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1 **Influence of number of azo bonds and mass transport limitations**
2 **towards the elimination capacity of continuous electrochemical**
3 **process for the removal of textile industrial dyes**

4
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15
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28 **ABSTRACT**

29 This study focusses on the electrochemical decomposition of synthetic azo dyes (RO16,
30 RR120 and DR80) using stainless steel electrodes, which is efficient, cost effective and
31 industrially driven process. The experiments were carried out in a continuous electrochemical
32 reactor and the effects of influencing parameters (initial concentration of dye, electrolyte
33 concentration, pH) governing the process efficiency was studied. The interaction between the
34 influencing parameters was investigated using Response Surface Methodology (RSM) and the
35 regression value obtained for the generated model was above 0.9 for all the three dyes. The
36 elimination capacity of electrochemical reactor was studied for the continuous removal of azo
37 dyes with different ranges of concentration (100 - 400 mg L⁻¹) and flow rate (0.1 - 0.5 L h⁻¹).
38 The maximum elimination capacity was obtained at a flow rate of 0.5 L h⁻¹ for 300 mg L⁻¹ of
39 initial concentration of dye for RO16 and RR120 whereas it was 0.5 L h⁻¹ for 400 mg L⁻¹ of
40 DR80. Further, a general dimensionless current density relation has been established for stirred
41 tank reactor and allowed characterizing the relationship between kinetics and mass transport
42 contributing to the overall reaction rate. The results quantitatively confirmed that the rate of
43 electrochemical decolorization increased with the increasing initial dye concentration and flow
44 rate due to the mass transport limitation. As newly established, the decolorization is also
45 directly linked to the number of azo bonds.

46

47 **Keywords:** *Azo dyes; Electrochemical process; Response Surface Methodology; Continuous*
48 *mode; Elimination capacity; Dimensionless current density*

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50

51

52 1. INTRODUCTION

53 Rapid industrialization, continuous growth of population and over exploitation of natural
54 resources has created an imbalance in the ecosystem. It has also intensified the environmental
55 issues associated with water, air and land. Enormous increase in the growth and development
56 of industries created a global demand for water due to its excessive consumption as it cannot be
57 substituted for its wide range of industrial applications. But the prevailing water crisis has
58 created an increasing awareness on the limited access to freshwater resources. The United
59 Nations World Water Development report released in 2018, forecasts that by the year 2050
60 nearly 3.6 to 4.6 billion people will be facing severe water stress.

61 On the other hand, due to the negligence in the implementation of stringent policies
62 towards industrial water treatment as well as lack of efficient technologies in large scale has
63 created an another dimension of water stress in terms of quality. Large amount of water and
64 chemicals are consumed by the textile hubs for the wet processing of materials and
65 simultaneously significant volume of contaminated effluent is discharged (Hasanbeigi and
66 Price, 2015). Consumption of such contaminated resources will have a direct impact on the
67 health status of the human. Among such micropollutants, azo dyes creates a major havoc to the
68 environment and the public health because of their toxic nature due to the presence of aromatic
69 amine groups (Holkar et al., 2016). Schneider et al., reported on the mutagenic nature of textile
70 dyes by studying the genotoxic activity of azo dyes (Schneider et al., 2004). Additionally,
71 allergic contact dermatitis and respiratory diseases are known to be caused by textile dyes
72 (Gürses et al., 2016). However, azo dyes are predominantly used by majority of the Indian
73 textile industries as it is economic and also acts as an effective chromophore. The available
74 literature demonstrates an extensive number of treatment methodologies involving physical
75 methods like adsorption (Brahmi et al., 2019; Shahnaz et al., 2020a, 2020b; Sharma et al.,
76 2020), chemical (Jegan Durai et al., 2020) and biological processes (Padmanaban et al., 2016)

77 as well as some of the new emerging techniques like advanced oxidation process and
78 photoelectrocatalysis (Aquino et al., 2013). Though there are plethora of research publications
79 on developing process for the decolorization of textile dyes, still in industries those
80 technologies are not in practice. Most of the developed process in the laboratory conditions
81 fails during scale up or during experimenting with real industrial effluent. The possible reasons
82 could be: (a) process development using pH indicators and stains; (b) the industrial effluent is a
83 complex mixture of different classes of dyes like monoazo, diazo, polyazo, Reactive and
84 Direct; (c) the industrial effluent pH is alkaline in nature; (d) high salt concentration in the
85 industrial effluent; (e) large volumes to handle at short time, i.e. high treatment capacity
86 requirement. To face these multiple constraints, developing a cost-effective technology remain
87 a challenge. A streamlined approach need to be followed during the process development for
88 the decolorization or degradation of dyes by using chemical engineering tools and
89 methodology.

90 Over the past decades, electrochemical processes have gained an increasing interest among
91 the environment researchers in treating various micro and macro pollutants from various
92 industries and especially dyes (Brillas and Martínez-Huitle, 2015). In direct electrolysis, at the
93 anodic surface, direct exchange of electrons takes place with the pollutants, thereby it
94 destabilises or degrade the pollutants whereas in indirect electrolysis, the exchange of electrons
95 with the pollutants is mediated by active species. The chain of redox catalysis takes place from
96 anodic surface to pollutants through series of electroactive species generated reversibly or
97 irreversibly (Panizza and Cerisola, 2009). Non-active anodes can even produce physisorbed
98 hydroxyl radicals ($\cdot\text{OH}$) that are available for indirect oxidation of the majority of organic
99 compounds that can enhance the degradation and mineralization efficiency (Mousset et al.,
100 2018). Upon the superiority of this mechanism, numerous articles proposed their
101 implementation for dyes elimination (Brillas and Martínez-Huitle, 2015). However, such

