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Abstract

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

Key words

Electrokinetics, sediment, remediation, pollutants, toxicity, copepod

1. Introduction

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

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

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

2. Materials and methods

2.1 Experimental set up and procedures

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

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

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

2.2 Analytical methods

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

The extraction of PAHs was carried out by means of a microwave assisted extractor (MAE method: Microwave Assisted Extraction). After lyophilization, 5 g of natural dry sediment (before or after treatment) was weighed and mixed with a solution of 40 mL of acetone /toluene (1:1) solvent in a special Teflon tube dedicated for the extractor (MarsX, CEM corporation). The heating temperature raised to 130 ° C in 5 minutes with the power of 1200 W for 6 extractions at the same time. Then, this temperature was maintained during 25 minutes prior to sample cooling. The liquid phase was then filtered with syringes and PTFE filters of 0.2 µm opening. A concentration step was required before analysis: a keeping solvent (60 µL of octanol) was introduced into the recovered eluents which were evaporated completely by using a miVac system (vacuum concentrator). The keeping solvent was then re-diluted with 1440 µL of toluene to give a final sample volume of 1.5 mL. Then, 990 µL were collected from the sample, in which 10 µL of a mixture of two internal standards (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_2). 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 (≈ 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 µm 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-µm mesh size; 1-m diameter) and were directly
168 passed through two sieves (500 and 100-µm 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−1). 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−1) 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+ ions in the anode compartment which made the sediment pH decreased to 5.57 near the
192 anode, and at the same time OH- 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 ± 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, pH>8 (Fig. 2a), saponin biosurfactant (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

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

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

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

alkaline environment (EDDS is not a weak acid unlike CA) overall the sediment sample in the electrokinetic cell (Fig. 2a) where no dewatering was observed during more than 600 hours treatment. The 'flushing' effect on electric current was important at each restart (Fig. 2b). This is attributed to the reset of EDDS-Na_3 ions in the sediment sample during the two days' rest. However, for the third and fourth cycles, the 'flushing' effect became shorter. EDDS-Na_3 ions migrated rapidly towards the two electrodes ($EDDS^{3-}$, Na-$EDDS^{2-}$, Na_2-$EDDS^{-}$ moved to anode, Na^+ moved to cathode) and thus the current became stable again very quickly.

3.1.3 Cumulative electroosmotic flow

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

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

main direction of EOF toward the cathode. However, this increase was inhibited after an elapsed time in EK1 and EK2 tests carried out with high concentration (0.2 M) of CA.

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

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

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

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

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

As noted previously, at the same concentration of 0.1 mol/L of chelating agent (EK 3 and EK 4 tests), the weak acid (citric acid) produced a higher cumulative EOF than the weak base (Na_3EDDS) (Fig. 3f). At the beginning phase, the sediment was over-saturated, the cumulative EOF in EK 4 test increased much rapidly than in EK 3 test because of a high pH environment and a more intensive electric current. It was reported (Pazos et al., 2010) that the electro-osmotic flow decreased as the concentration of surfactant increased. Moreover, a larger hydrated ionic radius of cations (such Na+ in EK 4) made the zêta potential less negative, leading to a smaller value of EOF (Kaya and Yeliz, 2005; Song et al., 2016). Finally, the cumulative EOF in EK 4 test could not be as great as in EK 3 test, but it was still higher than in EK0 test (water as electrolyte). Furthermore, the phenomena of dehydration and rehydration described before did not exist for EK4 test using EDDS, because EDDSNa_3 being a basic solution, the EOF overall the specimen sections was high without any fluctuation. So the cumulative EOF curves for both anode and cathode involved the same trend (Fig. 3e), and so the four slices after treatment were as humid as they were before.

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 mAm^{-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

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

3.2.2 Effect of different biosurfactants on contaminants removals

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

It can be added that the nonionic saponin had a smaller size of micelles than rhamnolipid in a CA solution. Anionic rhamnolipid molecules can form large micellar aggregates with a diameter of about 2.5 μm at pH = 3 (Lebron-Paler, 2008). These large aggregates could not entirely pass through the filter membrane (0.45 μm) which was used in this study. Consequently, there were fewer rhamnolipid micelles entering inside the sediment sample which so provided a less efficient removal result than using saponin. In addition, saponin is a 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 $mol.L^{-1}$ 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).

442

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 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^{2+} cations moving toward the cathode.

491 The best removal 75.8%) overall the metals was obtained for Cr in 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 of 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 pollutants removals obtained after all EK
496 tests carried out in different conditions and also energy consumption during 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 regard to metals 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, metals
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 metals removals provided by these
507 experiments are better than that reported by Iannelli et al. (2015) from large scale test 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 pollutants concentration and sustainable remediation can be achieved
512 with a moderate energy cost (200 kWh/Ton), without including additives 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.

