Consumption (kWh/ton)
	Cd	Cr	Cu	Pb	Zn	Σ16PAH	Σ7PCB	

EK0	4.5	34.5	6.6	2.1	0	0.6	0	189.47
EK1	9.1	17.9	5.9	2.9	3.1	17.4	25.1	281.57
EK2	14.4	15.8	5.7	4.4	5.8	29.2	38.2	313.15
EK3	12.7	27.8	1.6	5.3	1.9	13.1	50.2	221.05
EK4	12	75.8	2.0	14.4	3.1	5.2	38.7	568.42
EK5 <sup>a</sup>	38,6	8,48	8,67	33,39	51,60	54.4	-	352.63
EK6 <sup>a</sup>	34,93	8,49	5,60	28,84	50,18	48.1	-	205.26
EK7	24.3	45.1	36.4	12.5	20.1	-	-	221.05

760 <sup>a</sup> Aged sediment

## **Abstract**

This paper aims to present a contribution to the debate on learning styles and the learning process discussing some classic learning styles theories: Kolb's experiential learning theory and learning style model, Honey and Munford's Learning Style Model, Felder and Silverman's learning styles and the VARK model. We propose to link them with the learning process by exploring knowledge derived from other areas, such as Biology and the Neurosciences, to broaden the horizons of understanding on the subject. This reflection was developed as part of the ERASMUS+ research project IC-ENGLISH – Innovative Platform for Adult Language Education. After exploring theories, we present a brief view of the interconnection in the cerebral cortex to support our conclusions, suggesting an integration of learning styles approaches for a more successful learning process.

**Keywords:** learning styles, learning process, interconnection, cerebral cortex.

## **Introduction**

Learning, in the strict sense of the term, is an essential process for human beings, for cultures and for the success of educational systems. Formal education integrates the subjects to their environment, enables the development of cognitive and social skills, gives access to the cultural heritage accumulated by the history of humanity, and enables the advancement of this heritage, through the creation of new knowledge.

With the recent advances and the debate over lifelong learning, formal adult education has gained space, as well as interest, in the mechanisms underlying the learning process of this audience. Nowadays, it is widely accepted that people use different avenues to learn; have preferences for different stimuli and that they facilitate the learning process. Thus, while some are comfortable with written texts, readings, debates, and written output, others prefer images, videos, drawings, schemes, or practical, reality-centered tasks with a concrete purpose.

According to Cassidy (2004), in the last four decades, many studies have been conducted on learning styles. Coffield, Moseley, Hall, and Ecclestone (2004) identified more than 70 learning styles theories developed in the three decades preceding the study. These theories, in most cases, correspond to questionnaires, applied on a large scale by the industry, to identify students' learning styles, the relationship between students' and teachers' learning styles (Naimie, Siraj, Piaw, Shagholi & Abuzaid, 2010; Massa & Mayer 2006; Tuan 2011; Awla, 2014) whether by physical or virtual means. Among the best known are Dunn and Dunn's (1990) Learning Styles Model, Kolb's (1984, 1985) Learning Styles Inventory, and Honey and Mumford's (1992) Learning Styles Questionnaire.

With the wide dissemination of questionnaires, the expression "learning styles" has received different concepts and approaches, according to the focus chosen by its students (Kazu, 2009), as well as strong criticism of the scientific evidence of the correlation between learning styles, methodological choice and improvement of learning (Pashler, McDaniel, Rohrer & Bjork, 2008, Scott, 2010). There are also expressions used as synonyms, but which designate different processes. In this sense, when reviewing the literature in the area, it is common to find terms like learning style and cognitive style used as synonyms. However, they have different meanings and relate to different levels in the learning process. According to James and Gardner (1995, p. 20),

learning styles is "the complex manner in which, learners most effectively perceive, process, store, and recall what they are attempting to learn". Conversely, cognitive style refers to "an individuals' natural, habitual, and preferred way (s) of absorbing, processing and retaining new information and skills" (Reid, 1995: viii).

Learning styles corresponds to "generalized differences in learning orientation based on the degree to which people emphasize the four modes of learning process" (Kolb, 1984, p.76). Among the various concepts available, we will use Kolb's (1984) here for the theoretical support that precedes it and that we present below.

## **1 Kolb's Experiential Learning Theory and Learning Styles Model**

Kolb's learning styles model is supported by Kolb's Experiential Learning Theory (ELT), a comprehensive theory of learning and adult development. Kolb (1984), Kolb and Kolb (2013) explain that ELT is built on propositions of some prominent scholars, namely John Dewey, Kurt Lewin, Jean Piaget, Lev Vygotsky, William James, Carl Jung, Paulo Freire, Carl Rogers and Mary Parker Follet.

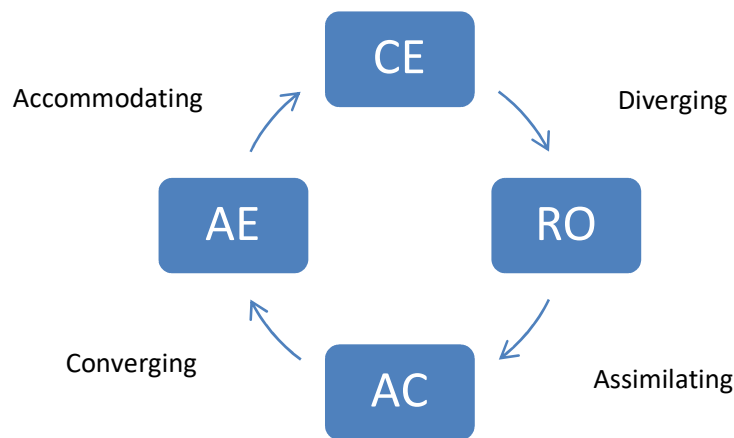
For Kolb (1984) and Kolb and Kolb (2013) learning should be considered a process and not only for the results obtained. It is facilitated when students have the opportunity to test and retest their beliefs, knowledge and ideas on a given topic, and add new and refined ideas. Learning is a holistic process of adaptation to the world that requires the ability to resolve dialectically conflicts between modes of adaptation to the world - reflection / action and feeling / thinking. Learning is therefore

the process of knowledge creation which requires the synergy between social knowledge and personal knowledge.