102 advanced electro-oxidation processes involve expensive materials such as boron-doped
103 diamonds (BDD) materials that proved to be currently the best option for long-term and real
104 applications (Nidheesh et al., 2019). Contrastingly, when using active anode, i.e. without
105 available $\cdot\text{OH}$ for indirect oxidation, the electrochemical degradation of dyes wastewater could
106 still occur, mainly by electron transfer reaction coupled with a dissociation chemisorption step
107 (Mohan et al., 2007). The efficiency of direct anodic oxidation of dyes benefits from the
108 presence of several functional groups (e.g. azo bonds) on their molecules that make them
109 electroactive for direct electron transfer (Michaelis, 1935). Moreover, the advantage of active
110 anodes (e.g. graphite, stainless steel) is their low cost compared to non-active materials, while
111 their efficiency towards dyes removal could remain still competitive in terms of cost-efficiency
112 (Mohan et al., 2007). This type of oxidation has been further tested as a viable alternative for
113 the degradation of textile dyes owing to their cost-effectiveness, eco-friendly nature and ability
114 to produce less sludge (Bassyouni et al., 2017). Moreover, electrocoagulation process has also
115 demonstrated to be effective for dye wastewater treatment by using cheap aluminium or iron
116 based- sacrificial anode for coagulant generation (Arslan-Alaton et al., 2008). A synergy by
117 using a non-active anode such as stainless steel that can act both as sacrificial anode and as a
118 role of direct electro-oxidation could be therefore interesting (Arslan-Alaton et al., 2008). The
119 presence of chloride at sufficient high concentration ($> 0.6 \text{ g L}^{-1}$) has shown to favour both the
120 mediated oxidation with active chlorine (Cl_2 , ClOH) and the electrocoagulation mechanism
121 with iron-based anode (Hakizimana et al., 2017). Since dye effluents contain high content of
122 chloride, this could be interesting to combine electro-oxidation with electrocoagulation for
123 such application (Hakizimana et al., 2017).

124 In order to proceed with this approach, better understanding on the electrochemical process,
125 the influence of molecular structure of dyes as well as the competition study between charge
126 transfer and mass transport is required for such heterogeneous process. The main objective of

127 this study is therefore to provide answers to these issues for the first time, by developing a
128 continuous stirred electrochemical reactor for the decolorization of textile dyes having different
129 number of azo bonds. An optimization of the technology is first proposed, by using One
130 Variable At a Time approach (OVAT) and Response Surface Methodology (RSM) in batch
131 mode. Then the effectiveness of the process in terms of elimination capacity, current efficiency
132 and energy consumption has been assessed under continuous mode. A general expression of
133 dimensionless current density is suggested for stirred tank cell design, as a way of better
134 quantitatively describe the competitiveness between charge transfer and mass transport
135 phenomena.

136

137 **2. MATERIALS AND METHODS**

138 **2.1. Chemicals used**

139 In this study, industrially used azo bond containing dyes of different classes were used.
140 Reactive Orange 16 (RO16), Reactive Red 120 (RR120) and Direct Red 80 (DR80) were taken
141 as the model dyes and were procured from Sigma-Aldrich, India. The physico-chemical
142 properties of the dyes are given in Table SM-1. Other chemicals such as sodium chloride
143 (NaCl), hydrochloric acid (HCl) and sodium hydroxide (NaOH) of laboratory grade were
144 purchased from HiMedia Laboratories, India. Simulated dye solution was prepared by
145 dissolving the industrially used azo dyes (RO16, RR120 and DR80) in aqueous medium and
146 was diluted to the specified concentration as released in the industrial effluent. Sodium chloride
147 is used as the supporting electrolyte in the process, since Cl^- is a predominant inorganic species
148 at high concentration in most of dyes effluents (Hakizimana et al., 2017). The pH of the
149 solution was adjusted using 1 N NaOH (basic) and 1 N HCl (acidic).

150

151

152 2.2. Electrochemical reactor and dye decolorization analysis

153 A cylindrical lab scale reactor made up of borosilicate glass with a net volume of 1500
154 cm³ was used for the electrochemical decolorization of synthetic wastewater. Stainless steel
155 electrodes (both anode and cathode) (Kristeel brand) with an immersed surface area of 17 cm²
156 were used. The inter-electrode distance between the anode and cathode was fixed as 4 cm for
157 all the experimental runs. For all the experiments the voltage was maintained within the ranges
158 of 3.8 - 4.0 V (previous unpublished data) using a variable DC power supply (Sciencetech
159 Technologies), corresponding to an average applied current density of 47 mA cm⁻². These
160 values fall in the range of optimal current density found in a previous study using stainless steel
161 sacrificial anode for dye wastewater (Arslan-Alaton et al., 2008). A magnetic stirrer (Remi)
162 was used for the stirring of solutions (100 rpm). The experiments were conducted at room
163 temperature. Block diagram of the electrochemical reactor is shown in the graphical abstract.
164 Sludge were also generated during the electrocoagulation mechanism at the stainless steel
165 anode, according to Eq. (1) and Eq. (2) (Arslan-Alaton et al., 2008):



168 The sludge was then separated using centrifugation at 8000 rpm for 5 min. The decolorization
169 of dyes was monitored by change in absorbance and measured λ_{max} as specified in the Table
170 SM-1 using a UV-Visible spectrophotometer (Eppendorf, Germany). The percentage of
171 decolorization and concentration of dye decolorized were calculated based on Eq. (3):

$$172 \quad \% \text{ removal in terms of decolorization} = \left(\frac{A_i - A_t}{A_i} \right) \times 100 \quad (3)$$

173 where A_i and A_t are absorbance at initial time and absorbance at time t , respectively.

174

175

176

177 **2.3. Batch process optimization – OVAT**

178 A batch mode was chosen as a preliminary step to determine the effects of pH,
179 electrolyte concentration and initial concentration of dye on the electrochemical decolorization
180 of synthetic wastewater. This investigation was carried out in order to determine the optimum
181 operating conditions for achieving maximum percentage of dye decolorization. For better
182 understanding of the influencing factors, individual set of experiments were performed for all
183 the three dyes (RO16, RR120 & DR80) within the specified range of reaction conditions (pH:
184 3.0 - 11.0, electrolyte concentration: from 0.1 to 0.5 M and initial concentration of dye: from
185 100 to 500 mg L⁻¹). Working volume of 500 mL was fixed for all experiments. The treated
186 samples collected at periodic time intervals were subjected to centrifugation (5000 rpm, 5 min)
187 for separating the sludge particles generated during the electrochemical process.

188

189 **2.4. Batch process optimization – RSM**

190 RSM is one of the structured statistical methods for designing experiments, generating
191 models, understanding variable effects on the response and also for improving the response
192 using optimal conditions (Amani-ghadim et al., 2013). In this study, modified face centred
193 central composite design (CCF) with alpha value 1.0 was used to analyze the interaction
194 between the influencing parameters and also on the selection of optimum variables for
195 maximizing the decolorization of synthetic azo dyes. Initial concentration of dye, pH and
196 reaction time for the electrochemical process were the selected factors to be studied using
197 RSM. In case of direct dyes, pH was excluded as it had no significant effects on decolorization.
198 The experimental design for the decolorization of azo dyes is shown in Table 1.