3.4 Toxic effect of EK-treated sediment on Eurytemora affinis

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

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

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

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

4. Conclusions

The electrokinetic remediation studies reported in this paper investigated the efficiency of different enhancing additives (chelating agents, surfactants and biosurfactants) on the removal of contaminants (metals, PAHs and PCBs) from fresh and formerly deposited sediments. The results showed that mixtures of a biodegradable chelating agent (citric acid) combined with biosurfactants (rhamnolipids, saponin) or the synthetic Tween 20 are promising candidates for EK multi-decontamination because they did not induce ecotocicity after EK treatment. Longer treatment time for clay and carbonate rich sediments seemed necessary for reaching significant contaminants removal, because of the important buffering effect of carbonates, which delayed the acidification of the sediment specimen. Saponin was more efficient than Rhamnolipid because of its nonionic and head/tail ratio (smaller size of micelles) characteristics. Citric acid combined with nonionic surfactants provided a significant improvement of pollutants removal. Citric acid may not be the best biocompatible chelating agent but in moderate concentration, it could provide an interesting efficiency. 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)	Anolythe	Catholyte	Duration (days)
EK0	1 (5d on / 2d off)	Pure water	Pure water	28
EK1	1 (5d on / 2d	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[a]	1 (continuous)	Tween 20 (0.004M) + Citric Acid (1M)	Tween 20 (0.004M) + Citric Acid (1M)	22
EK6[a]	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[a]	38,6	8,48	8,67	33,39	51,60	54.4	-	352.63
EK6[a]	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 [a] 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.

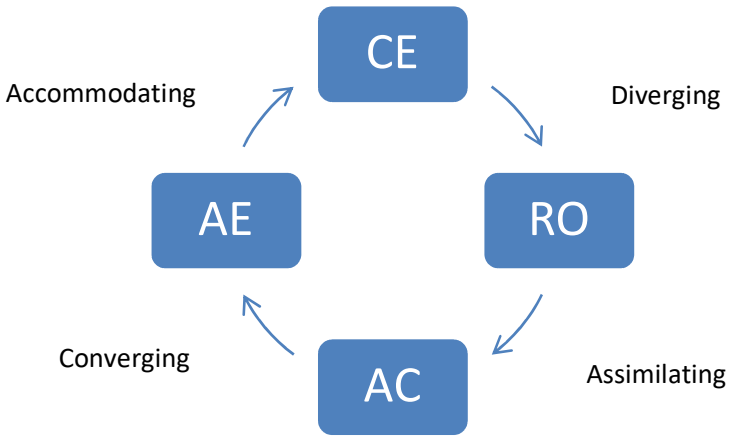
For Kolb (1984) and Kolb and Kolb (2013) learning should be considered a process and not only for the results obtained. It is facilitated when students have the opportunity to test and retest their beliefs, knowledge and ideas on a given topic, and add new and refined ideas. Learning is a holistic process 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

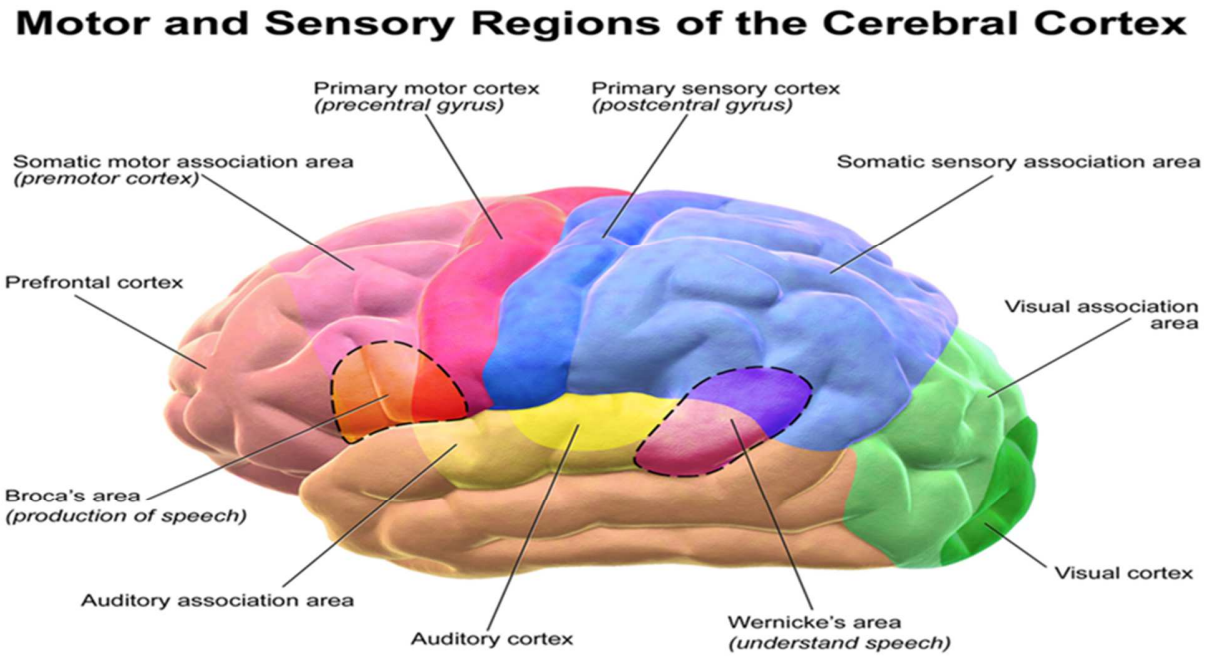
The discussion about learning styles and the effectiveness of their identification to improve learning may have in Biology and Neuroscience points of common interest for a broader dialogue. Although they are different areas from those that focus on the topic of learning styles, the knowledge produced 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



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.

