

Valorization of the use of Waste Agricultural Materials for the Anodic Oxidation of Amaranth Red (E123) using SS/PbO₂ Anodes Elaborated by Pulsed Mode Current

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1 **Valorization of the use of waste agricultural materials for the anodic oxidation of Amaranth Red (E123)**
2 **using SS/PbO₂ anodes elaborated by pulsed mode current**

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8
9 **Abstract**

10 The present paper aims to valorize the use of cheap agricultural waste materials for polluted water
11 decontamination. An evaluation of the efficiency of coupling anodic oxidation (AO) using SS/PbO₂ electrodes
12 with biosorption by *Luffa cylindrica* (*L.C*) for the removal of Amaranth Red (E123) from aqueous solution was
13 investigated. The effects of pH, contact time, and initial concentration were studied. The regeneration of *L.C* was
14 estimated based on biosorption /desorption tests. The performance of the coupling process was evaluated based
15 on the color, chemical organic carbon (COD), Total organic carbon (TOC) removals, the energy consumed, and
16 the time required for the degradation of Amaranth. A comparison between the efficiency of the AO and the
17 coupling process for the increase of the lifetimes of the anodes used was done. 54.1, 97.8, and 99.9% of 50 mg.L⁻¹
18 of Amaranth were removed respectively after 85, 65, and 50 min by biosorption, AO, and coupling AO with
19 biosorption. An increase in the percentages of COD, TOC, germination indexes (GI), and Amaranth removals
20 were observed when adopting the coupling process. Furthermore, a decrease in the release of Pb²⁺ ions was
21 observed confirming the good stability of the elaborated anodes during the coupling process. Atomic absorption
22 analysis showed that the Pb²⁺ ions reached about 0.020 mg.L⁻¹, after the total removal of Amaranth dye (60 min)
23 and 0.051 after (80 min) respectively, for coupling AO with biosorption and the AO process. These values are
24 inferior to those allowed by the Standards. Phytotoxicity tests confirmed the possibility of the reuse of the treated
25 solutions.

26 **Keywords:** Anodic oxidation, Coupling, Biosorption, *Luffa cylindrica*, Amaranth

27 **1. Introduction**

28 The discharge of wastewater laden with polluting substances into the receiving environment without or with
29 unsuitable treatment is a cause for growing concern given the undesirable effects; it can have on the environment
30 and the health of living beings (Iloms et al. 2020). The protection of water resources against this growing

31 pollution is the subject of several research studies for the implementation of more efficient, inexpensive, and
32 environmentally friendly technologies (Othmani et al. 2020b). The decontamination of water resources can have
33 various origins; they can be inorganic or organic (Garcia-Segura et al. 2015). Wastewater is characterized by
34 strong variations in pH, high concentration of organic matter , and high chemical oxygen demand (Choi et al.
35 2017). Some compounds are easily degradable chemically or biologically, others are recalcitrant to conventional
36 treatment methods and there is a need to seek more adequate treatment systems (Elaiassaoui et al. 2016). Up to
37 date, plenty of methods have been used in the cure of contaminated water including cheap alternatives like
38 biosorption and expensive ones like electrochemical processes (Fernandes et al. 2016; Elaiassaoui et al. 2019).
39 Electrochemical treatment, especially anodic oxidation, is generally applied for the treatment of refractory
40 organic compounds present in high concentrations (Ghime and Ghosh 2019). It offers a performing ability for
41 wastewater decontamination from a variety of hazardous pollutants (Panizza and Cerisola 2009). However, the
42 electrochemical process depends crucially on the nature and the stability of the electrode used (Othmani et al.
43 2019). The anodic oxidation can be more effective when using performing electrodes able to produce a large
44 amount of reactive hydroxyl radicals $\cdot\text{OH}$ (Nurhayati 2012). In other words, when using a high anode
45 overvoltage of O_2 , like PbO_2 , SnO_2 , TiO_2 , RuO_2 , IrO_2 , diamond doped with boron supported on Si or Ti (BDD)
46 etc...(Ghime and Ghosh 2019). SS/ PbO_2 anodes have a high over potential for oxygen generation combining
47 high conducting ability and performing electrochemical activity (Morsi et al. 2011; Othmani et al. 2019).
48 However, the short lifetime of the deposited layer of PbO_2 into the substrate these last can be one of the main
49 drawbacks of their use (Mohd and Pletcher 2006). In this context, several methods have been devoted to this
50 utility. However, most of them are expensive and required the use of several products and types of equipment.
51 Among the proposed solutions; the doping methods have been successfully applied for enhancing the stability of
52 the elaborated electrodes (Dao et al. 2020). Coupling two efficient processes to enhance the effectiveness of each
53 process alone has been successfully applied. Among the performing coupling processes studied, we can cite
54 coupling ultrasonic cavitation with electrochemical oxidation, which leads to enhance the effectiveness of the
55 studied parameters like the reaction rate, the energy consumed, and the removal efficiency. (Barros et al. 2014).
56 Others have chosen to modify the PbO_2 electrodes with an environmentally friendly conductive carbon black.
57 The results showed an increase of about 24.66% in the removal efficiency of metronidazole compared to the raw
58 PbO_2 electrodes. Furthermore, an improvement in the current efficiency and the generation of hydroxyl radicals
59 was achieved (Wang et al. 2020). Based on the literature most of the solutions proposed for the enhancement of
60 the stability of electrodes based on PbO_2 are oriented for the doping methods. However, more cheap and clean

61 alternatives can take place for this utility. Among these alternatives the one proposed by (Othmani et al. 2019)
62 who have offered a new alternative based on the use of alternating current (AC) instead of direct current (DC)
63 for the anodic oxidation of methylene blue (MB) using SS/PbO₂ and Pb/PbO₂ electrodes. Results showed an
64 enhancement of the stability of the used electrodes. Furthermore, atomic absorption analysis confirmed the
65 decrease of the release of (Pb²⁺) ions to much lower values compared to DC and those allowed by the Standards.
66 A year later, the same team has proposed a cheap alternative based on coupling biosorption using *L.C* with AO
67 using SS/PbO₂ anodes. Results showed that 98.7 and 80.02% of MB were removed, respectively, after 60 and
68 120 min for AC and DC when using the coupling process. Otherwise, 62.84 and 46.87 % of the same dye were
69 removed by the AO process, respectively, after 120 and 180 min for AC and DC (Othmani et al. 2020a). These
70 findings encourage the use of cheap agricultural waste materials for the removal of more hazardous pollutants.
71 According to the literature, the production of azo dyes is estimated at around 350,000 tons per year (Pagga and
72 Brown 1986; Radhakrishnan 2014). In practice, this category of dye is currently the most common. It represents
73 more than 50% of worldwide production (Khadhraoui et al. 2009). During the dyeing procedures, 10-15% of the
74 dyes used in the initial quantities can be lost and discharged without prior treatment in the effluents (Singh and
75 Arora 2011). These latter are carcinogenic and refractory (Bauer et al. 2001; Barros et al. 2014). Therefore,
76 Amaranth Red (E123) was chosen as a model in this study. Many points were studied in the present paper. First,
77 we tried to encourage the use of cheap and abundant agricultural waste materials for hazardous pollutant removal
78 to replace the use of expensive adsorbent. Second, enhance their capacity uptake and reaction speed by coupling
79 biosorption with anodic oxidation. Third, to enhance the lifetime of the elaborated electrodes used and to
80 minimize the generation of Pb²⁺ ions by a safe and economic method based on the coupling process. The
81 characterization of the biosorbent used and the SS/PbO₂ anodes were done using X-ray diffraction (XRD) and
82 scanning electron microscopy (SEM). Quantitative and qualitative characterization of the used *L.C* was reported
83 based on their point zero charges (pHpzc), surface functionality, functional groups, and elementary
84 decomposition. The evaluation of the quality of the treated water after purification was done based on the color,
85 chemical oxygen demand (COD), and total oxygen-carbon (TOC) removals. Finally, the possibility of the reuse
86 of the treated water and the anodes used was evaluated by phytotoxicity tests. The release of Pb²⁺ ions was done
87 measured using atomic absorption spectrophotometry. The possibility of the regeneration of the used *L.C* was
88 done based on biosorption/desorption tests. Finally, a prediction of the possible pathway of the removal of
89 Amaranth dye by AO and AO coupling biosorption was done.