In the historical-cultural postulate of learning in which the theory is inserted, Kolb (1984) uses the Vygotskian concept of Proximal Development Zone to ground a new concept, that of 'experiential learning', directed towards adult learning. This concept is based on the assumption that learning is built from the experience lived in context, in interaction with the knowledge that each individual has already accumulated at a given moment. Human beings live integrated in natural, cultural and historical environments that give them the necessary elements to enable them to construct their knowledge. In this framework, experiences can be transformed into learning and this, in turn, expands the knowledge that each one already has. However, not every experience results in learning. Learning is a mental process oriented toward a purpose, which requires conscious reflection. Learning is "the process whereby knowledge is created through the transformation of experience. Knowledge results from the combination of grasping and transforming experience."(Kolb, 1984, p.41).

From these assumptions, Kolb (1984) then presents an explanatory structural model of learning and an instrument of identification of learning styles, directed to the formation of adult professionals, known as the Kolb cycle, as can be seen in Figure 1.

**Fig 1.** Kolb's experiential learning cycle



Source: adapted from Kolb (1984), Kolb and Kolb (2013).

As seen in the diagram, Kolb's experiential learning cycle represents an ideal dynamic view of learning, oriented toward dialectically resolving the two opposite forms of experiencing (reflection / action) and transforming experiences into knowledge (feeling / thinking).

**1. Concrete experience** - (feeling) refers to the contact with concrete problems to be solved, referenced in the accumulated world knowledge and already developed mental structures;

**2. Reflective observation** - consists of the internal action of identifying characteristics, grouping and organizing information, establishing connections, searching for similar concepts, analyzing information that contributes to the solution of the problem.

**3. Abstract conceptualization** - (thinking) here is where concepts are formed and generalized, from the comparison with similar realities, which results in a synthesized set of knowledge about the problem.

**4. Active experimentation** - is the external application, in unpublished practical actions, of the experiences felt, reflected and conceptualized in the previous phases of the cycle.

The combination of cycle modes gives rise to Kolb's learning styles and Kolb Learning Styles Inventory - LSI - (Kolb, 1971, 1976) in its various versions (Kolb, 1985, 1999, Kolb & Kolb, 2013).

A learning style is therefore the combination of preferences among the four modes of learning; the point at which the learner enters the learning cycle, that is, the individual way in which each individual combines the two modes of experience / reflection / action and turns it into knowledge (feeling / thinking). Since learning is here considered a process, in construction and continuous reconstruction, which occurs through the interaction of the individual's knowledge with the knowledge of the environment, the learning style is not a fixed psychological or cognitive trait, but rather the result of the interaction between the person and the environment (Kolb & Kolb, 2013). Kolb detects the following styles:

**Diverging** - the learning style derived from the CE / RO combination. Individuals with this style have a preference for visual stimuli, concrete situations, combined with diverse information. They feel comfortable with group work, discussion and constant feedback.

**Assimilating** - characterized by the preference for visual and mental (RO / AC) stimuli. Learners with this style deal more easily with analysis, explanations, theories, texts and all kinds of material that allow analysis and reflection.

**Converging** - is the learning style of people who identify with practical tasks and deductive reasoning to solve a given problem (AC / AE). These learners have a preference for direct and practical guidance and learning tasks.

**Accommodating** - is the learning style identified by the preference for making plans, projecting the future, creating prospects for situations, from stimuli involving thinking and doing (AE / CE).



Individuals with this style handle challenging activities easily, take risks, and solve problems intuitively (Kara, 2009).

## **2 Honey and Munford's Learning Styles Model**

Kolb's (1984) experiential learning theory and his model of learning styles are the foundations for the learning styles model developed by Honey and Munford (1992). The Honey and Munford Model - Learning Styles Questionnaire - LSQ - establishes learning styles from the strategies used by learners to capture and transform information. They are: Activist, Reflector, Theorist and Pragmatic, corresponding to the AE, RO, AC and CE strategies of the Kolb cycle, respectively.

**Activist** learners learn best in situations of concrete action, where experimentation, learning by making mistakes and being correct is favored. Group discussion activities, problem-solving, puzzles and brainstorming are stimuli that favor the learning of activist individuals.

**Reflectors** share a style of learning that prefers a combination of observation and thinking to learn. They consider many possibilities and implications in an act before taking a decision. Activities that give them time to investigate and think, go back and observe, review what happened, without deadlines, are preferred by reflectors.

**Theorist** learners are more comfortable with learning from explanatory models, theories, statistical data, analysis and synthesis. These learners need to understand the logic behind the actions. Activities of discussion, reading, case studies, with stimuli that allow them time to think, seek

theoretical explanations, formulate models and base problem solving are the most suitable for these learners.

**Pragmatist** learners apply to practice analytical knowledge to create new things and solve problems. Activities with a clear link between topic and real need, techniques applied to current problems and clear guidelines offer the stimulus preferred by pragmatists.

### **3 Felder and Silverman's learning styles**

Felder and Silverman (1988) developed an instrument to identify learning styles, i.e. the Index of Learning Styles (ILS). These authors consider learning styles to be the preferences and qualities of individuals as they receive and process information. Thus, they established a model that measures the approximation of preferences between the categories Active / Reflective, Sensitive / Intuitive, Visual / Verbal, Sequential / Verbal using a pre-established scale. The ILS underwent several reformulations, which resulted in the design of a questionnaire (Felder & Soloman, 1991) to identify students' learning styles in the four categories previously identified by Felder and Silverman (1988). In 1997, the instrument was made available on the Internet for free use (Schmitt & Domingues, 2016).