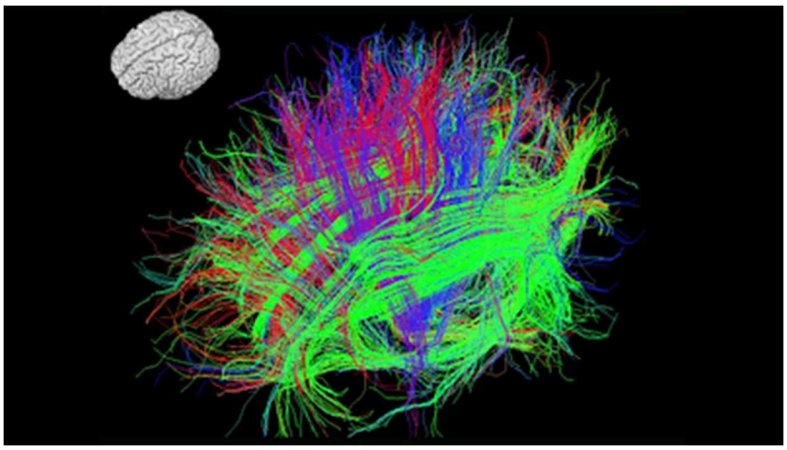
The interconnection between the areas of the brain is confirmed by studies in Neuroscience. Research carried out by Dehaene et al. (1999) on exact sums (e.g. 3 + 4 = 7) point to the activation of the left-lateralised area in the inferior frontal lobe, an area of the brain commonly associated with language. Conversely, when the sunm 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 retrival 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 2nd and 4th grades, and at the end, in 9th and 10th 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 & Munford, 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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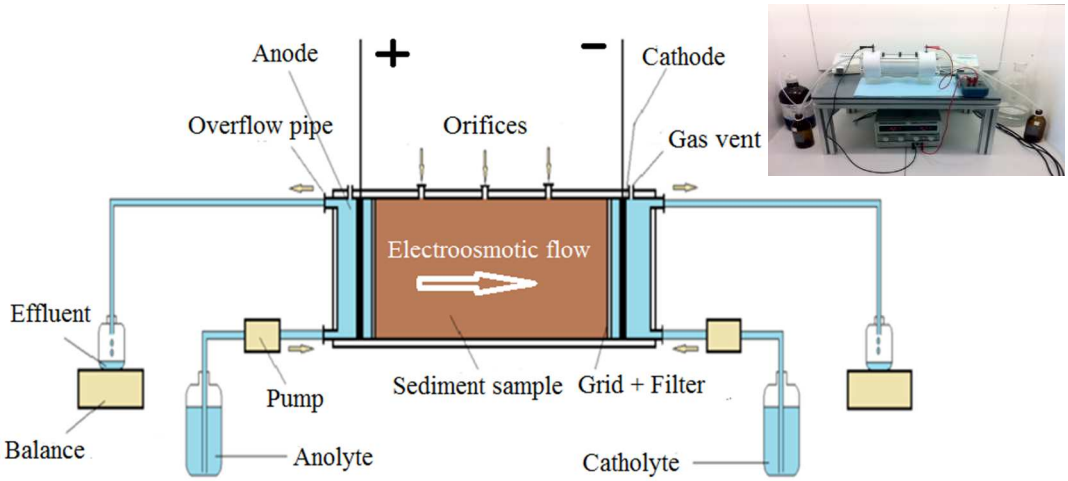

Anode
+
−
Cathode
Overflow pipe
Orifices
Gas vent
Electroosmotic flow
Effluent
Pump
Sediment sample
Grid + Filter
Balance
Anolyte
Catholyte