90 **2. Materials and methods**

91 **2.1. Preparation of *L.C***

92 The used *L.C* has a Tunisian origin. It is composed of 54% of cellulose, 11% of lignin, 5% of pectin, 7% of fats
93 and waxes, and 23% hemicelluloses (Othmani et al. 2020b). The preparation of this biosorbent consisted of
94 cutting the fibers finely, washing those last several times to remove all impurities, and drying them at 70°C until
95 the material was completely dried constantly. The dried sample was ground and sieved to obtain a uniform
96 particle size using an electric shifter. The chosen particles have a diameter of 250 µm.

97 **2.2. Elaboration of SS/PbO₂ by pulsed mode current**

98 A plate of stainless steel (SS) of 2 mm thick, with circular geometry and area 12.56 cm² were used for the AO
99 process in the presence and absence of *L.C*. The electrodes were then coated with a chemically inert resin
100 (Araldite 50-50); the electrical contact was ensured by a conductive wire protected by a pyrex tube.

101 The elaboration of SS/PbO₂ electrodes was done in a bath containing 0.5M of HNO₃ (Sigma –Altrich ,
102 purity:95%) and 0.5M of Pb(NO₃)₂ Panerac Quimica, SA(purity: 99%). A total of 900 pulses (height =30
103 mA/cm², width =1s, relaxation time=5s at zero current) were applied for each anode for 34 min (Naim et al.
104 2009).

105 **2.3. Schematic of coupling anodic oxidation with biosorption**

106 The experiments used for the Amaranth Red (E123) removal by biosorption has been performed in triplicate in a
107 batch reactor by adding 0.5 g of *L.C* in 0.5 L of Amaranth solution (pH= 2, 7, and 10; C₀=10 mg.L⁻¹, T=25°C,
108 and t=100 min). The same experiments were used for the AO coupling biosorption by adding an electrical
109 mounting comprising a DC source and a voltmeter (J=25 mA.cm⁻²). As for the experimental procedure used for
110 the anodic oxidation tests; it has been performed in a batch reactor. The electrochemical cell consisted of a
111 Plexiglas reactor with PbO₂ supported on SS as an anode and SS as a cathode. The surfaces of anodes and
112 cathodes were fixed at 12.56 cm² and the inter distance gap between the anode and the cathode was fixed at 2
113 cm. Table SM-1 presents some properties of Amaranth Red (E123).

114 The stock solution of Amaranth Red (E123) (purchased from Sigma-Aldric, purity≥ 99.5%) was prepared by
115 dissolving 1 g of the dye in 1 L of distilled water. Test amaranth red solutions were prepared by diluting the
116 stock dye solution.

117 The desired concentrations were obtained by successive dilution. The adjustment of pH was done using dilute
118 HCl (0.1 M) or NaOH (0.1M) (purity 95–97%) solution before biosorption. During the experiments,
119 concentrations were determined by UV visible spectrophotometer (Perkin Elmer Lamda 25) using quartz
120 cuvettes at λ=520 nm based on the following equation (Elaiassaoui et al. 2016)

121
$$\text{Color removal (\%)} = \frac{(C_0 - C_t)}{C_0} \times 100 \quad (1)$$

122 Where

123 C_0 is the initial dye concentration (mg.L^{-1}) and C_t is the dye concentration at any time (mg.L^{-1}).

124 **2.3.1. Estimation of the retained amount of dye by the *L.C***

125 The amount of Amaranth retained by the *L.C* was estimated based on Eq.(2) : (Othmani et al. 2020b)

126
$$Q_e = \frac{C_0 - C_t}{m} \times V \text{ (mg.g}^{-1}\text{)} \quad (2)$$

127 Where

128 Q_e is the adsorbed quantity at equilibrium time, C_0 and C_t (mg.L^{-1}), correspond respectively to the initial and
 129 remaining concentration of Amaranth at any time (mg.L^{-1}), V is the volume of solution (L) and m is the mass of
 130 *L.C* (g). At equilibrium, $C_i = C_e$, and $Q = Q_e$ (Kesraoui et al. 2016)

131 **1.3.2. Desorption study**

132 The regeneration of *L.C* was estimated based on a desorption test in different pH media. 3g of the biosorbent
 133 obtained after the AO and the AO coupling biosorption of the maximum retained concentration of Amaranth
 134 were recovered after use by filtration and dried in an oven. The obtained samples were placed in 0.5 L of
 135 distilled water. After that the pH was fixed at 2, 7, and 10 to evaluate the ability of these samples to desorb in
 136 different pH media. The desorbed quantity is calculated as follow:

137
$$Q_d = \frac{C \times V}{m} \quad (3)$$

138 Where

139 Q_d is the desorbed amount (mg/g), C is the concentration at each instant t (mg/L), V is the volume of the
 140 solution (L), and m is the mass of the fibers (g).

141 The desorption rates were calculated according to Eq.(4)

142
$$\text{TD(\%)} = \frac{Q_{de}}{Q_{ae}} \times 100 \quad (4)$$

143 If $\text{TD} > 50\%$, the retention of Amaranth by the *L.C* is weak which means it is physisorption,

144 If $\text{TD} < 50\%$ the retention of Amaranth by the *L.C* is important which means it is chemisorption.

145 The evaluation of all experiments was performed based on various parameters, like chemical Oxygen Demand
 146 (COD), Total Organic Carbon (TOC), and Germination Indexes (GI).

147 **2.4. COD and TOC removals**

148 The % COD removal was determined by a photometric method as follow (Barros et al. 2014)

$$149 \quad COD \text{ removal } (\%) = \frac{COD_0 - COD_t}{COD_0} \times 100 \quad (5)$$

150 COD₀ and COD_t are the initial oxygen chemical demands before and after fixed time t of electrolysis treatment
151 (mg.L⁻¹ O₂).

152 The measure of TOC was determined by a TOC analyzer (HACHIL, 550-TOC-TN model) and the TOC removal
153 was estimated as follow:

$$154 \quad TOC \text{ removal } (\%) = \frac{TOC_0 - TOC_t}{TOC_0} * 100 \quad (6)$$

155 Where, TOC₀ and TOC_t are respectively the initial total organic carbon before and after fixed time t of
156 electrolysis treatment (ppm C.O.)

157 **2.5. Average current efficiency (ACE)**

158 The quantity of current used during the degradation of the organic matter was estimated based on the ACE
159 calculated according to Eq (7) (Othmani et al. 2019)

$$160 \quad ACE (\%) = (COD_0 - COD_t) \times \frac{F \cdot V}{8 \cdot I \cdot t} \times 100 \quad (7)$$

161 Where I: is the applied current (A), t: is the electrolysis time (min), F: is the Faradic constant (96.487 Cmol⁻¹), V:
162 is the solution volume (L) and 8 is the number of electrons exchanged per mole of O₂.

163 **2.6. Energy consumption (EC)**

164 The energy consumed (EC) during the electrolysis was estimated as follows (Elaissaoui et al. 2019)

$$165 \quad EC (\text{KWh} \cdot \text{g}^{-1} \text{COD}) = \frac{I \cdot V \cdot t}{\Delta \text{COD} \cdot V_s} \quad (8)$$

166 Where

167 I: is the applied constant current (A), V: is the average cell potential value volt, t: is the electrolysis time (h),

168 ΔCOD₀: COD are the experimental measurements (g /L O₂), V_s: is the solution volume (L).

169 **2.7. Phytotoxicity tests**

170 The efficiency of the coupling process was evaluated based on the possibility of the reuse of the treated water
171 using SS/PbO₂ anodes. Therefore, a phytotoxicity test was done to test the inhibitory effect of the tested water on
172 the germination and growth potential of lettuce based on the GI (%) calculated as follow:(Louhichi et al. 2019)

173 The reference is distilled water.

$$174 \quad GI (\%) = \frac{\text{number of seeds sprouted in the sample}}{\text{number of seeds sprouted in the reference}} * \frac{\text{average length of root in the sample}}{\text{average root length in the reference}} * (100) \quad (9)$$

175 **2.8. Atomic absorption spectrophotometry**

176 The concentration of Pb^{2+} ions released within the solutions after the AO and coupling AO with biosorption was
177 dosed according to the standard method(Perkin 1996); using a Graphite Furnace Atomic Absorption
178 Spectrometry (NovAA800, Analytik Jena GmbH).

179 **2.9. Morphological and structural Characterizations**

180 SEM was performed using a JEOL JSM 5400 scanning microscope after coating them with gold using a JEOL
181 JFC-1199E ion sputtering device for the characterization of *L.C* and without coating for the characterization of
182 the SS/PbO₂ anodes used.