199

200

201

Table 1 Experimental design for decolorization of azo dyes by RSM-CCF

a) Reactive dyes (RO16 and RR120)					
Factor	Units	Low Actual	High Actual	Mean	Std. Dev
A = Initial concentration of dye	mg L ⁻¹	100	1000	550	318.29
B = pH	-	3.0	11.0	7.0	2.828
C = Time	min	5	15	10	3.536
Response	Units	Model	Transformation	Mean	Ratio
Y₁ = Concentration of RO16 decolorized	mg L ⁻¹	Quadratic	Base 10 log	204.52	57.496
Y₂ = Concentration of RR120 decolorized	mg L ⁻¹	Quadratic	Inverse Sq Rt	265.27	12.89
b) Direct dye (DR80)					
Factor	Units	Low Actual	High Actual	Mean	Std. Dev
A = Initial concentration of dye	mg L ⁻¹	100	1000	550	318.29
B = Time	min	5	15	10	3.536
Response	Units	Model	Transformation	Mean	Ratio
Y₃ = Concentration of DR80 decolorized	mg L ⁻¹	Quadratic	Power	492.79	10.88

202

203

204

205 **2.5. Decolorization of azo dyes – Continuous process**

206 The decolorization of the azo dyes was monitored during continuous electrochemical
207 treatment. The simulated dye solution was pumped into the continuous reactor via peristaltic
208 pump with a predetermined flow rate (ranging from 0.1 to 0.5 L h⁻¹). For all the experimental
209 runs, hold-up volume of the reactor was maintained as 700 mL by providing similar flow rates
210 at both the inlet and outlet. This experiment was performed with various dye concentrations
211 (100, 200, 300 and 400 mg L⁻¹) at pH 11.0 for all the three dyes. The electrolyte (salt)
212 concentration was maintained using 0.5 M NaCl. The reactor efficiency was calculated by the
213 elimination capacity for different inlet loading rates using Eq. (4) and Eq. (5).

$$214 \quad \text{Inlet loading rate (mg (Lh)}^{-1}) = \frac{C_{in}Q}{V} \quad (4)$$

$$215 \quad \text{Elimination capacity (mg (Lh)}^{-1}) = \frac{(C_{in}-C_{out})Q}{V} \quad (5)$$

216 where C_{in} and C_{out} are inlet and outlet concentration of dye respectively, Q is the
217 volumetric flow rate (L h⁻¹) and V is the holdup volume of the reactor (L).

218

219 **3. RESULTS AND DISCUSSION**

220 **3.1. Characterization of dye – Changes in absorption spectra**

221 The characterization and the suitability of the kinetics of dye decolorization assessment by the
222 spectrophotometric method is carried out as a preliminary step. 100 mg L⁻¹ of simulated
223 solution was prepared individually for all the three dyes (Operating conditions: pH 11.0, 0.5 M
224 NaCl, 4 V) and subjected to electrochemical process for 10 min. The result of changes in
225 absorption spectra of samples before decolorization (0th min) and after decolorization is shown
226 in the Fig. SM-1. The UV-Visible spectrophotometric analysis of non-decolorized RO16 dye
227 shows two prominent peaks at 490 nm and 390 nm, RR120 shows at 510 nm and 290 nm and
228 DR80 shows at 540 nm and 290 nm respectively. The peak in the visible region corresponds to
229 the conjugated structure of azo bond (chromophores) and peak in the UV region is attributed to

230 the aromatic structure (Padmanaban et al., 2018). The dye solutions subjected to
231 electrochemical process lost its colour and it is confirmed from the disappearance of prominent
232 peaks without apparition of interfering peaks that could come from the matrix and
233 intermediates generated with electrolysis time. It further confirms the reliability to use this
234 method for the following batch and continuous mode studies, by considering that the
235 absorbance measured at wavelength giving maximal absorbance of the dye was link only to the
236 concentration of the studied dye and not to any other species that could absorb also at this
237 wavelength.

238

239 **3.2. Batch process optimization – OVAT**

240 Most textile industries produce effluent that need to be neutralized from highly alkaline pH
241 prior to discharge or reuse. With respect to effluent treatment plants, the pH of the influent
242 coming to the plants may be of diverse range of pH and it has to be brought near to the pH of
243 the process employed in the treatment plant. The effect of pH (3.0 - 11.0) on the process of
244 decolorization was studied through five different batch experiments at 100 mg L⁻¹ of initial
245 concentration of dyes (RO16, RR120 & DR80) with 0.5 M of electrolyte concentration at 4 V.
246 At 6th min, the process of decolorization comes to an equilibrium. Table 2 depicts the
247 percentage of dye decolorization at 6th min for different pH. For the reactive and direct dyes,
248 percentage of decolorization increased while moving from acidic condition to alkaline
249 condition. Close examination of the results indicates that nearly 100% of decolorization was
250 achieved at pH 11.0. At pH > 7.5, the rate of Fe²⁺ oxidation into Fe(OH)₂(s) (Eq. (6)) is
251 increased, which subsequently increase the production of Fe(OH)₃(s) (Eq. (7)) and can
252 therefore increase the electrocoagulation efficiency (Hakizimana et al., 2017).

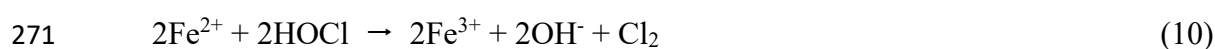


255 Knowing that the pH of majority of textile wastewaters (cotton fibre) lies within the range 8.0-
256 12.0 (Correia et al., 1994), pH adjustment won't be required to operate at optimal pH. Hence,
257 pH 11.0 is considered to be the optimum pH for the decolorization of azo dyes by
258 electrochemical process with the employment of stainless steel electrodes.

259 The effect of electrolyte was studied at various concentrations ranging from 0.1 to 0.5 M
260 NaCl. From Table 2, it is shown that the percentage of decolorization for the solution with an
261 initial dye concentration of 100 mg L⁻¹ and pH 11.0 increases with the increasing electrolyte
262 concentration. Eq. (8) and Eq. (9) shows that the active chlorine species (Cl₂, ClOH) (Mousset
263 et al., 2020)) generated from Cl⁻ oxidation could have contributed in the indirect
264 electrochemical process of azo dyes:



267 Similar kinds of results have been also reported with active anode that was not made of
268 mixed metal oxide but with a carbon-based material (Mousset et al., 2020). In addition, the
269 formation of active chlorine has shown to increase the formation of Fe³⁺ (Eq. (10)), that then
270 enhance the electrocoagulation process (Hakizimana et al., 2017):



272 For reactive dyes, 0.5 M NaCl was the optimum electrolyte concentration for achieving
273 100% of dye decolorization, while the maximum of decolorization was already reached at
274 0.3M with DR80. Therefore, the supporting electrolyte concentration was fixed at 0.5 M for the
275 subsequent experiments as the real time textile industrial effluent has a mixture of reactive and
276 direct dyes. This is further representative of the range of concentrations given in real dye
277 wastewater (Arslan-Alaton et al., 2008).