Fig.1

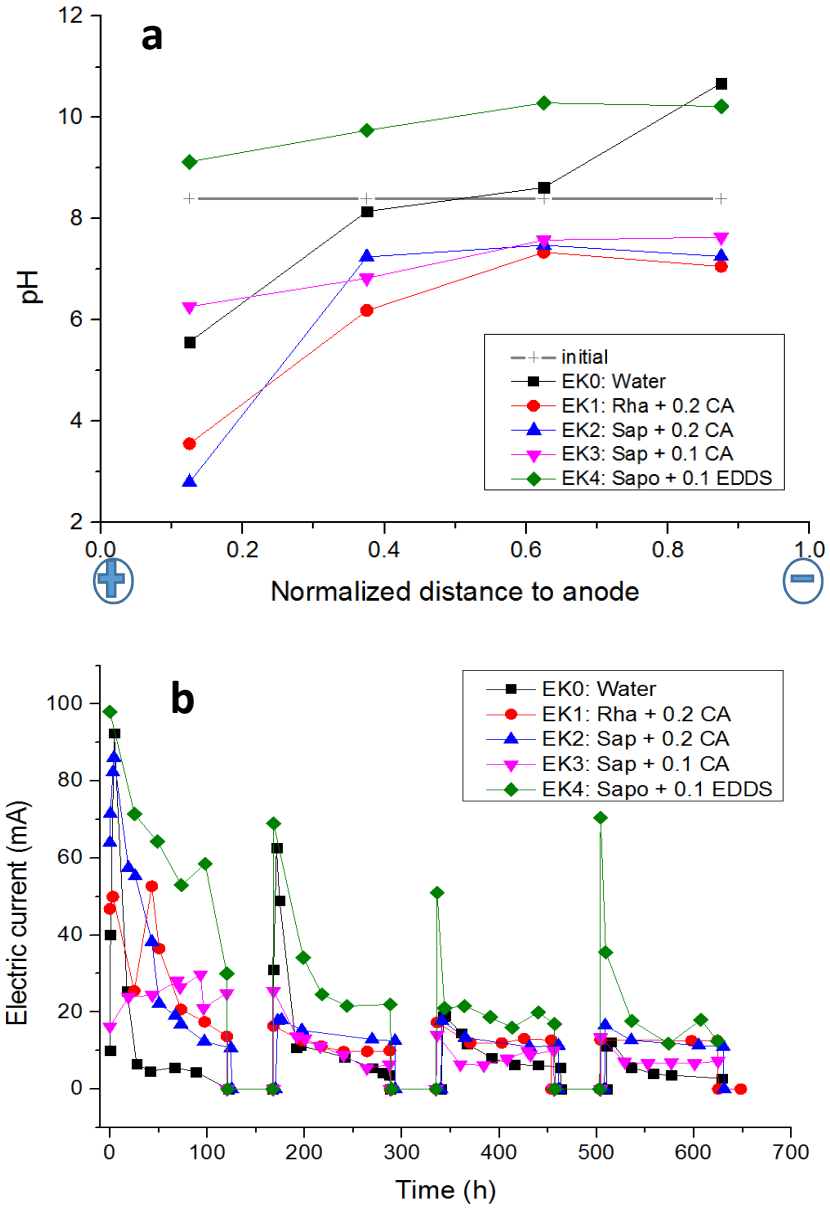

a
pH
Normalized distance to anode
initial
EK0: Water
EK1: Rha + 0.2 CA
EK2: Sap + 0.2 CA
EK3: Sap + 0.1 CA
EK4: Sapo + 0.1 EDDS
b
Electric current (mA)
Time (h)
EK0: Water
EK1: Rha + 0.2 CA
EK2: Sap + 0.2 CA
EK3: Sap + 0.1 CA
EK4: Sapo + 0.1 EDDS