183 EDS was planned to assess the surface elemental compositions of *L.C* using a JEOL JSM 5400 scanning
184 microscope. EDS was performed after coating them with gold using a JEOL JFC-1199E ion sputtering device.

185 XRD characterizations of the elaborated SS/PbO₂ anodes were done using an X-ray diffractometer D8 Advance
186 (Bruker, (CNRSM)) and a Diano, Ka Co radiation at a wavelength of 1.54 nm using the Debye method
187 (Holzwarth and Gibson 2011).

188 **3. Results and discussion**

189 **3.1. Surface characterization of *L.C* and SS/PbO₂ anodes**

190 The performance of the biosorption process is depending on the chemical, structural, morphological, and surface
191 properties of the used biosorbent (Adewuyi 2020). Thus, having an idea about the surface of biosorbent used can
192 facilitate the prediction of the main reactions that may occur during the removal of Amaranth dye by biosorption
193 and biosorption coupling AO. According to (Othmani et al. 2020b), *L.C* fibers have an amphoteric character based
194 on their zero charge point (pH_{PZC}) which is equal to 7.38 ± 0.0002 . These findings were confirmed by the
195 chemical surface properties of these fibers determined by Boehm titration. Results have shown an affinity
196 between the acidic function and the basic one, where they reached respectively $(1.510 \pm 0.005, \text{ and } 1.560 \pm$
197 $0.0008) (\times 10^{-4} \text{ mmol/g})$. The identification of the surface functionality of the used *L.C* will enhance the deep
198 understanding of the main mechanism that may occur during the retention of the Amaranth dye. On the other
199 hand, and according to results found by EDS illustrated in Table 1, *L.C* is mainly composed of Carbon (54.46%
200 of C), and Oxygen (40.6% of O). These high percentages of these compounds suggest the existence of C-O and
201 C=O groups specific to aromatic ring type and alcoholic function. Furthermore, some impurities in low
202 concentration are also present as shown in table SM-2.

203 As for the SEM micrograph shown in Fig.1, it showed that the *L.C* presents a rough porous structure and a
204 homogeneous appearance which is formed by bonded multicellular fibers (Boynard and D'Almeida 2000).
205 Therefore, this porous structure of *L.C* leads to the retention of Amaranth Red (E123).

206 3.2. SEM and XRD characterizations of SS/PbO₂ anodes

207 Fig.2 specific to the XRD and SEM of SS/PbO₂ anodes shows the presence of small crystalline particles and
208 pyramidal ones (Li et al. 2016) attributed respectively to α -PbO₂ form and β -PbO₂ specific to electronic
209 conduction and electrochemical reduction capacity (Zhou and Gao 2007; Othmani et al. 2019).

210 3.3. Effect of pH

211 The effect of pH on the removal of Amaranth Red (E123) by biosorption, AO, and biosorption coupling AO was
212 studied over a pH of 2, 7, and 10 as shown in Fig.3. As said earlier, the pH_{PZC} of *L.C* =7.38, therefore the surface
213 of *L.C* is positively charged at pH values below pH_{PZC} and should be able to adsorb negatively charged species.
214 At the same time at pH values above 7.38 *L.C* can adsorb positively charged species (Mbarki et al. 2020) . The
215 best results for AO, biosorption , and coupling AO with biosorption were obtained for pH =2 and reached
216 respectively, 97.8, 54, and 98.7% which can be explained as follow: As the Amaranth Red (E123) is an anionic
217 azo dye with predominantly negative charges at acidic pH (Ahmad and Kumar 2011) and based on the fact that
218 for pH under 7.38, the dominant functional groups of *L.C* are positively charged and therefore attract strongly
219 the negatively charged species. However, with the increase in pH to 7 and 10, the surface of *L.C* becomes more
220 negative and therefore the attraction between the adsorbate and the *L.C* decreased gradually resulting in a
221 decrease in the % of removal of Amaranth. For pH=10 the low % of Amaranth removal can be due to the
222 presence of an excess of OH⁻ in the solution. This last can enter into competition with the adsorbate for the
223 available sites onto the *L.C* and therefore decline the uptake capacity. For the AO of Amaranth Red (E123), the
224 efficiency of the process was more accentuated for pH=2. The electrolysis is controlled by material transport and
225 side reactions (such as the evolution of oxygen) which begin with the oxidation of amaranth. However, these
226 reactions can also produce other oxidants capable of contributing to the oxidation process and therefore of
227 participating in the mineralization of pollutants. According to the literature, two main parameters strongly
228 influence the electrochemical degradation of Amaranth ; the type of electrolyte used in the electrochemical cell
229 and the solution pH (Barros et al. 2014). As the best results were obtained at pH=2, the possible pathway of the
230 Amaranth Red (E123) degradation can be described as follow: The degradation of the Amaranth molecule by the
231 ·OH radical oxidation generated by the SS/PbO₂ anodes starts by the division of N=N- bond, which produces
232 aromatic molecules of lower molecular weight (Silva et al. 2008). According to previous studies, the main

233 byproducts generated are two primary amines (Zhang et al. 2009) and some oxidation products detected during
234 the mineralization of aromatic compounds like phenol, quinone, malonic, and oxalic acid (Pogacean et al. 2018).
235 Concerning the coupling process, a combination between the possible pathway of the retention of Amaranth dye
236 onto the available sites of *L.C* and the electrochemical degradation of this last has taken place in harmony.
237 Therefore, the removal of Amaranth was faster than each process alone. The presence of *L.C* has given some
238 relaxation time for the SS/PbO₂ anodes which decreased the energy consumed and the mass loss of Pb²⁺ into the
239 solution. This behavior has minimized one of the main drawbacks of the use of anodes based on PbO₂ which is
240 the toxicity generated during the electrolysis. Furthermore, a decrease in the required time for the removal of
241 Amaranth dye was observed indicating the efficiency of the coupling process. These findings must be confirmed
242 by the adsorption atomic analysis, SEM, and SRX analysis of SS/PbO₂ anodes after use.

243 **3.4. Effect of concentration**

244 The effect of concentration on the removal of Amaranth Red (E123) by biosorption in batch mode, AO and AO
245 coupling biosorption was evaluated over a range between [10-100] mg.L⁻¹, pH=2, C_{Na₂SO₄}=0.1M, J=25 mA/cm²,
246 m_{*L.C*}=0.5g, V=0.5 L, T=25°C, and t=100 min. As shown in Fig.4, the effect of concentration influences
247 differently the removal of Amaranth Red (E123) when adopting the AO, the biosorption, and the coupling
248 process. For the biosorption process, the increase in the initial concentration from 10 to 100 mg.L⁻¹ has shown
249 two main phases. An increase in the % of Amaranth removal until reaching 50 mg.L⁻¹, indicating fast removal
250 phase; indicating a rise in the number of ions in solution involving a higher biosorption capacity (Othmani et al.
251 2017). However, for concentration higher than 50 mg.L⁻¹, a gradual decrease in the removal efficiency was
252 observed indicating a decrease in the capacity uptakes of the used *L.C* confirmed by the slowdown of the
253 removal speed. Therefore, up to 50 mg.L⁻¹ of Amaranth, a relation of proportionality was obtained between the
254 initial concentration and the removal efficiency. These findings can be explained by the decrease in the number
255 of the available sites onto the *L.C* (Othmani et al. 2020a). Therefore, the maximum biosorption capacity of
256 phenol with raw *L.C* is fixed to 50 mg.L⁻¹; and the saturation phase was fixed at 85 min (Shahryari et al. 2010).
257 Also, the accumulation of Amaranth on the surface of *L.C* can be another reason for the decline in the removal
258 efficiency (Othmani et al. 2020b). Furthermore, researchers have explained the fast removal speed of the
259 pollutant at the first stage of biosorption to the transfer of external mass and the slow one to the phenomenon of
260 diffusion (internal mass transfer) (Ghaedi et al. 2014; Liu et al. 2018). As for the AO process the same behavior
261 was observed for the removal of Amaranth dye where the maximum % of removal was observed for a
262 concentration of 50 mg.L⁻¹ after 65 min. The increase in concentration leads to a decrease in process efficiency.

263 The degradation of Amaranth Red (E123) was promoted by the hydroxyl radicals formed at the SS/PbO₂ surface
264 from the water oxidation and other weak oxidizing species formed in the sulphate medium. The efficiency of the
265 process depends mainly on the ability of the SS/PbO₂ anodes to produce [•]OH reagents (Skoumal et al. 2008).
266 The electrochemical oxidation of Amaranth Red (E123) can be divided into two main stages (Baddouh et al.
267 2019); the first one consists of the formation of hydroxyl radicals (OH[•]), which is evolved at the anode (M=
268 SS/PbO₂) upon water discharge reaction (Eq.(10))



270 In the second stage the (OH[•]) radical adsorbed on the surface of SSPbO₂ anodes as shown in (Equation 10) and
271 hence the hydroxyl radical oxidized the Amaranth molecules.