278

279

Table 2 Decolorization of azo dyes – One Variable At a Time approach: Effect of pH, Effect of Electrolyte Concentration (NaCl), Effect of Initial Concentration of dye

pH	% of dye decolorized		
	RO16	RR120	DR80
3.0	53	79	84
5.0	57	89	86
7.0	61	85	90
9.0	87	93	98
11.0	100	97	100

*Initial conc. of dye = 100 mg L⁻¹; Electrolyte concentration = 0.5 M;
Voltage = 4 V; Run time = 6 min*

Electrolyte Concentration (M)	% of dye decolorized		
	RO16	RR120	DR80
0.1	18	9	39
0.2	21	33	72
0.3	23	63	100
0.4	47	83	100
0.5	90	100	100

*Initial concentration of dye = 100 mg L⁻¹; pH = 11.0;
Voltage = 4 V; Run time = 6 min*

Initial Concentration of dye (mg L⁻¹)	Concentration of dye decolorized (mg L⁻¹)		
	RO16	RR120	DR80
100	100	99	100
200	90	115	199
300	117	119	300
400	107	122	391
500	164	240	488

*pH = 11.0; Electrolyte concentration = 0.5 M;
Voltage = 4 V; Run time = 6 min*

280

281 The effect of initial concentration of dye on the decolorization of azo dyes by
282 electrochemical process was studied by varying the concentrations from 100 to 500 mg L⁻¹.
283 The results from Table 2 explains the decolorization potential of the process with respect to
284 different dyes. The concentration of dye decolorized increased with increase in the
285 concentration of azo dyes. At high initial concentration of dye (500 mg L⁻¹), 33% (164 mg L⁻¹)

286 of RO16 and 48% (240 mg L⁻¹) of RR120 were decolorized, whereas 97% of DR80 (488 mg L⁻¹) was removed. From this study, it is interesting to note that as the complexity of dye increases
 287 ¹) was removed. From this study, it is interesting to note that as the complexity of dye increases
 288 with respect to number of azo bonds, the kinetics of decolorization is raising, as further
 289 discussed in section 3.4.

290 In addition, the amount of generated sludge was around 5.1 g h⁻¹ in optimal condition,
 291 which is not negligible and highlighted the contribution of electrocoagulation mechanism in the
 292 removal efficiency. Still, the amount of sludge produced was 3 times less than with aluminium
 293 sacrificial anode in another study to reach complete colour removal (Arslan-Alaton et al.,
 294 2008).

295

296 **3.3 Batch process optimization – RSM**

297 **3.3.1 Experimental design and statistical analysis**

298 The effect of interaction between the influencing factors on the decolorization of the
 299 azo dyes (RO16, RR120, DR80) by electrochemical process and the design parameters based
 300 on the RSM-CCF are shown in Eqs. (11) - (13). Based on RSM designs for all the three dyes,
 301 the data were fitted into the second order polynomial equation and the empirical relationship
 302 between the dependent and independent parameters involved in the decolorization of dyes were
 303 established.

$$304 \text{ Concentration of RO16 dye decolorized} = +228.02 + 74.27A + 56.58B + 78.00C + 27.26AB + \\ 305 52.51AC + 8.26BC - 38.24A^2 - 25.80B^2 - 47.77C^2 \quad (11)$$

$$306 \text{ Concentration of RR120 dye decolorized} = +323.44 + 122.31A + 53.32B + 97.87C + 46.98AB \\ 307 + 77.02AC + 26.21BC - 108.59A^2 + 16.03B^2 - 23.76C^2 \quad (12)$$

$$308 \text{ Concentration of DR80 dye decolorized} = +549.41 + 360.54A + 99.24B + 123.16AB - \\ 309 47.69A^2 - 74.99B^2 \quad (13)$$

310 Box-Cox plots and diagnostic plots for RO16, RR120 and DR80 are given in the
 311 supplementary data Fig. SM-2, SM-3 and SM-4 respectively. The Box-Cox transformation has
 312 been employed to improve the normality of residuals and the plots suggested a transformation
 313 in all the models: Base 10 logarithmic transformation for RO16, Inverse square root
 314 transformation for RR120, Power transformation for the DR80. The transformed and reduced
 315 model equations are given in Eqs. (14) - (16).

$$316 \text{Log}10(\text{Concentration of dye decolorized}) = +2.32 + 0.30A + 0.29B + 0.36C - 0.18BC - 0.29B^2 \\ 317 - 0.23C^2 \quad (14)$$

$$318 1.0/\text{Sqrt}(\text{Concentration of dye decolorized}) = +0.055 - 0.024A - 6.946E-003B - 0.014C + \\ 319 3.863E-003BC + 0.024A^2 + 8.460E-003C^2 \quad (15)$$

$$320 (\text{Concentration of dye decolorized})^{0.5} = +23.40 + 9.32 A + 1.92 B + 2.29AB - 3.52 A^2 - 1.52 \\ 321 B^2 \quad (16)$$

322 Analysis of variance (ANOVA) for the RSM models of all the three dyes are
 323 consolidated in the Table 3 and supplementary data are shown in the Table SM-2, Table SM-3
 324 and Table SM-4. The significance of each coefficient can be determined by the F-value and p-
 325 values. The effect on the response increases with larger magnitude of F-values and smaller P-
 326 values. The P-Value of models generated for all the three dyes is less than 0.0001 and this
 327 indicates the significance of the parameters in the model. From the results, it was observed that
 328 for the decolorization of RO16, three linear terms (A, B, C), two quadratic terms (B^2 , C^2) and
 329 an interactive term (BC) are determining, whereas for the decolorization of RR120, three linear
 330 terms (A, B, C), two quadratic terms (A^2 , C^2) and an interactive term (BC) are significant. For
 331 all the three dyes, diagnostic plots such as predicted versus experimental helps to judge the
 332 adequacy and significance of the model. Normality of the residuals is determined using the
 333 normal probability plot. In this plot, the distribution of the residuals lies close to the trend lines
 334 and this shows minimum disperse effect. Though the lack of fit in the model is significant for

335 RO16 and DR80, all the centre point experiments are performed independently for all the three
 336 dyes to study the fitness of the model with respect to other error analysis parameters which
 337 suggest the model is fit in respective transformations (Muniyasamy et al., 2020).