The pairs of learning styles established by ILS are:

**Active** – these learners prefer to work in a group, strive for learning from actions; or **Passive** - prefer to work alone or in small groups; learn better by thinking about the problems/issues before them.

**Sensitive** – these learners prefer the concrete, the sensitive, the real facts; or **Intuitive** - these are more conceptual, like theories, explanations and syntheses.

**Visual** – these learners prefer activities involving images, visual representations; or **Verbal** - prefer written information, reading and commentary.

**Sequential** – these learners prefer processes segmented into well-defined parts that follow linear thinking; or **Global** - need a holistic perspective to process the information.

#### **4 The VARK model**

Another instrument developed to identify students' learning styles and to enhance their learning was developed by Fleming (2001), based on mapping learning styles. According to this author, the VARK technique - Visual, Aural, Read, Kinesthetic - corresponds to the four channels used by individuals to receive and process information:

**Visual** – individuals who favour the visual aspect learn best from pictorial information and descriptions such as drawings, graphics, and images. They organize the reasoning better with the use of lists and diagrams. For these learners, the most indicated activities are lectures, slide presentations, diagrams, graphics, videos and images, resolution of exercises, surveys or any other materials that contain visual information.

**Aural** - these individuals use the auditory pathway to learn better. They prefer information with sounds and audio guidance, such as spoken instructions, discussions, oral presentations, conversations, music, audio and video information, music and role plays.

**Read / writing** - learners using this style prefer written and reading information as a means of learning. They usually resort to notes, diagrams and all sorts of writing to learn better. Activities involving texts, reading, abstraction production, essays, articles, comments or any other type of written stimuli are preferred by these individuals.

**Kinesthetic** - People with this learning style need movement, sensory touch and interaction with the environment to acquire information and create knowledge. Activities such as hands-on classes, problem solving, case studies, demonstrations or physical activities are best suited for learners using this pathway.

## **5 Integrating approaches**

The discussion about learning styles and the effectiveness of their identification to improve learning may have in Biology and Neuroscience points of common interest for a broader dialogue. Although they are different areas from those that focus on the topic of learning styles, the knowledge produced there can contribute to the enrichment of what we know about the complex process that is human learning.

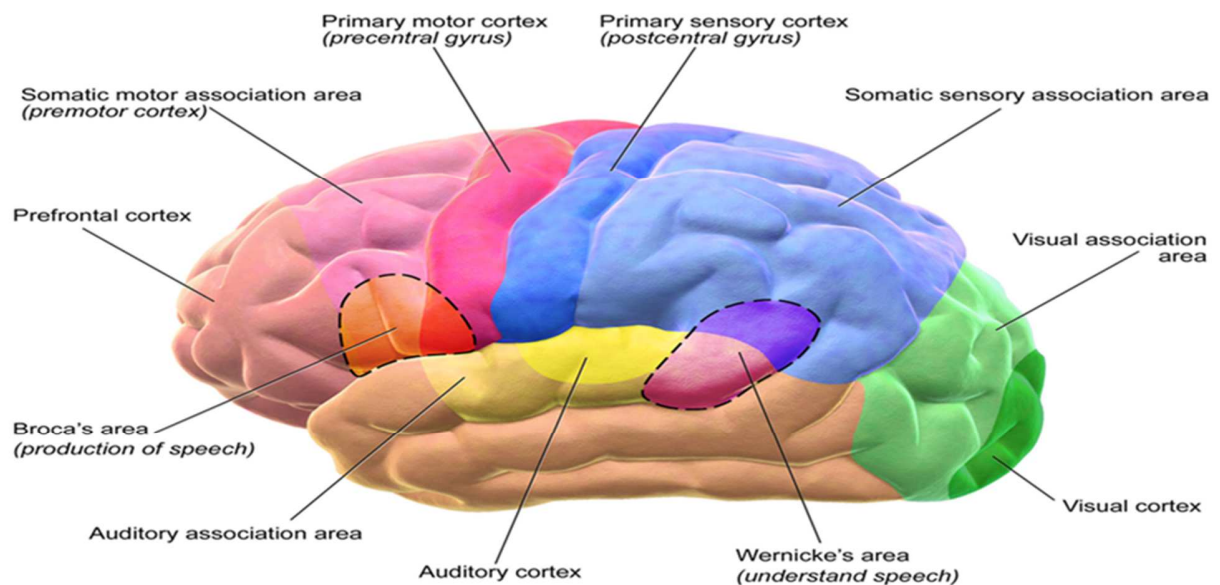
Much is known today about brain structure and its functioning, although scholars in the field recognize that they are still at the beginning of this discovery process, and that there is much more to know.

In terms of structure, Biology has divided the human brain into overlapping layers with distinct functions. The most superficial layer is the cerebral cortex, which is divided into large areas,

responsible for processing the external stimuli that are captured by the sense organs, as shown in Figure 2.

Figure 2

## Motor and Sensory Regions of the Cerebral Cortex



Source: Blausen.com staff (2014). "Medical gallery of Blausen Medical 2014". WikiJournal of Medicine 1 (2).

Each part of our cerebral cortex specializes in receiving and processing stimuli coming from different external points, and then producing an output. As seen in Figure 2 above, at the back of the brain is the visual cortex, responsible for image recognition and formation; next to it is Wernicke's area, responsible for understanding spoken or written words. This, in turn, is connected to the auditory cortex, which receives and processes sound information in general. Further ahead is Broca's area, the part responsible for speech articulation; it is here where the muscles are

activated for the production of speech. The higher mental functions (concentration, planning, judgment, expression of emotions, creativity) are processed in the prefrontal cortex, while the motor cortex processes and activates motor actions and the sensory cortex takes care of sensitive information.