273 R: organic compound (Amaranth Red (E123))

274 The increase of the performance of the AO at first stages until reaching the concentration of 50 mg.L⁻¹ can be
275 due to the association of Amaranth Red (E123) molecules to form clusters of low diffusivity; this lowers the rate
276 of pollutant diffusion to the surface of SS/PbO₂ anodes. However, the decrease in the rate of hydroxyl radical's
277 formation leads to a decrease in the rate of Amaranth oxidation. Therefore, the % of dye removal decreases.
278 Similar behavior was observed by (Baddouh et al. 2019) for the removal of MB by AO SnO₂ anodes. As for
279 coupling AO with biosorption the variation of the effect of concentration is similar to each process alone. Both
280 processes have taken place; the presence of DC has played two main roles. At the initial stage of the coupling
281 process, it increased the speed of the fixation of Amaranth dye onto the available sites of *L.C*; the presence of the
282 electric field has increased the disorder in the solution and consequently the mobility of the Amaranth molecules
283 which increased the electrostatic interaction between these last and the functional groups of *L.C*, and therefore,
284 favored their retention by the *L.C*. When the entire available sites were full, DC placed his initial role for the AO
285 process, thus it favored the contact between the SS/PbO₂ anodes and the target molecules and accelerated the
286 production of [•]OH, which was week at the initial stage due to the presence of a large number of vacant sites onto
287 the biosorbent surface. These findings can be affirmed by the dissolution of Pb²⁺ during the electrolysis process
288 by the absorption atomic analysis.

289 **3.5. Evaluation of the efficiency of the AO and coupling AO with biosorption for the removal of** 290 **Amaranth: Calculation of % of color, ACE, EC, TOC, and COD removals**

291 Both AO and coupling AO with biosorption by *L.C* for the removal of Amaranth dye were evaluated based on
292 the ability to remove the color, COD, TOC and the variation of ACE, and the EC.

293 Based on results illustrated in Fig.5.a,b, and c; TOC, COD, and color removals have shown the same variation,
294 an increase in the percentages of removal was observed indicating the performance of both processes. However,
295 the variation of the average current efficiency (ACE) which presents the fraction of current required for the
296 degradation of Amaranth and its sub-products, and the energy consumed (EC) have shown different variations as
297 shown in Fig.5.d; a gradual increase over the time was observed for the EC by both processes used for the
298 removal of Amaranth. However, results achieved for the coupling process were better than those obtained for the
299 AO. The EC passed from $(0.07 \text{ to } 0.29) \times 10^3$ and from $(0.09 \text{ to } 0.56) \times 10^3$ (kWh. g⁻¹COD) respectively, for the
300 coupling process and the AO. The variation of ACE was inversely proportional to the variation of EC. As seen in
301 Fig .5.e, specific to the variation of % ACE; a decline in ACE was observed as a function of the electrolysis time
302 for both processes indicating the presence of secondary reactions including the oxygen evolution. Similar
303 findings were obtained in the literature where some researchers have attributed this variation to the formation of
304 refractory products and the decrease in the organic matter (Panizza and Cerisola 2005; Steter et al. 2014;
305 Sasidharan Pillai and Gupta 2015). Moreover, these percentages are lower in the case of the coupling process
306 which confirmed the positive effect played by the *L.C* which decreased the secondary reactions and the possible
307 by-produced produced during the reaction. These findings can be explained more by the germinations tests and
308 the atomic absorption analysis which will test the toxicity of the solutions treated.

309 **3.6. Evaluation of the quality of the treated water**

310 **3.6.1. Germination tests**

311 The performance of biosorption, AO, and biosorption coupling with OA was evaluated by phytotoxicity tests of
312 the raw and treated Amaranth solution was carried out using the germination test of *Lactuca Sativa* seeds. A
313 concentration of 10 mg.L⁻¹ was chosen for a pH = 2, T=25°C, and after treatment of 80 min. The germination
314 inhibition results obtained are shown in Fig.6. The reference is distilled water. As seen the initial germination
315 index (GI) of Amaranth dye is 35%, an increase in this value was observed after the removal of this dye by
316 biosorption, AO, and coupling AO with biosorption. The GI% has reached about 86% higher than the other
317 processes, which presented a predicted result since biosorption is safe and environmentally friendly. As for the
318 AO, it reached about 54% and for the coupling process about 72%. These findings indicated that the entire
319 percentages are higher than 50% and therefore decay in the toxicity of the tested solutions was achieved
320 (Buchmann et al. 2014). Furthermore, these rates confirmed the decrease in the amounts of by-products formed
321 by the oxidation of amaranth on the SS/PbO₂ anodes (Elaiassaoui et al. 2016). The high values reached in the case
322 of the coupling process compared to the AO can be explained by the positive effect played by the *L.C* which

323 favored the retention of Amaranth by the available sites on its surface and therefore minimize the amount of the
324 by-products formed. Similar behavior was observed for the removal of methylene blue when using the same
325 process (Othmani et al. 2020a).

326 **3.6.1. Atomic Absorption**

327 Dealing with results registered in table SM-2, the presence of detectable Pb^{2+} in solution begins before 50 and 20
328 min of the total degradation of Amaranth respectively for the AO the coupling process. These findings
329 emphasized the positive effect plays by the *L.C* which enhanced the stability of the anodes by decreasing the
330 contact between these last and the Amaranth and favoring at the same time the retention of the major
331 concentration of this dye. These observations confirmed the explanation given for the effect of concentration on
332 the removal of Amaranth from the solution. Therefore, coupling AO with biosorption by *L.C* fibers can offer a
333 performing alternative for the removal of hazardous pollutants by cheap and safe alternative. The Pb^{2+} ions
334 reached about $0.020 (\pm 0,002 \text{ mg.L}^{-1})$, after the total removal of Amaranth dye (60 min) and $0.051 (\pm 0,002 \text{ mg.L}^{-1})$
335 after (80 min) respectively, for coupling AO with biosorption and the AO process. These values are lower than
336 those allowed by the Tunisian Standards (NT 106.02, 1989).

337 **3.7. Test of the efficiency of the coupling process on the stability of the SS/PbO₂ anodes**

338 The efficiency of the SS/PbO₂ anodes is linked to the stability of oxide layers during electrolysis. Generally,
339 PbO₂ electrodes have a major drawback which is the deposit corrosion; this corrosion can lead to a loss of
340 efficiency of the electrode. To evaluate the efficiency of the AO and the coupling process on the increase of the
341 lifetime of the SS/PbO₂ anodes during the removal of Amaranth dye, SEM and XRD characterizations after the
342 use of anodes were performed. As seen in Fig.7.a after the use of SS/PbO₂ anodes for the AO of Amaranth, the
343 SEM image of SS/PbO₂ anodes shows the same structure showed before use with the appearance of some big
344 holes specific to the detachment of the PbO₂ layer from the substrate. As for the SEM image specific to the
345 anodes used for the coupling process (Fig.7.b), it shows two different parts like it are divided into two different
346 aspects, indicating a heterogeneous structure due to the electrolysis treatment, and this can ensure that both
347 processes have taken place for the removal of the Amaranth dye in the case of the coupling process. Based on
348 these SEM images and XRD diffractograms, it well noticed that the coupling process has enhanced the stability
349 of the deposited PbO₂ layer on the SS substrate due to the relaxation time offered to the used anodes by the
350 biosorption process which decreased the contact between the Amaranth dye with the anodes and favor their
351 retention by the dominant positively charged sites of *L.C*. These findings can explain the extinction of the major
352 electronic conduction and electrochemical reduction peaks of PbO₂ as shown in the specific diffractogram

353 obtained for the anodes after the removal of Amaranth by AO. Therefore, we can confirm the effectiveness of
354 the coupling process on the increase of the stability of the anodes used.