Fig. 2

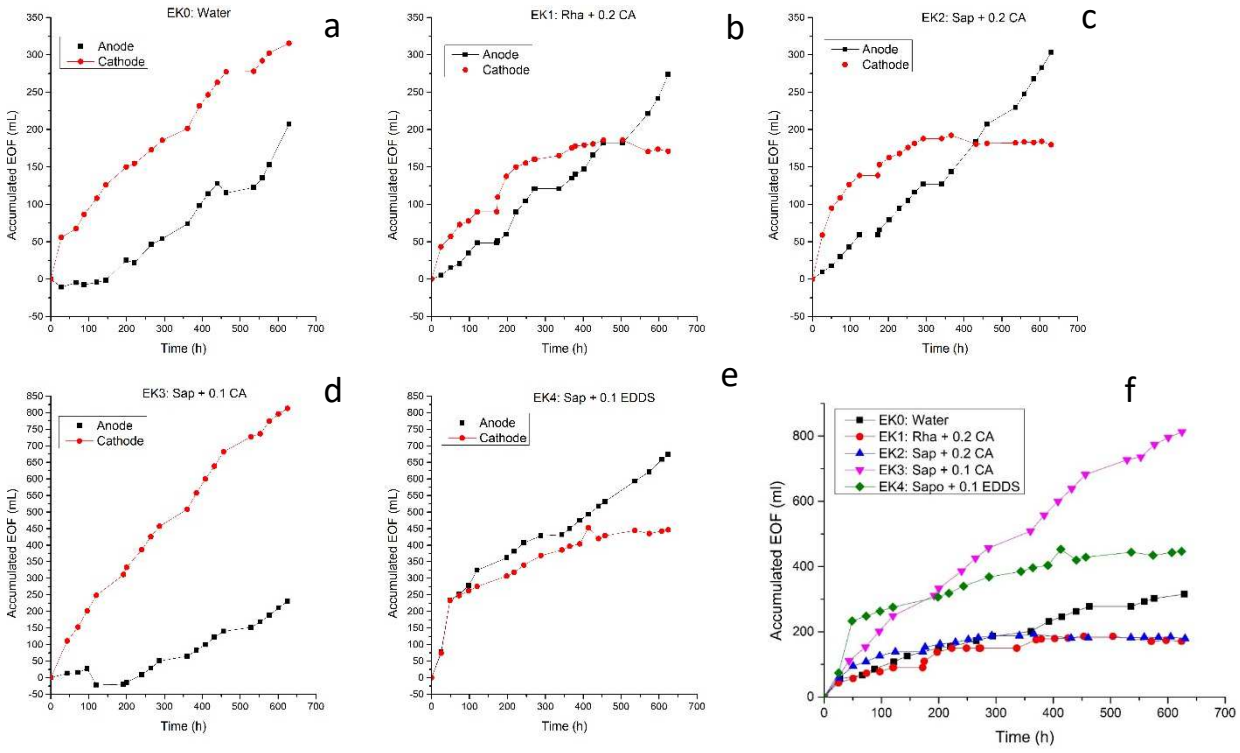

a
EK0: Water
Anode
Cathode
Accumulated EOF (mL)
Time (h)
b
EK1: Rha + 0.2 CA
Anode
Cathode
Accumulated EOF (mL)
Time (h)
c
EK2: Sap + 0.2 CA
Anode
Cathode
Accumulated EOF (mL)
Time (h)
d
EK3: Sap + 0.1 CA
Anode
Cathode
Accumulated EOF (mL)
Time (h)
e
EK4: Sap + 0.1 EDDS
Anode
Cathode
Accumulated EOF (mL)
Time (h)
f
EK0: Water
EK1: Rha + 0.2 CA
EK2: Sap + 0.2 CA
EK3: Sap + 0.1 CA
EK4: Sapo + 0.1 EDDS
Accumulated EOF (ml)
Time (h)

Fig. 3

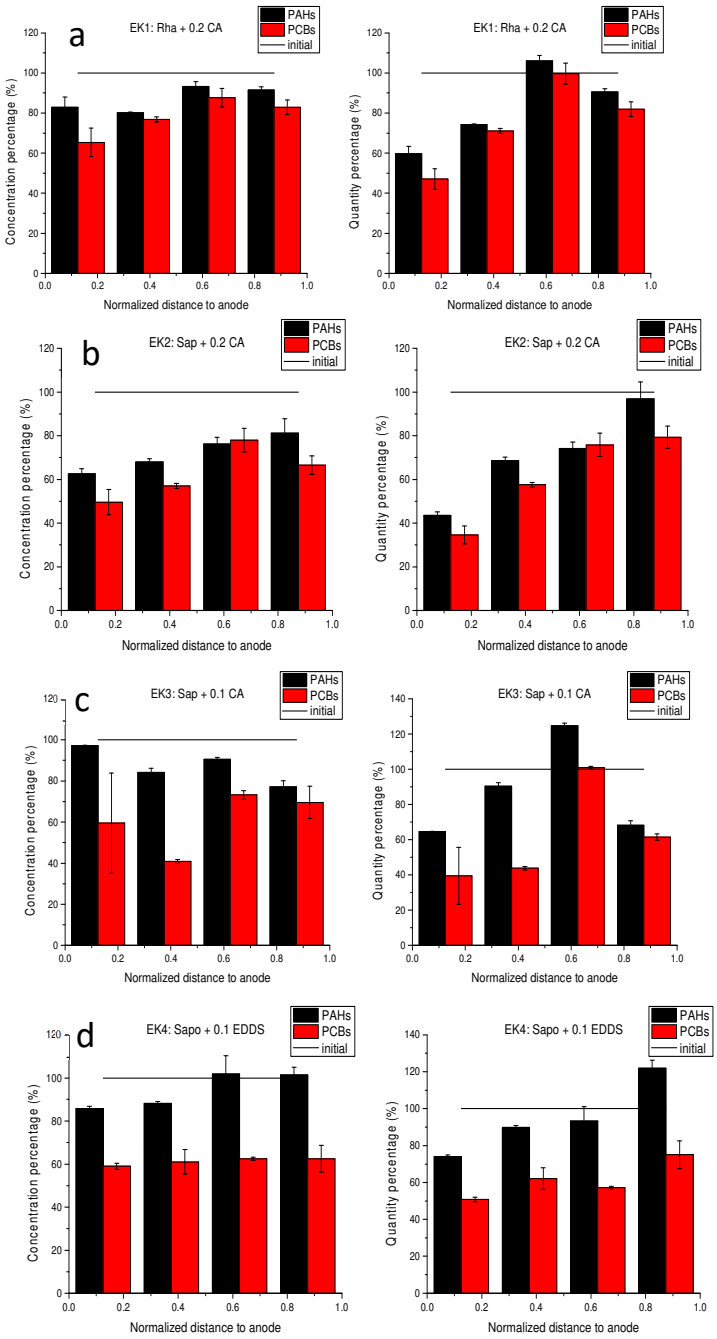

a
EK1: Rha + 0.2 CA
PAHs
PCBs
initial
Concentration percentage (%)
Quantity percentage (%)
Normalized distance to anode
b
EK2: Sap + 0.2 CA
c
EK3: Sap + 0.1 CA
d
EK4: Sapo + 0.1 EDDS