Note that specific cortexes (visual, auditory, sensory, motor) integrate broader regions, areas of visual, auditory, motor and sensory association, respectively; that is, there are specific centers for the different information, but these work within a broader specific area. It is this integration that enables, for example, recognition of forms or texture, understanding language signs, planning motor actions and modulating sensory impulses (Orhan & Arslan, 2016). Despite the specialty of each of the areas, it is known that they work intensely interconnected to transform the information captured by the sense organs into knowledge.

In a simplified example of the path between an auditory input and the verbal output equivalent to the question "What day is it?" and an appropriate answer, we would have the following process:

1. The sound is picked up by the auditory area and sent to Wernicke's area, where the comprehension of the spoken language is processed, namely, the meaning of the words, their sequence in the sentence. In order to do so, 2. memory is used, that is, knowledge already accumulated about the language and the world. Next, 3. the motor area and Broca's area come into play, which voluntarily trigger a set of muscles in the throat and face to vocalize the appropriate response.

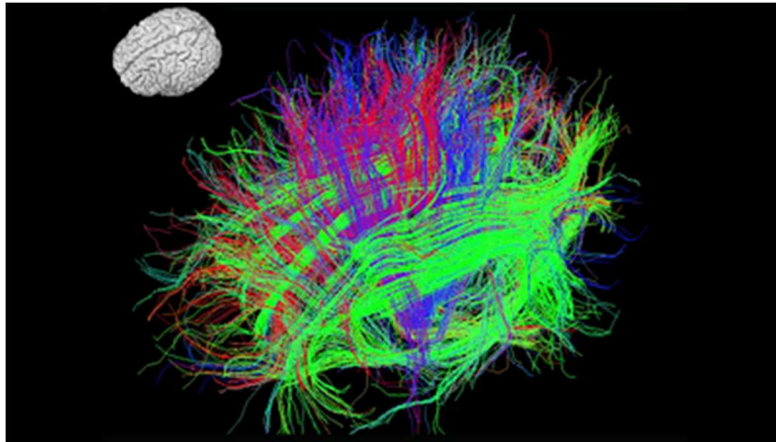
The interconnection between the areas of the brain is confirmed by studies in Neuroscience. Research carried out by Dehaene et al. (1999) on exact sums (e.g.  $3 + 4 = 7$ ) point to the activation of the left-lateralised area in the inferior frontal lobe, an area of the brain commonly associated with language. Conversely, when the sum was approximate (e.g.  $3 + 4 = 8$ ), this area did not show

any activity. According to the researchers, this is because exact sums involve the retrieval of knowledge on the number intensively acquired previously. This information is usually stored in the areas of the brain responsible for language.

Another study conducted by Shaywitz and Shaywitz (2005), on young adults followed longitudinally, found different types of neural paths to support reading. The authors used brain images to analyse the neural connections of three groups: 1. persistently poor readers (PPR) thus named for their low reading skills at the beginning of the study, in the 2<sup>nd</sup> and 4<sup>th</sup> grades, and at the end, in 9<sup>th</sup> and 10<sup>th</sup> grade. 2. accuracy-improved poor readers (AIR), thus characterised for meeting the criteria for poor reading at the beginning of the study, but not at the end; and 3. nonimpaired readers (NIR), those who showed no evidence of poor reading performance at any stage of the study. Analysing the brain connections developed by the three groups, the researchers found different neural paths: NRI readers demonstrated connectivity between the left hemisphere posterior and anterior reading systems. In contrast, PPR readers showed connectivity between the left posterior reading systems and right prefrontal areas often associated with working memory and memory retrieval.

In Figure 3, we can see a suggestive image of how interconnection between the areas of the brain works.

**Figure 3.** Interconnections in the brain



Source: Damásio, H. (s.d.) cited by Damásio, A. (2019).

The image, produced from the observation of a living brain, shows the constant intercommunication between the various parts of the brain, characteristic of brain activity. The lines, in figurative colors, indicate the direction of the movements of said activity and suggest the connection between the various parts of the brain in information processing. This intense activity continually enlarges and modifies the brain itself and its ability to learn.

The ability to change from experience at structural, functional and morphological levels is called cerebral plasticity (Hebb, 1949; Kolb & Wishaw, 1998; Kandel, Schwartz, Jessel, Siegelbaim, & Hudspeth, 2013). Although the foundations for the concept of brain plasticity were first mentioned in the 19th century by James (1892, p. 135) when he spoke of the “organic matter, especially nervous tissue, seems endowed with a very extraordinary degree of plasticity”, it was technological development which allowed Neuroscience to observe, through images, changes in the brain structure, in the neurons and in the interconnectivity between areas of the brain (Rees, Booth & Jones, 2016).



The changes in brain structure derived from the ageing of the organism in childhood and adolescence, known as sensitive periods (Knowland & Thomas, 2014), were noted in various studies. Giedd et al. (1999) suggested, from a longitudinal study they conducted, that the volume of the brain only reaches its peak at the age of 14.5 years for boys and 11.5 years for girls. Other studies indicate that the volume of grey matter mass and of white matter mass changes during childhood (Lenroot & Giedd, 2006; Schmithorst & Yuan, 2010) and increases during the shift from to adolescence and adulthood (Giorgio et al., 2010).

Nevertheless, other than in the sensitive periods, the brain ability to change depending on the environment persists throughout life, albeit less intensely intensidade (Knowland & Thomas, 2014). In a study conducted by Draganski et al. (2004) on young adults, a significant increase in the volume of grey mass was observed in both brain hemispheres in areas that connect sight and motor control after three months of juggling practice. Also, after three months of the subject not training, the volume of that area went back to the initial level. Dehaene et al. (2010a, b) observed the brain activity of three groups of subjects: literate since childhood, illiterate and literate in adulthood. The researchers noted that a brain area related to image recognition (VWFA) was more active in the illiterate and the literate in adulthood than in the literate since childhood. Both studies are suggestive of the impact that learning a new skill – be it motor or cognitive – can have in changing the brain structure.