355 **3.8. *L.C* regeneration studies**

356 The regeneration ability of the used *L.C* through three consecutive biosorption/desorption cycles was performed
357 for a biosorbent mass of 3 g, an initial concentration of Amaranth of 10 mg.L⁻¹, V=0.5 L, and T=25°C. Tests
358 were carried out at different pH media; 2, 7, and 10. Based on Fig.8, the best desorption was obtained at pH=2
359 for the biosorption and biosorption coupling AO. As seen, at pH 7 and 10 all the desorption rates for the three
360 cycles were higher than 50% indicating that the retention forces of Amaranth by the *L.C* for both processes and
361 during the three cycles are weak. Thus at neutral and basic pH, the biosorption of Amaranth is physisorption
362 (Inyinbor et al. 2015). In other words, the linkages are Van Der Waals which can explain the easiness of the
363 desorption. Of course, the rates are approximatively the same with very low experimental errors since we have
364 the same number of sites and the capacity uptake is the same. At pH=2, all the desorption rates obtained for the
365 biosorption and the biosorption coupling AO were lower than 50% confirming that the retention forces of
366 Amaranth by both processes are strong and therefore it is chemisorption. In this case, the biosorption
367 mechanisms involved in this retention may be hydrogen-bonding formations, and n- π interaction (Tran et al.
368 2017). As seen after the desorption rates decreased slowly after three cycles of biosorption/desorption of
369 Amaranth dye by biosorption and biosorption coupling AO. It appears that the times required for the saturation
370 for the biosorption and biosorption coupling AO decreased by increasing the number of regeneration cycles
371 which can be dependent on the gradual decrease of the biosorption capacity from the first to the third cycle.
372 Despite this gradual decrease, these findings confirmed the good regeneration ability of the used *L.C* even after
373 three continuous cycles.

374 **3.9 A comparative study with reported literature**

375 The success of the alternative offered for the enhancement of the deposited PbO₂ layer on the target substrate
376 cannot be confirmed without comparing the main achievement with those illustrated in previous studies
377 Therefore, a comparative study of the stability of the PbO₂ layer onto a different substrate and their performance
378 for the degradation of some pollutants was given in the table SM-3. Based on the results collected coupling AO
379 using SS/PbO₂ anodes with biosorption by *L.C* has shown similar efficacy to those reached after doping the
380 anodes used.

381 **3.9. Possible pathway for the removal of Amaranth dye by coupling AO with biosorption**

382 An assumption of the pathway of the removal of Amaranth by the AO and coupling AO with biosorption was
383 proposed. Based on the literature the possible pathway for the degradation of Amaranth dye by AO under DC is

384 divided into two main steps: the first one as described in Fig.8 is specific to the formation of hydroxyl radicals
385 which is evolved at SS/PbO₂ anodes upon water discharge reaction, after that the hydroxyl radicals will be
386 adsorbed on the surface of the used anodes. The second step consists of the oxidation of the Amaranth dye by
387 these last. As for the coupling process, and based on results obtained during this study, the mechanism can be
388 divided into two stages. The first one is specific to the fixation of the Amaranth onto the available sites onto the
389 surface of *L.C* until the saturation phase. As the dominant functional groups onto the *L.C* are positively charged,
390 the main pathway of the fixation of Amaranth is the electrostatic interaction (especially that the Amaranth is
391 negatively charged at pH =2). The second one is specific to the AO process were the same mechanism that is
392 described before has taken place for the degradation of the remaining molecules of Amaranth dye.

393 **4. Conclusions**

394 Coupling anodic oxidation using SS/PbO₂ anodes electrodeposited by pulsed mode current with biosorption
395 by *Luffa cylindrica* has offered a cheap and effective alternative for the removal of Amaranth Red (E123) from
396 aqueous solution. The combination of both processes has enhanced the stability of the electrodeposited layer of
397 PbO₂ on the SS substrate giving similar performance to that of the doping methods. The results showed that the
398 presence of biosorbent allowed the retention of Amaranth by their available vacant sites which minimize the
399 dissolution of Pb²⁺ ions, increase the percentages of removal of Amaranth and decrease the required time for the
400 purification. During the coupling process direct current has played two main roles; it increased the contact
401 between the opposites charged species in solution which accelerated their retention of Amaranth dye by the
402 biosorbent used and enhanced the production of hydroxyl radicals which favors the degradation of the target
403 pollutant. The biosorption/desorption confirmed the good regeneration ability of the used *L.C* even after three
404 continuous cycles. Atomic absorption analysis confirmed the respect of the obtained concentrations of Pb²⁺ to
405 the Standards. The phytotoxicity tests confirmed the possibility of the reuse of the treated water where all the
406 germination indexes are higher than 50%. Therefore the sub-products produced during the degradation of
407 Amaranth dye are mineralized as confirmed by the high values of COT and COD. Thus the treated solutions can
408 load to any receiving water.

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412 **Conflict of interest**

413 The present paper is an original work with no conflict of interest of any kind.

414 **Ethical Approval:** Dr Amina Othmani confirms that this work is original and has not been published elsewhere
415 nor is it currently under consideration for publication elsewhere.

416 **Consent to Participate:** Not applicable.

417 **Consent to Publish:** Dr Amina Othmani agrees to publish this work.

418 **Authors Contributions:** The conceptualization, methodology, writing- original draft preparation, and editing
419 were done by Dr Amina Othmani

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422 **Availability of data and materials:** Applicable.

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548

Figures

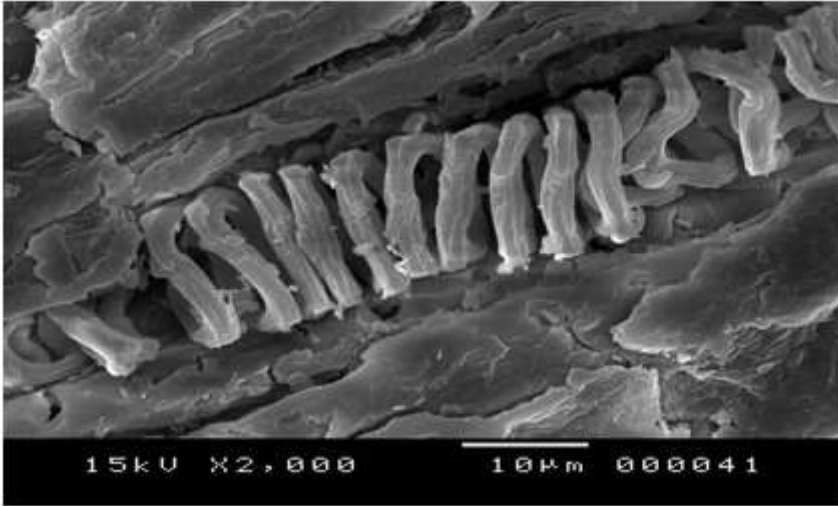


Figure 1

SEM of L.C

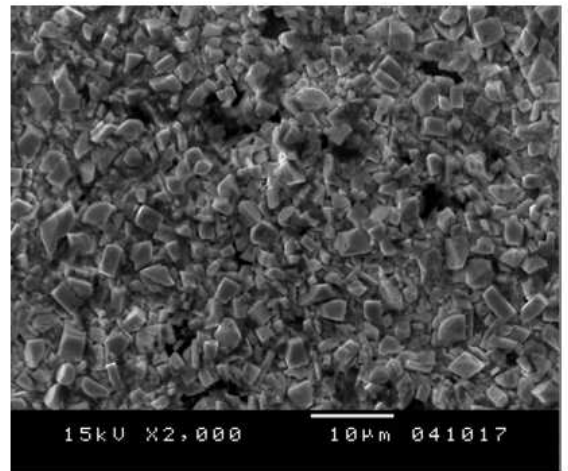
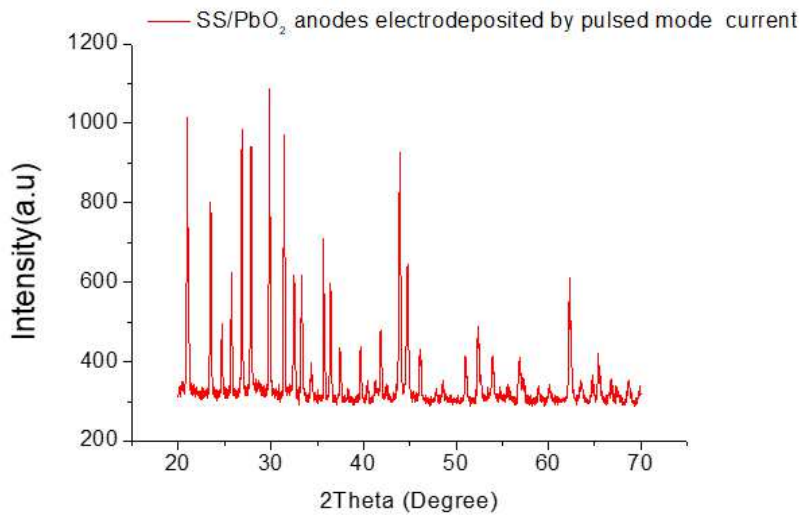