Fig. 4

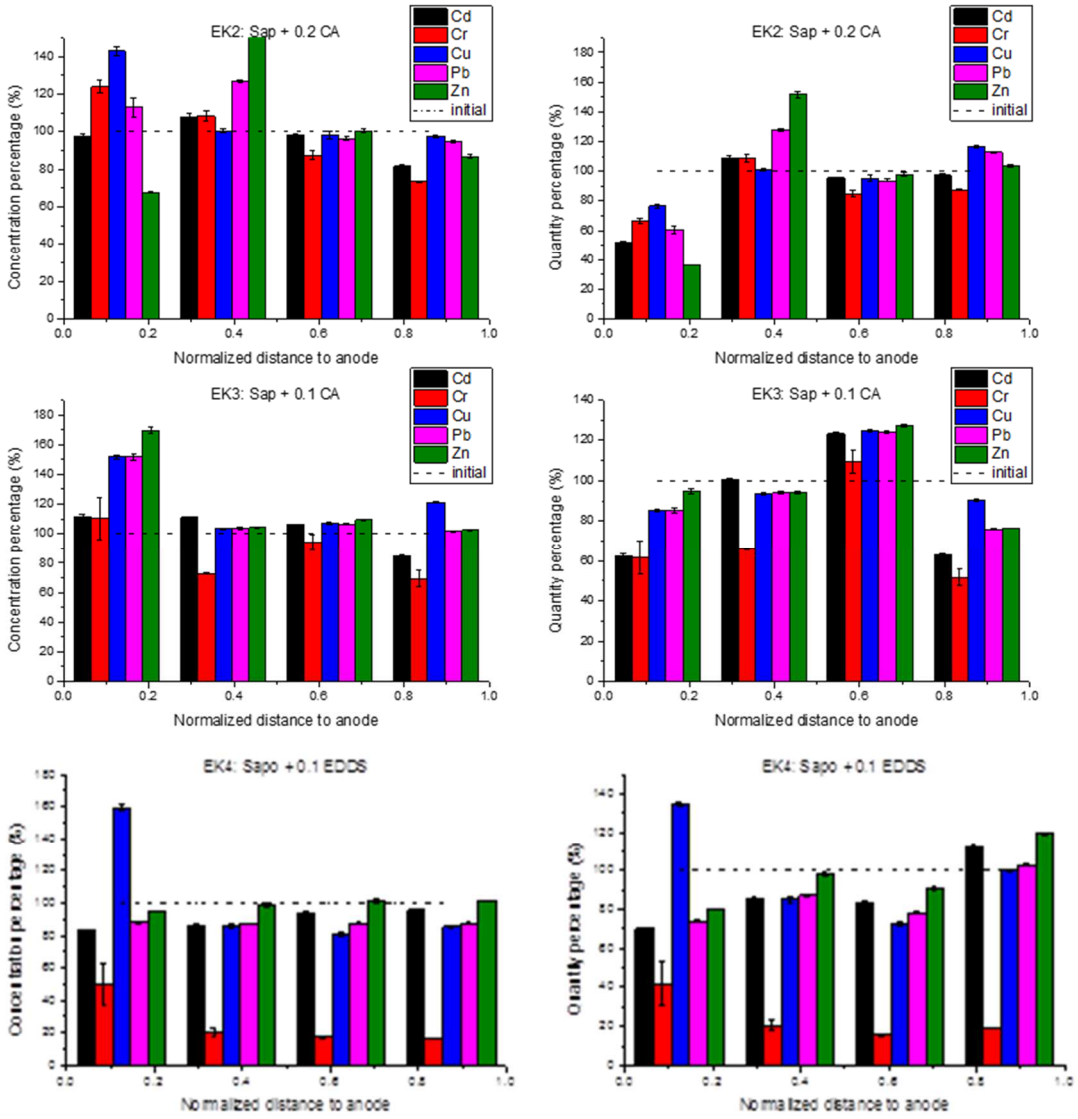

EK2: Sap + 0.2 CA
Concentration percentage (%)
Normalized distance to anode
Cd
Cr
Cu
Pb
Zn
initial
EK2: Sap + 0.2 CA
Quantity percentage (%)
Normalized distance to anode
EK3: Sap + 0.1 CA
Concentration percentage (%)
Normalized distance to anode
EK3: Sap + 0.1 CA
Quantity percentage (%)
Normalized distance to anode
EK4: Sapo +0.1 EDDS
Normalized distance to anode
EK4: Sapo +0.1 EDDS
Normalized distance to anode