## **Conclusion**

In this paper, we present the concept of learning styles and their theoretical foundations based on the theory of experiential learning by Kolb (1984). Among the many instruments for identifying

learning styles, we chose to present LSI (Kolb, 1971, 1976), LSQ (Honey & Mumford, 1992), ILS (Felder & Silverman, 1988) and VARK (Fleming, 2001) due to their similarity in the conception of learning and the theoretical paradigm that supports them.

Also, we have established a link between the learning styles and the knowledge coming from Biology and the Neurosciences, in order to broaden the debate on the subject. From the theories and models presented, we draw some considerations that can contribute to the debate about the topic among teachers.

1. In order to learn, we use different external channels, through which we capture information, which is then processed internally in articulation with the knowledge we already have, the environment and the time in which we live. Although they are not discussed in this text, we add here the widely known psychological and affective issues involved in learning.

2. With this we highlight the individuality of the process and the paths chosen by each subject in the construction of knowledge. For students, knowing their learning style can help them make learning more attractive by prioritizing how they organize their activities and the types of input they are more stimulated by. For teachers, recognizing that there are different ways of learning favors a change in the very conception of learning and the traditional model of education, which is almost always rooted in an approach to didactics that prioritizes visual and auditory information.

3. The knowledge that we offer today, coming from the constructivist and socio-interactionist learning theories, articulated with new developments in Biology and the Neurosciences, indicate that learning happens through the continuous interaction of endogenous and exogenous factors. The process changes, because it changes the accumulated knowledge and, with it, individuals' own learning ability and strategies.

Based on this analysis, it seems therefore restrictive to choose a single learning style, in other words, to focus on a single type of stimulus for the organization of learning activities as a presupposition for better learning. While recognizing individuality and the preferences of the subject, providing students with different stimuli, equivalent to the various styles explained here, will constitute the most appropriate methodology to the construction of learning.

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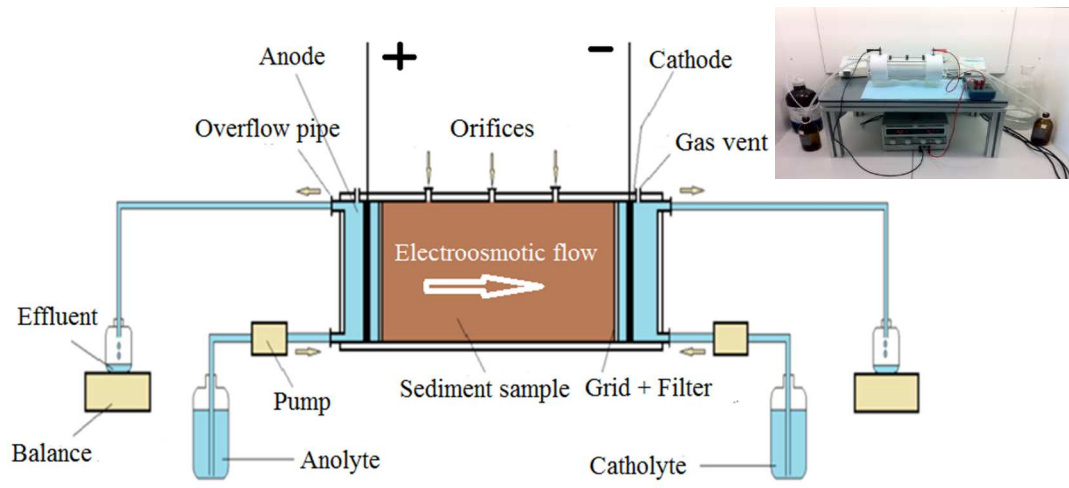


Fig.1



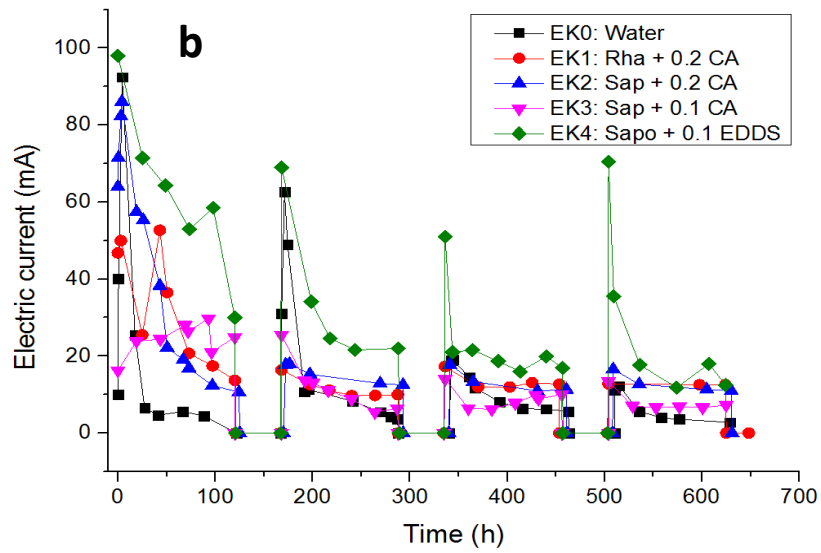
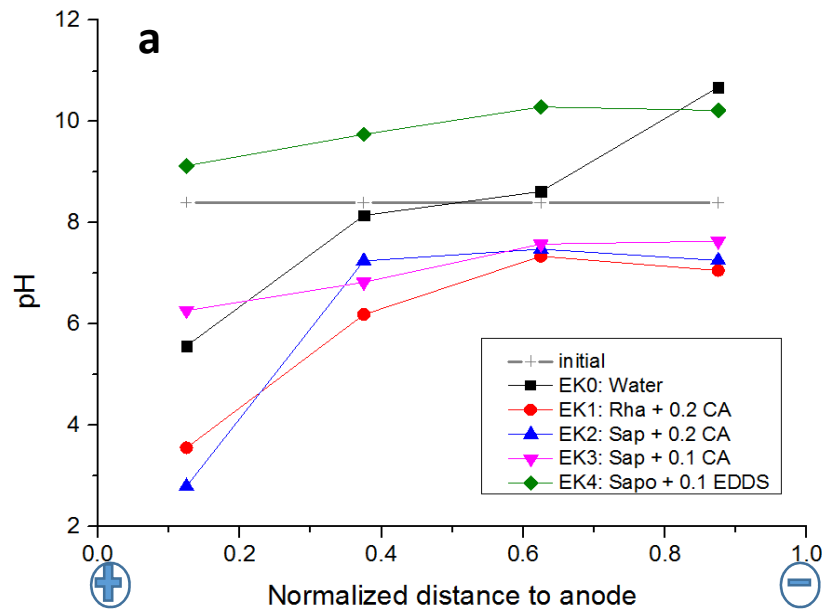