Figure 2

XRD and SEM of SS/PbO₂ anodes

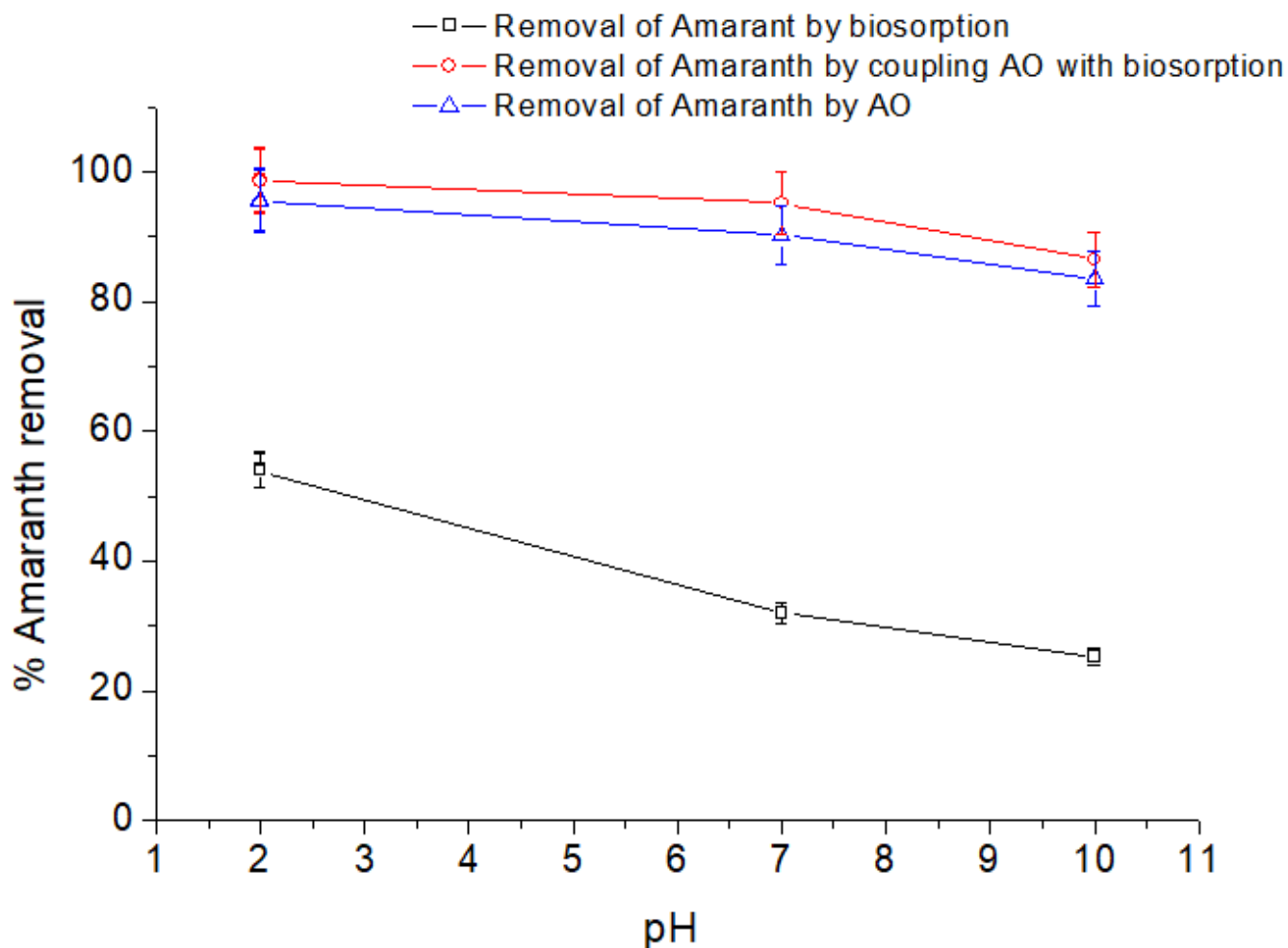


Figure 3

Effect of pH on the removal of Amaranth, $C_0=10 \text{ mg.L}^{-1}$, $t=100 \text{ min}$, $T=25^\circ\text{C}$, $C_{\text{Na}_2\text{SO}_4}=0.1\text{M}$, $J=25 \text{ mA/cm}^2$, $m \text{ L.C}=0.5 \text{ g}$, $V=0.5 \text{ L}$

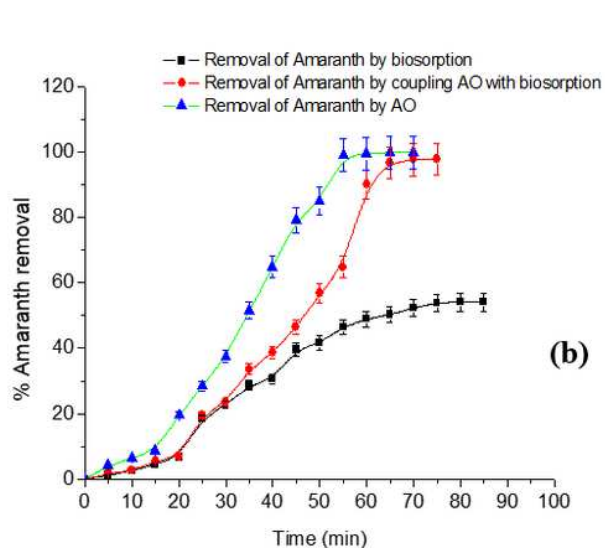
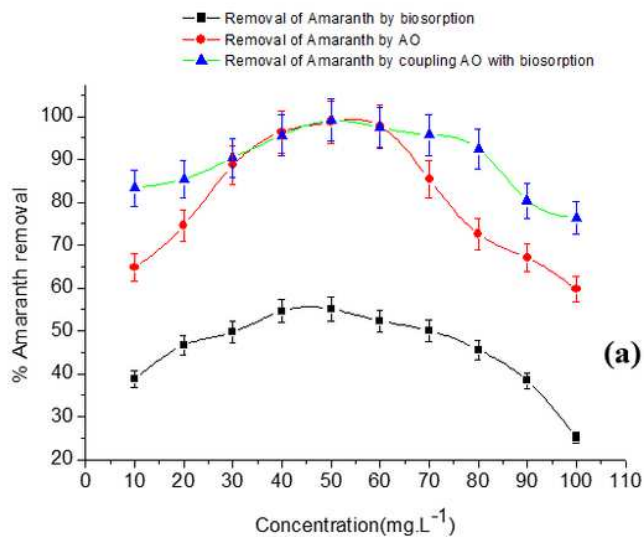


Figure 4

Effect of (a) initial concentration , (b) contact (and electrolysis) time on the removal of Amaranth by biosorption AO, and coupling AO with biosorption, $T=25^{\circ}\text{C}$, $\text{CNa}_2\text{SO}_4=0.1\text{M}$ $\text{pH}=2$