Fig. 5

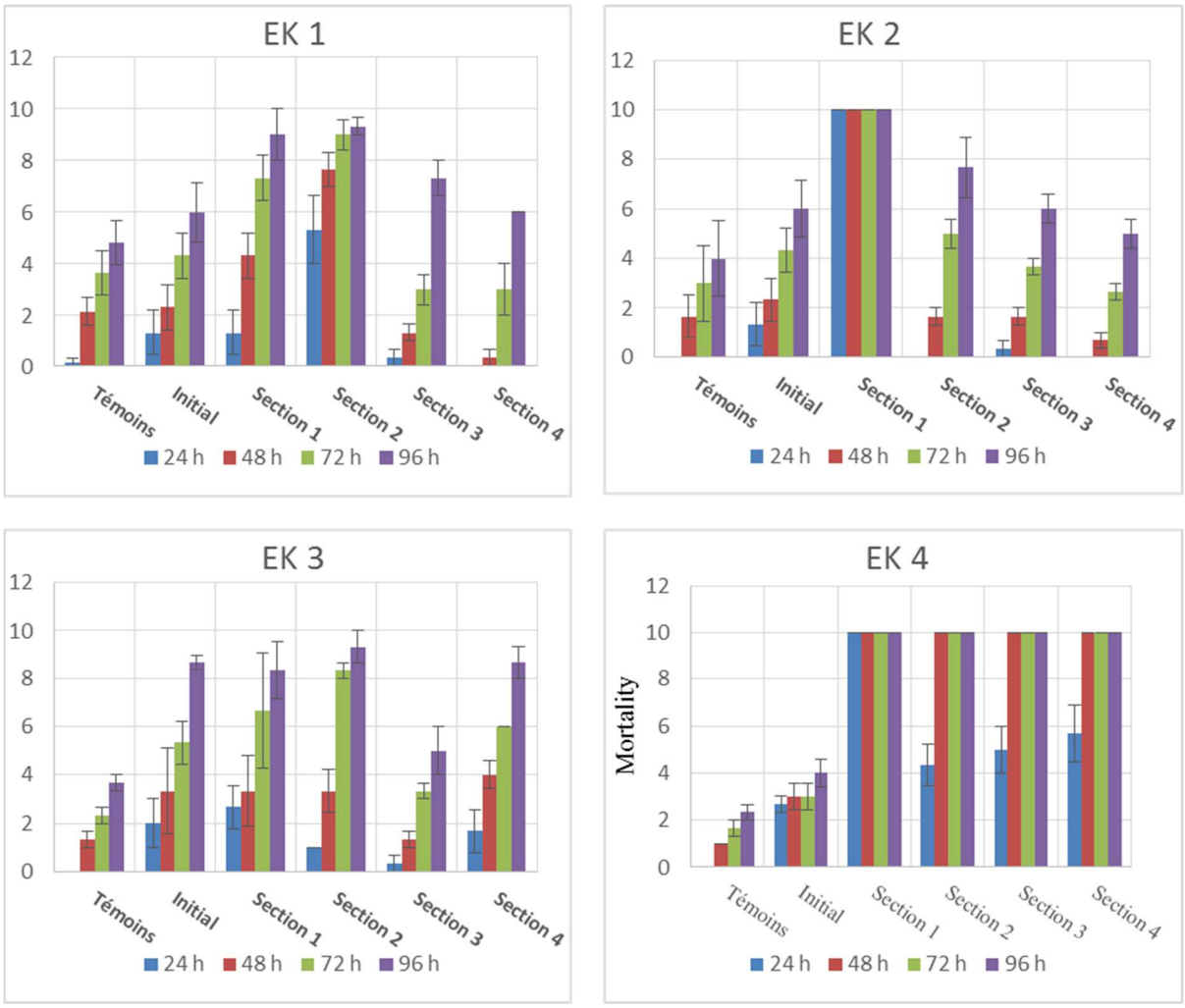

EK 1
EK 2
EK 3
EK 4
Mortality
0
2
4
6
8
10
12
Témoins
Initial
Section 1
Section 2
Section 3
Section 4
24 h
48 h
72 h
96 h

Fig. 6

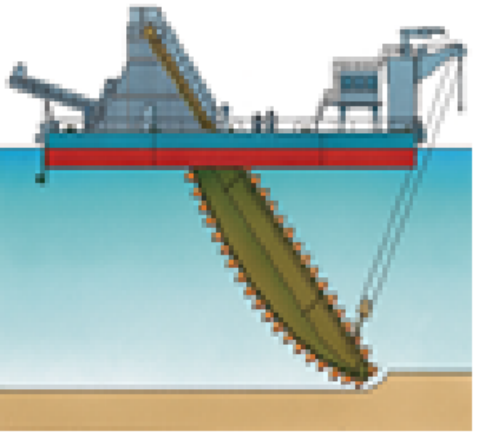
Table 1. Summary of performed tests parameters