338

Table 3 CCF Model parameters for the decolorization of azo dyes from the
 Analysis of Variance

Parameters	RO16	RR120	DR80
Model (P-value)	<0.0001	<0.0001	<0.0001
Significant Parameters & Interactions	A, B, C, BC, B ² , C ²	A, B, C, BC, A ² , C ²	A, B, AB, A ² , B ²
R ²	0.9277	0.9856	0.9879
Adjusted R ²	0.8943	0.9790	0.9792
Adequate Precision	20.32	40.365	32.645
Coefficient of variation (%)	7.74	5.34	4.97

339

340 3.3.2 Analysis of response surface – Operational parameters

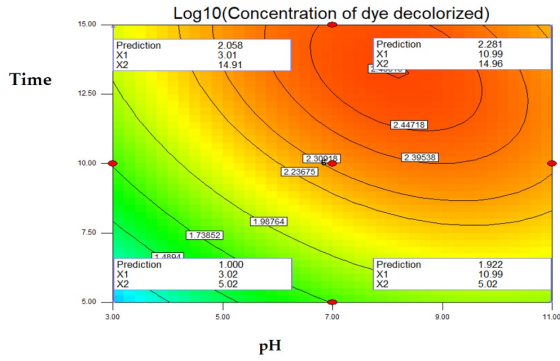
341 The interactive effects between operational parameters are explained by two dimensional
 342 (contour) and three dimensional plots as shown in Fig. 1.

343 *Interactive effects of pH and time*

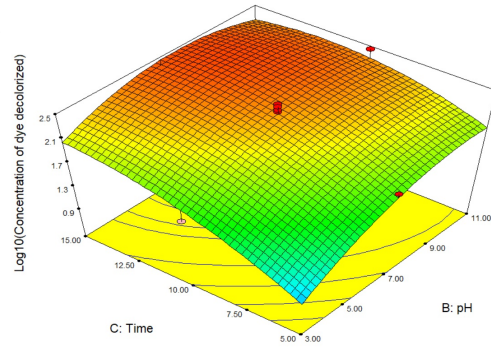
344 The interactive effects between pH and time are significant in the decolorization of reactive
 345 dyes (RO16, RR120). From the contour plot of RO16 (Figs. 1a and 1b), it can be interpreted
 346 that maximum concentration of dye decolorization was obtained at alkaline pH and at a
 347 reaction time for about 15 min. In the case of RR120 (Figs. 1c and 1d), at pH 11.0 the
 348 concentration of dye decolorization increased from 223 to 494 mg L⁻¹ with respect to the

349 increase in time from 5 to 13 min. Thus, for both reactive dyes increase in pH and time has
 350 maximized the concentration of dye decolorization.

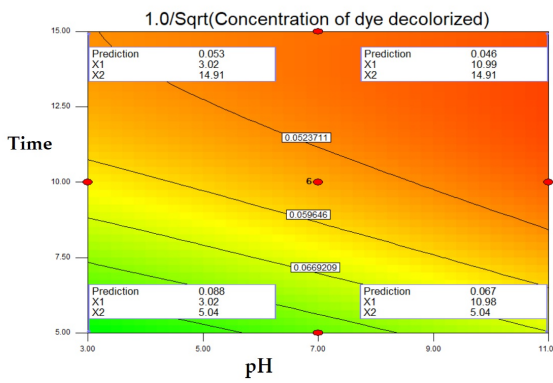
a



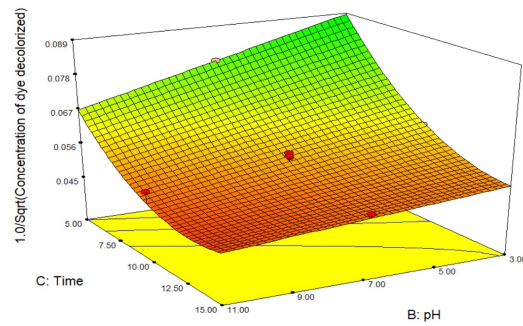
b



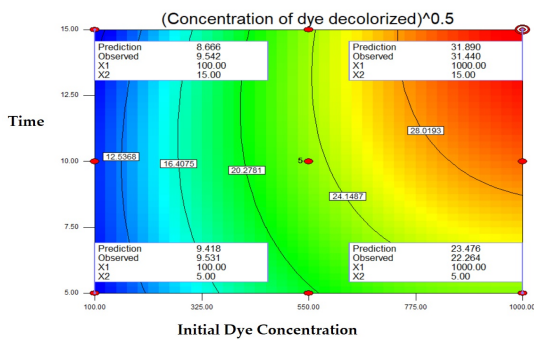
c



d



e



f

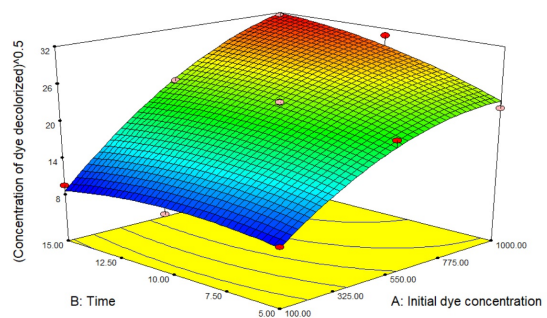


Fig. 1 CCF based Contour 2D and 3D Response surface plots: RO16 (a&b), RR120 (c&d) and DR80 (e&f)

351

352

353 ***Interactive effects of initial concentration of dye and time***

354 The interactive effects between initial concentration of dye and time are significant in the
355 decolorization of DR80 (Figs. 1e and 1f). Maximum concentration of dye decolorization was
356 obtained with an increase in both the initial concentration of dye and time. The concentration
357 of dye decolorized increased from 703 to 989 mg L⁻¹ during 10 to 15 min with an increase in
358 the initial concentration of dye from 550 to 1000 mg L⁻¹.