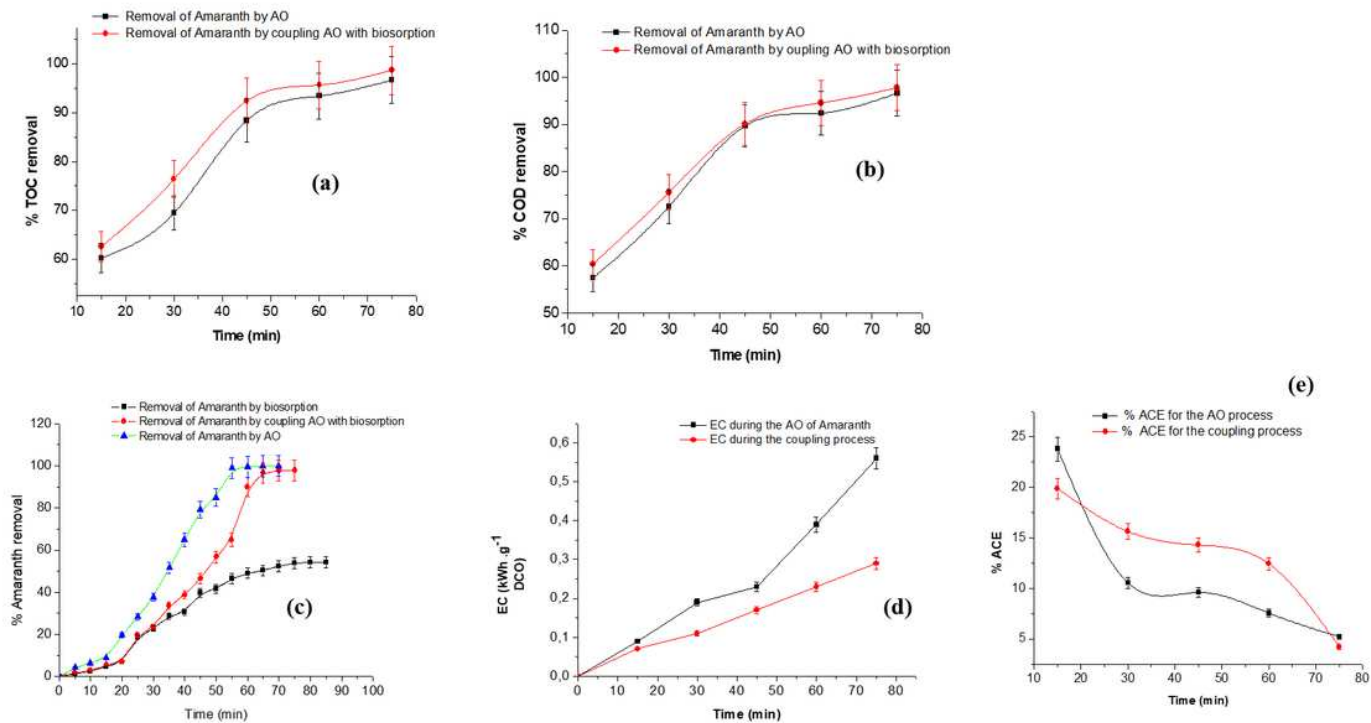


Figure 5

Evaluation of (a) % TOC, (b) % COD; (c) % Amaranth removal , (d) % EC, and (e) %ACE achieved during the removal of Amaranth by AO and coupling AO with $\text{C}_0=10\text{ mg.L}^{-1}$, $\text{J}=25\text{ mA.cm}^{-2}$, $T=25^{\circ}\text{C}$, $\text{CNa}_2\text{SO}_4=0.1\text{M}$, $\text{pH}=2$, $T=80\text{ min}$

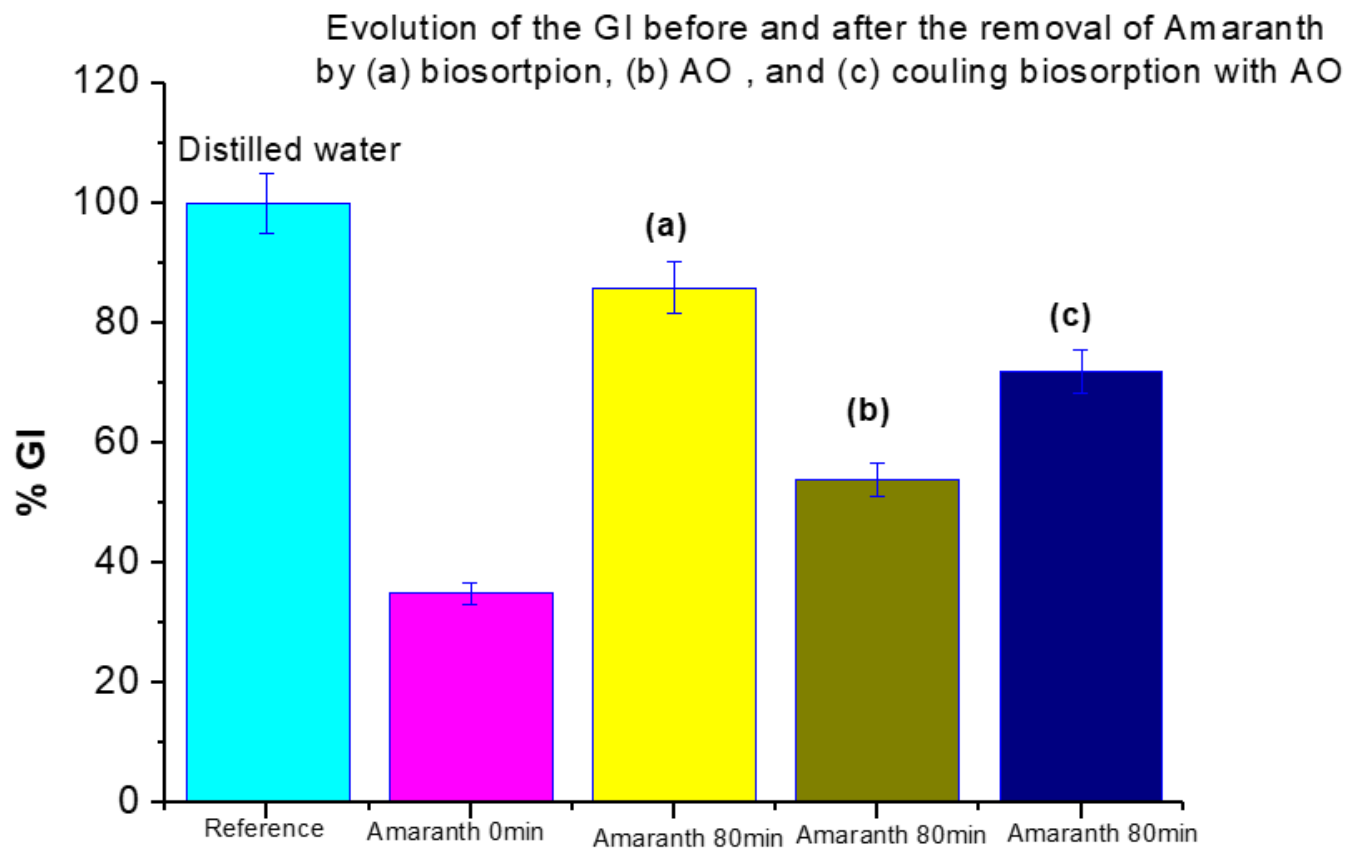


Figure 6

Evolution of the germination index (% GI) before and after removal of Amaranth dye by differ processes