Fig. 2

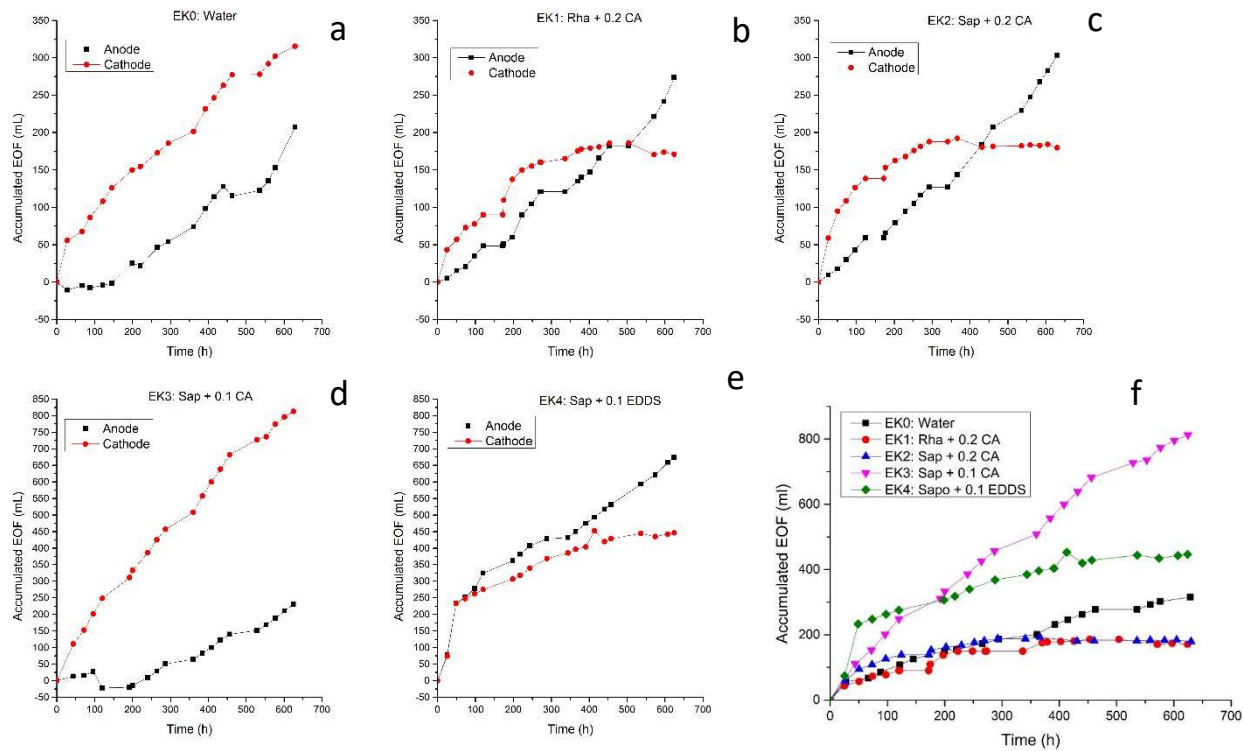


Fig. 3

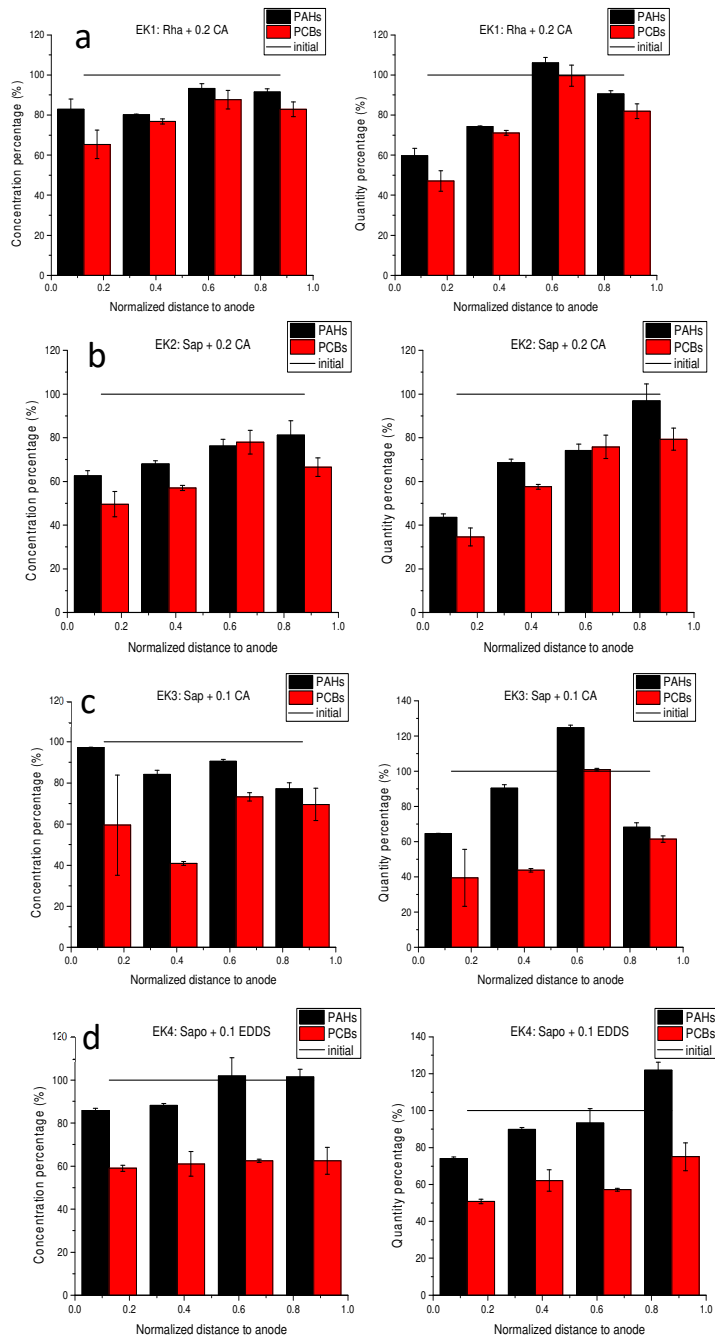


Fig. 4

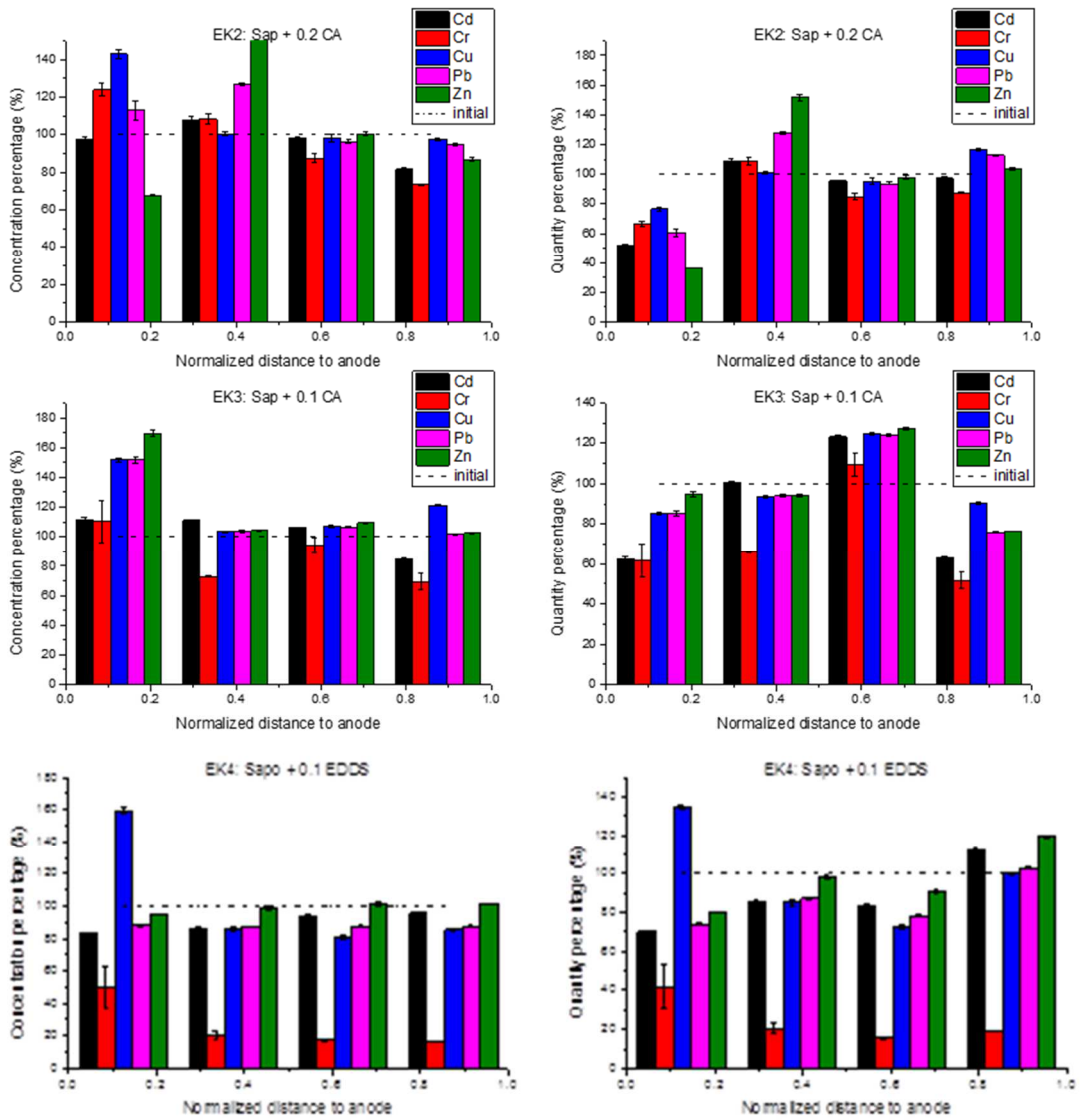


Fig. 5

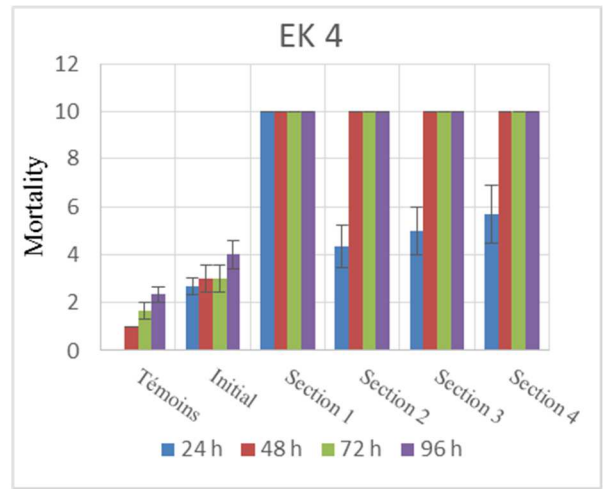
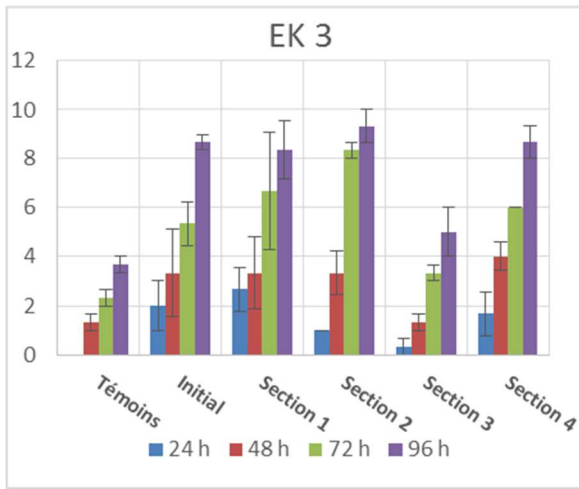
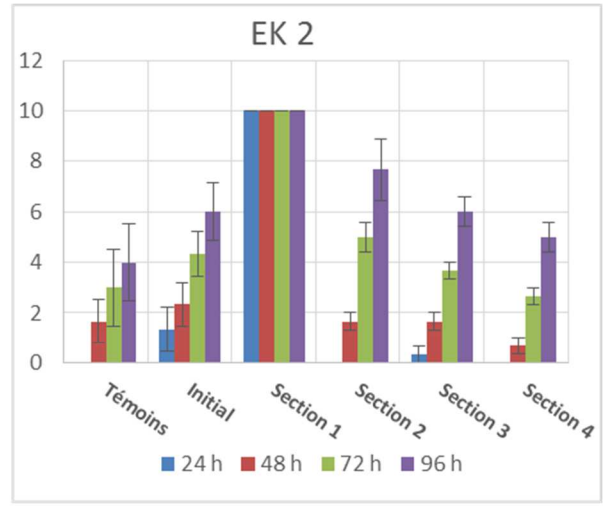
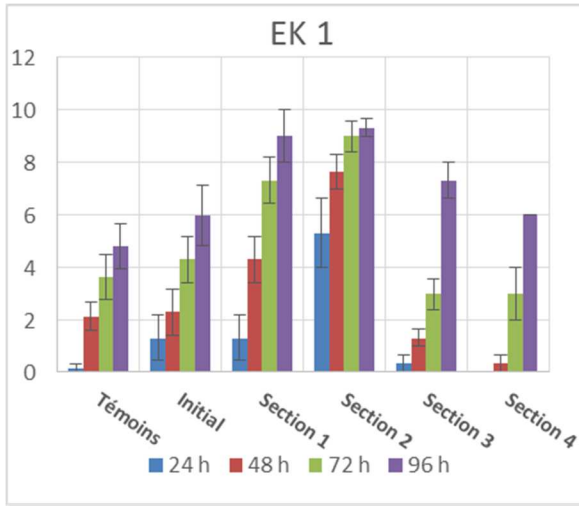


Fig. 6

**Table 1.** Summary of performed tests parameters

Test	Voltage (V/cm)	Anolyte	Catholyte	Duration (days)
EK0	1 (5d on / 2d off)	Pure water	Pure water	28
EK1	1 (5d on / 2d off)	Rhamnolipid (1.1 g/L) + Citric Acid (0.2M)	Rhamnolipid (1.1 g/L) + Citric Acid (0.2M)	28