359

360 **3.4 Electrochemical treatment of azo dyes under continuous mode**

361 The elimination capacity of continuous electrochemical treatment was studied for all
362 the three dyes with different concentrations (100 - 400 mg L⁻¹), at varied flow rates (0.1 - 0.5 L
363 h⁻¹). The removal efficiency and elimination capacity of RO16, RR120 & DR80 respectively at
364 9th min was shown in the Table SM-5. The reactor efficiency was calculated using the inlet
365 loading rate. The results are compared based on the reaction time. In the case of 100, 200 &
366 300 mg L⁻¹ of RO16 dye concentration, the elimination capacity increased with the increase in
367 the inlet loading rate. For 300 mg L⁻¹ of RO16 with an inlet loading rate of 214 mg (L h)⁻¹, the
368 elimination capacity obtained was 113 mg (L h)⁻¹ (~ 52% of inlet loading rate is eliminated)
369 with residence time of 0.531 min. This was observed to be the maximum elimination capacity
370 for RO16. Similar pattern was observed in RR120. For 300 mg L⁻¹ of RR120 with an inlet
371 loading rate of 214 mg (Lh)⁻¹, the elimination capacity obtained was 159 mg L⁻¹ h⁻¹ (~ 74% of
372 inlet loading rate is eliminated) with residence time of 0.377 min. Elimination capacity
373 decreased in the different flow rates of both the reactive dyes (RO16 and RR120) at 400 mg L⁻¹
374 ¹. Interestingly, the maximum elimination capacity of DR80 was observed at 0.5 L h⁻¹ of 400
375 mg L⁻¹ concentration. 99% of inlet loading rate (280 mg (Lh)⁻¹) was removed with residence
376 time of 0.214 min.

377 To further understand the difference between the dyes removal efficiency, their
378 percentages removal efficiencies have been illustrated in Fig. 2 for different inlet
379 concentrations (100 - 400 mg L⁻¹) and flow rates (0.1 - 0.5 L h⁻¹). In all the conditions, the
380 removal yield of DR80 was higher than RR120, which was higher than RO16. For instance, the
381 removal efficiency equalled 23%, 48% and 99% at 400 mg L⁻¹ and 0.5 L h⁻¹. Moreover, the
382 average residence time for 1 mg L⁻¹ of RO16, RR120 and DR80 was found to be 0.531, 0.377
383 and 0.214 min respectively (Table SM-6), which corroborated the behaviour. This trend was in
384 agreement with the results obtained in batch mode, highlighting the influence of number of azo
385 groups on dye molecule considering that RO16, RR120 and DR80 have 1, 2 and 4 azo bonds,
386 respectively (Table 2). Thus, the higher the number of azo groups, the better the removal
387 efficiency. Interestingly, a linear relation was newly obtained between the number of azo bonds
388 and the removal efficiency as well as with the elimination capacity, giving slope values of 24.4
389 ($R^2 = 0.9988$) and 70.0 ($R^2 = 0.9988$), respectively (Fig. 3a). Moreover, the increase of inlet
390 concentration makes increase the removal efficiencies for RO16 and RR120, while the removal
391 efficiencies of DR80 were around $97.5 \pm 2.5\%$ for all the inlet concentrations. This means that
392 the kinetics were depending on the inlet concentrations. Another interesting feature is that the
393 removal efficiency was increasing with the flow rate, i.e when the retention time was
394 decreasing, for all the dyes whatever their inlet concentrations.

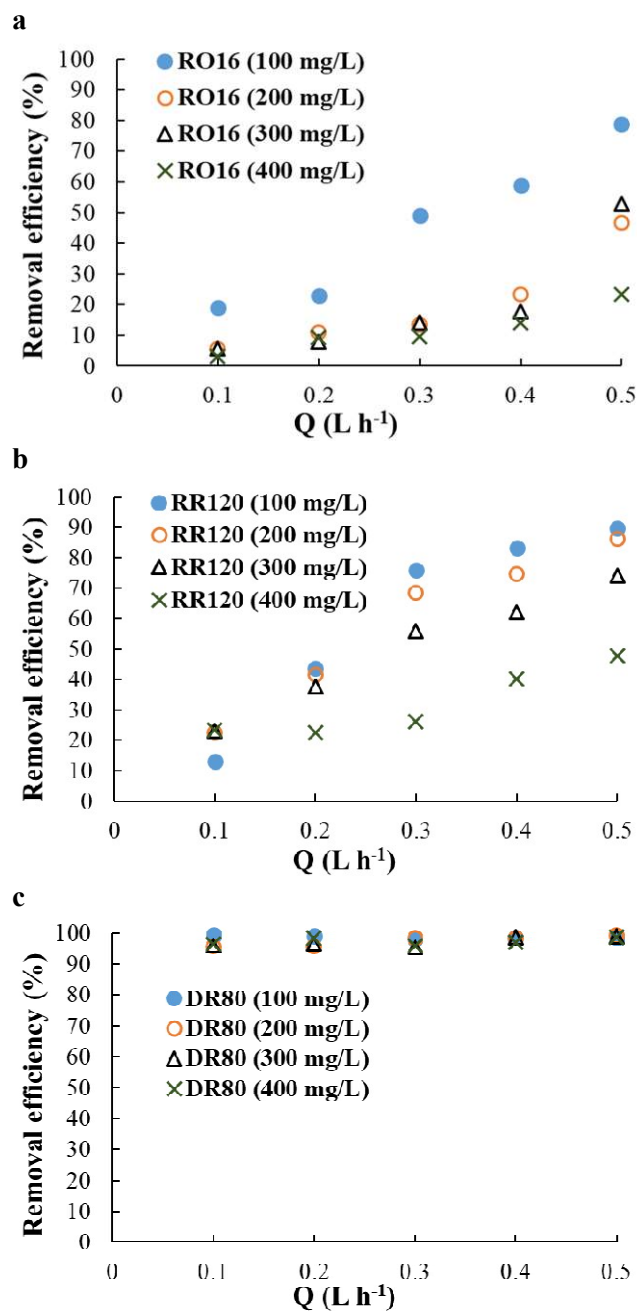


Fig. 2 Effect of flow rate and inlet concentration on the removal efficiency of RO16 (a), RR120 (b) and DR80 (c) dyes

395

396 To deeper understand the influence of flow rate, a comparison between the applied
 397 current density (j_{app}) value (47 mA cm⁻²) with the initial limiting current density (j_{lim}^0) values
 398 has been performed by calculating the dimensionless current density (α), as defined by Eq.
 399 (17) (Panizza et al., 2001):

400
$$\alpha = \frac{j_{appl}}{j_{lim}^0} \quad (17)$$

401 In addition, j_{lim}^0 can be expressed as function of Faraday constant (F), the mass
 402 transport coefficient (k_m) and the inlet COD (COD_{in}) Eq. (18) (Panizza et al., 2001):