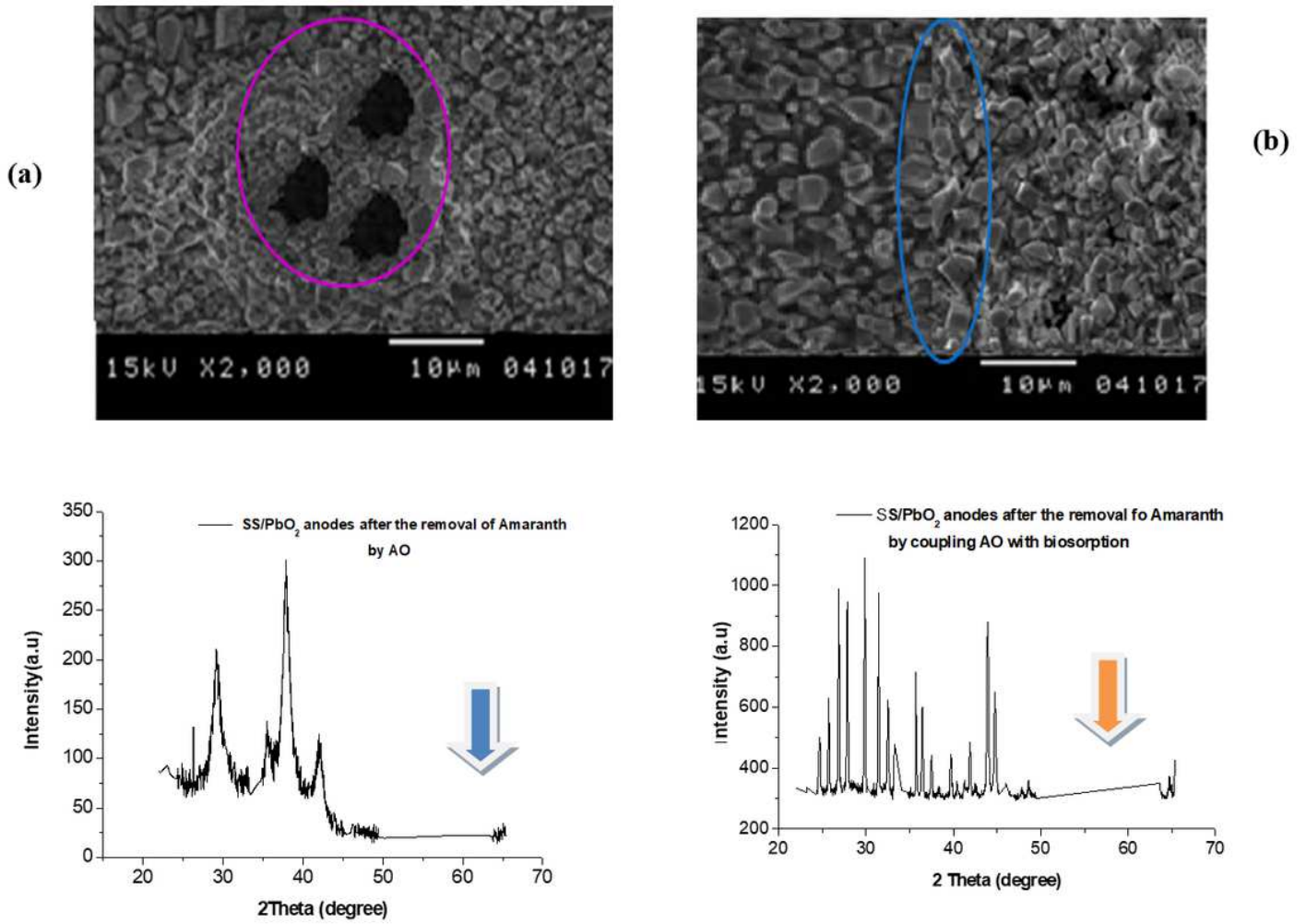


Figure 7

SEM images of SS/PbO₂ anodes after the removal of Amaranth dye by (a) AO, (b) coupling AO with biosorption

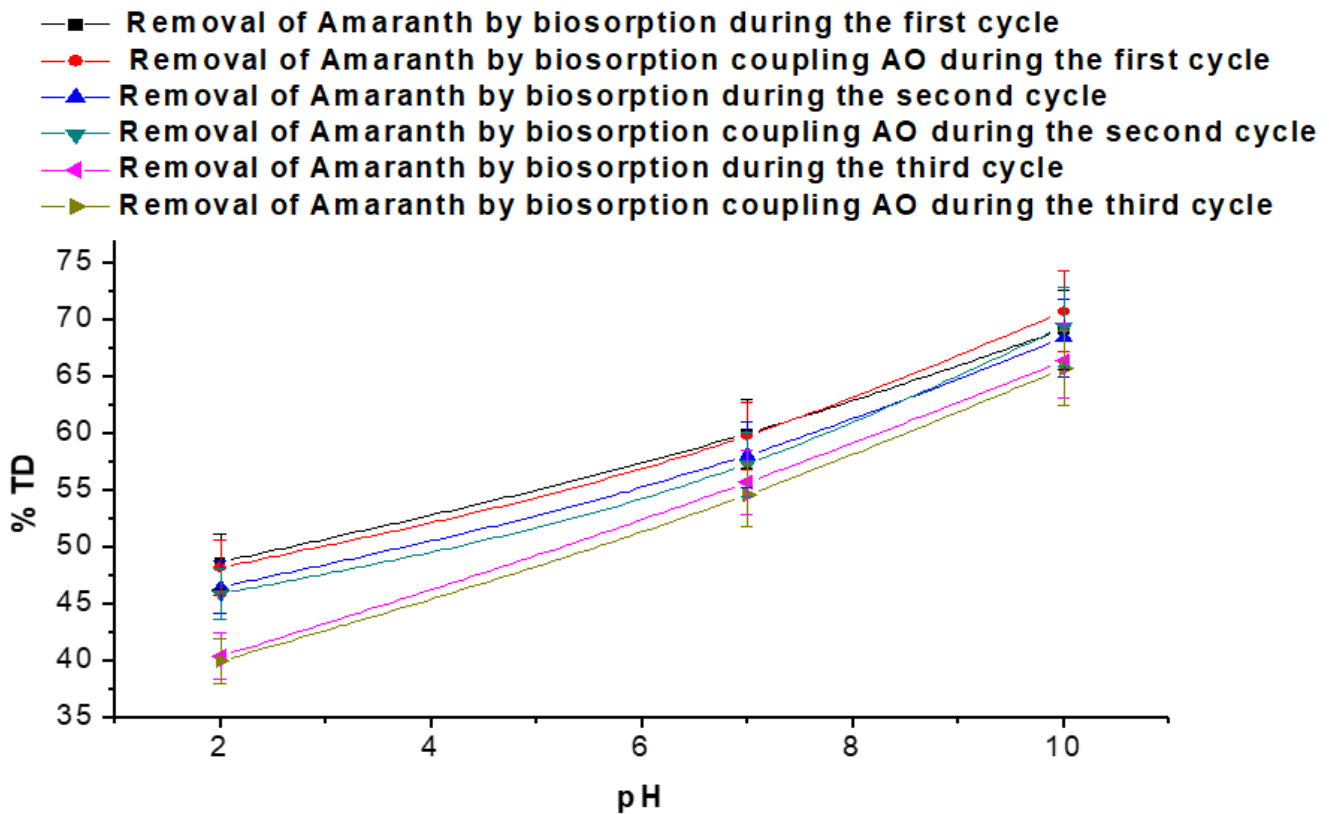


Figure 8

Evaluation of the desorption rate of L.C after the removal of Amaranth dye by AO and AO coupling biosorption after successive cycles (biosorption/desorption)

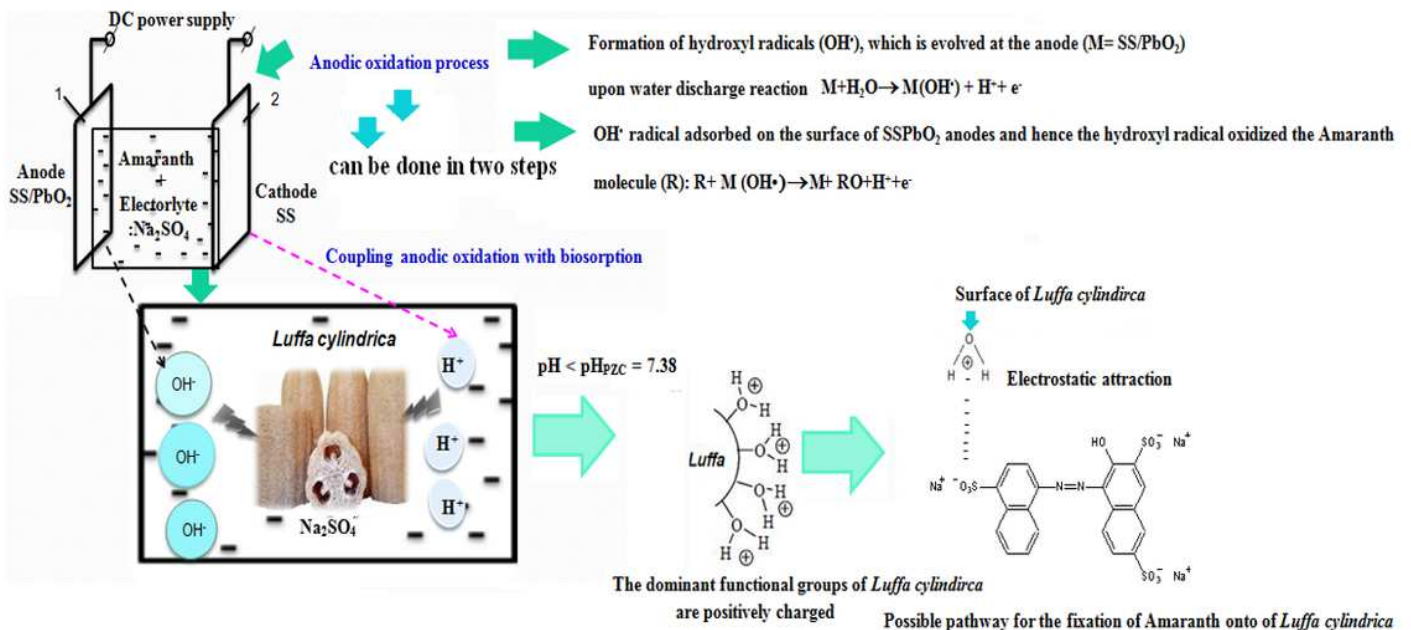


Figure 9

Proposed pathway for the removal of Amaranth by AO and AO coupling biosorption

Supplementary Files

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