EK2	1 (5d on / 2d off)	Saponin (0.85 g/L) + Citric Acid (0.2M)	Saponin (0.85 g/L) + Citric Acid (0.2M)	28
EK3	1 (5d on / 2d off)	Saponin (0.85 g/L) + Citric Acid (0.1M)	Saponin (0.85 g/L) + Citric Acid (0.1M)	28
EK4	1 (5d on / 2d off)	Saponin (5 g/L) + EDSS (0.1M)	Saponin (5 g/L) + EDSS (0.1M)	28
EK5 <sup>a</sup>	1 (continuous)	Tween 20 (0.004M) + Citric Acid (1M)	Tween 20 (0.004M) + Citric Acid (1M)	22
EK6 <sup>a</sup>	1 (5d on / 2d off)	Tween 20 (0.004M) + Citric Acid 0.1M)	Tween 20 (0.004M)+ Citric Acid (0.1M)	24
EK7	1 (continuous)	Pure water	Citric Acid (1M)	21

**Table 2.** Summarized removals of organic and inorganic pollutants and average energy consumption from EK tests

Test	Removals (%)							Energy Consumption (kWh/ton)
	Cd	Cr	Cu	Pb	Zn	Σ 16PAH	Σ 7PCB	
EK0	4.5	34.5	6.6	2.1	0	0.6	0	189.47
EK1	9.1	17.9	5.9	2.9	3.1	17.4	25.1	281.57
EK2	14.4	15.8	5.7	4.4	5.8	29.2	38.2	313.15
EK3	12.7	27.8	1.6	5.3	1.9	13.1	50.2	221.05
EK4	12	75.8	2.0	14.4	3.1	5.2	38.7	568.42
EK5 <sup>a</sup>	38,6	8,48	8,67	33,39	51,60	54.4	-	352.63
EK6 <sup>a</sup>	34,93	8,49	5,60	28,84	50,18	48.1	-	205.26
EK7	24.3	45.1	36.4	12.5	20.1	-	-	221.05

<sup>a</sup> Aged sediment