403
$$j_{lim}^0 = 4Fk_mCOD_{in} \quad (18)$$

404 By combining Eqs. (17) - (18), the following relation of α can be written Eq. (19):

405
$$\alpha = \frac{j_{appl}}{4Fk_mCOD_{in}} \quad (19)$$

406 In order to determine α , the value of k_m is required. k_m has been estimated considering
 407 the dimensionless Sherwood (Sh) number relation that can be defined as function of k_m , the
 408 equivalent diameter (d_h) and the diffusivity (D) Eq. (20) (Cañizares et al., 2006):

409
$$Sh = \frac{k_m d_h}{D} \quad (20)$$

410 Sh number can also be generally expressed as function of dimensionless Reynolds (Re)
 411 number and Schmidt (Sc) number. Eq. (21) (Anglada et al., 2010)), while Sc is defined through
 412 Eq. (22) (Cañizares et al., 2006) and Re in a stirred tank reactor can be determined considering
 413 Eq. (23) (Fitschen et al., 2019):

414
$$Sh = aRe^bSc^c \quad (21)$$

415
$$Sc = \frac{\nu}{D} \quad (22)$$

416
$$Re = \frac{a^2 N}{\nu} \quad (23)$$

417 where ν is the kinematic viscosity, d is the diameter of the stirrer, N is the rotation speed of the
 418 stirrer.

419 By combining Eqs. (20) - (23), the general expression of k_m is Eq. (24):

420
$$k_m = \frac{a}{a_h} D^{(1-c)} \nu^{(c-b)} (d^2 N)^b \quad (24)$$

421 Finally, the general dimensionless α relation in a stirred tank reactor is proposed as
422 follow by combining Eq. (19) and Eq. (24):

$$423 \quad \alpha = \frac{j_{appl} \frac{d_h}{a}}{4FCOD_{in}} D^{(c-1)} v^{(b-c)} (d^2 N)^{-b} \quad (25)$$

424 In this work, the values of d_h , d , D , N , v , a , b and c constants were considered equalled
425 to 10.5 cm, 2 cm, $10^{-9} \text{ m}^2 \text{ s}^{-1}$ (Scialdone et al., 2012b), 100 rpm, $8.917 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ at 25°C
426 (Engineering ToolBox, 2004), 0.228 (Selman and Tobias, 1978), 0.66 (Selman and Tobias,
427 1978) and 0.33 (Selman and Tobias, 1978), respectively. A k_m value of $1.7 \cdot 10^{-6} \text{ m s}^{-1}$ was
428 therefore obtained in this study. This value is in the same range of values given in literature for
429 a stirred tank reactor ($\sim 5.9 \cdot 10^{-6} \text{ m s}^{-1}$) (dos Santos et al., 2014; Mousset et al., 2019b; Rocha et
430 al., 2012). The COD_{in} values used for α calculation are reported in Table SM-7. The results of
431 dimensionless current density as function of the dyes and their inlet concentrations are
432 displayed in Fig. 3b. In all the cases, α was ranging from 18 to 102 and was always higher than
433 1, which means that j_{appl} was always higher than j_{lim}^0 . It can therefore be concluded that the
434 kinetics were under mass transport control all along the treatment (Mousset et al., 2019a;
435 Panizza et al., 2001). Knowing that the flow rate has an influence on k_m , it means that
436 increasing Q make increase k_m and therefore enhance the kinetics, since it is under mass
437 transport control. Thus, it explains the increase of removal efficiency with an increase of flow
438 rate in Fig. 4.

439

440

441

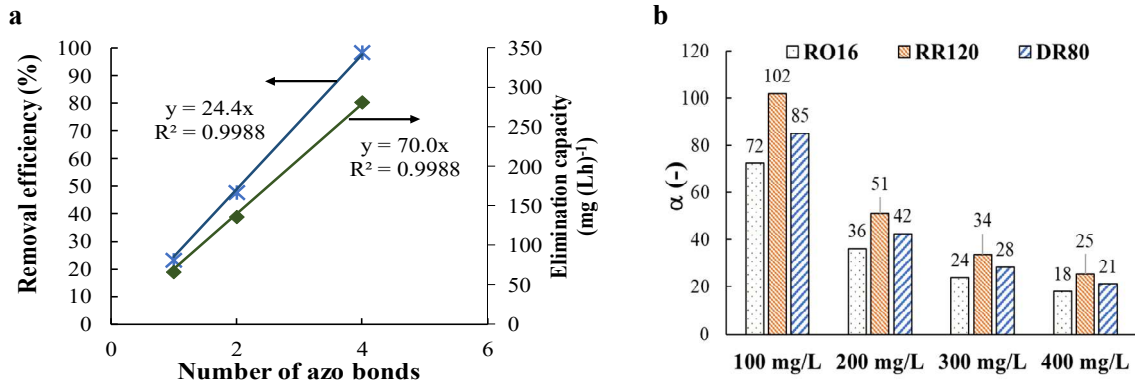
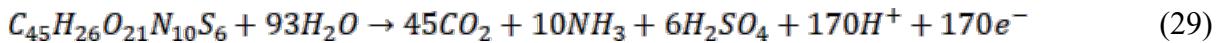
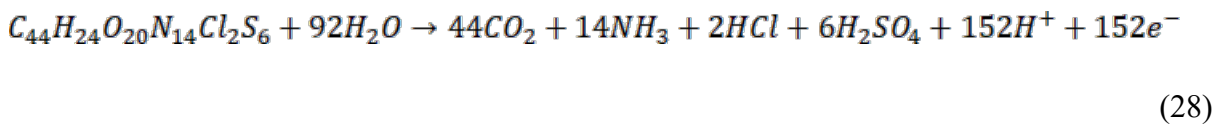
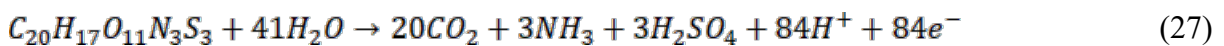


Fig. 3 Influence of number of azo bonds on the dyes removal efficiency and elimination capacity at 400 mg L⁻¹ and 0.5 L h⁻¹ (a), dimensionless current density as function of inlet concentration of RO16, RR120 and DR80 dyes (b)