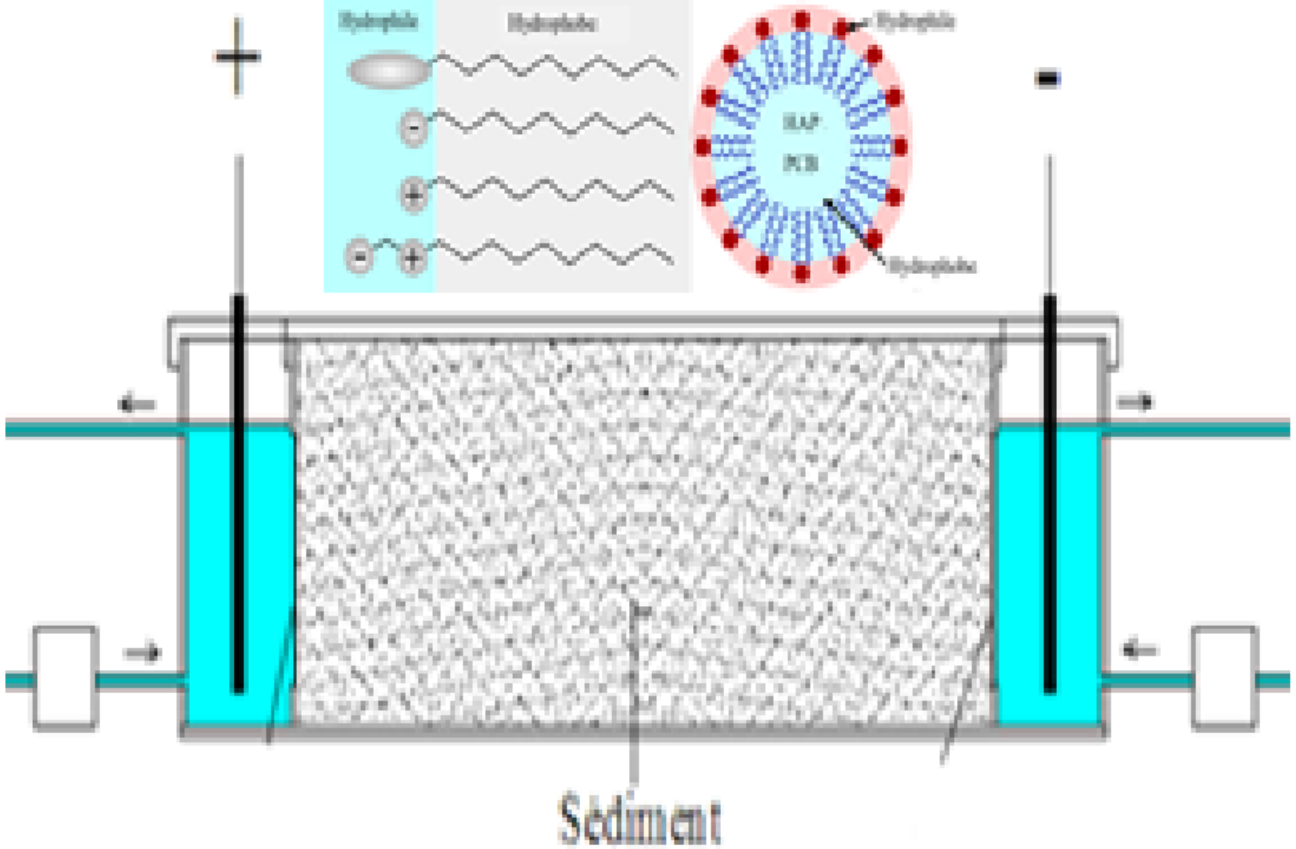
Test	Voltage (V/cm)	Anolythe	Catholyte	Duration (days)
EK0	1 (5d on / 2d off)	Pure water	Pure water	28
EK1	1 (5d on / 2d off)	Rhamnolipid (1.1 g/L) + Citric Acid (0.2M)	Rhamnolipid (1.1 g/L) + Citric Acid (0.2M)	28
EK2	1 (5d on / 2d off)	Saponin (0.85 g/L) + Citric Acid (0.2M)	Saponin (0.85 g/L) + Citric 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) + EDDS (0.1M)	Saponin (5 g/L) + EDDS (0.1M)	28
EK5[a]	1 (continuous)	Tween 20 (0.004M) + Citric Acid (1M)	Tween 20 (0.004M) + Citric Acid (1M)	22
EK6[a]	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[a]	38,6	8,48	8,67	33,39	51,60	54.4	-	352.63
EK6[a]	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

[a] Aged sediment




+
-
Hydrophile
Hydrophobe
Hydrophile
LAP
PCB
Hydrophobe
Sédiment


Eurytemora
affinis