To further assess the efficiency of the process, the current efficiency (CE) has been calculated considering a continuous mode using Eq. (26) (Scialdone et al., 2012a):

$$CE (\%) = 100 \times \frac{nF C_{in} X Q}{j_{appl} A} \quad (26)$$

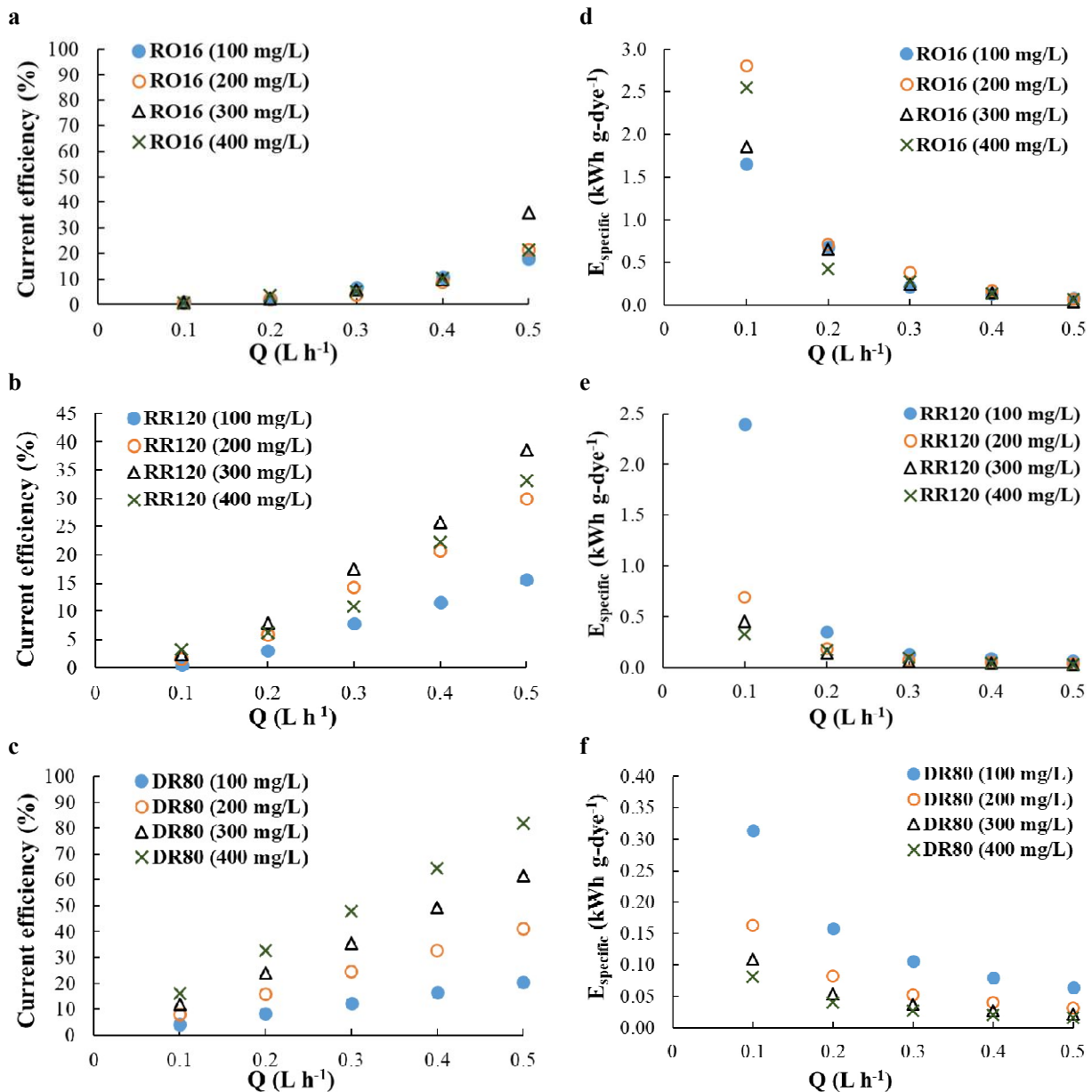
where A is the immersed surface area of the electrode (17 cm²), X is the conversion yield ((C_{in} - C_{out})/C_{in}) and n is the number of electron(s) required for the conversion of the dye into carbon dioxide by electrochemical combustion reaction that can be written as follow for RO16 (Eq. (27)), RR120 (Eq. (28)) and DR80 (Eq. (29)):



From Eqs. (27) - (29), it can be noted that the values of n for RO16, RR120, and DR80 were 84, 152 and 170, respectively. The specific electric energy consumption (E_{specific}) was also estimated in continuous mode (Eq. (30)) (Mousset et al., 2018):

$$E_{specific} = \frac{E_{cell} I}{C_{in} X Q} \quad (30)$$

where, E_{cell} is the cell potential (V) and I is the current intensity (A).



462

Fig. 4 Effect of flow rate and inlet concentration on the current efficiency (a, b, c) and the specific energy requirement (d, e, f) to remove RO16 (a, d), RR120 (b, e) and DR80 (c, f) dyes

465

Both current efficiency and specific energy have been plotted in Fig. 4 as function of flow rate and inlet concentration. The following rank of CE was obtained (from the highest to the lowest): DR80 (4% - 82%) > RR120 (0.45% - 33%) > RO16 (0.56% - 21%), whatever the inlet concentration and flow rate. This trend was in agreement with the removal efficiencies (Fig. 2).

469

470 The energy requirement followed the opposite relation order (from the highest to the lowest
471 E_{specific} value): RO16 (0.07 - 2.8 kWh g-dye⁻¹) > RR120 (0.033 - 2.4 kWh g-dye⁻¹) > DR80
472 (0.016 - 0.31 kWh g-dye⁻¹). At optimal condition for complete decolorization, the energy
473 consumption was around 6 kWh m⁻³ in this work against 11 kWh m⁻³ with aluminium anode
474 obtained in a previous study (Arslan-Alaton et al., 2008). This demonstrates the interest of
475 using stainless steel anode compared to aluminium electrode.

476 In addition, CE and E_{specific} were generally raising and decreasing respectively with the
477 inlet concentration, as a further confirmation of the kinetics dependency with the inlet
478 concentration. Moreover, CE values were increasing with the flow rate, while E_{specific} values
479 were decreasing, due to mass transport control.

480

481 4. CONCLUSIONS

482 This study investigates the electrochemical decomposition of synthetic azo dyes (RO16,
483 RR120 & DR80) using a continuous electrochemical reactor containing stainless steel
484 electrodes. The interaction between the influencing parameters was determined using RSM.
485 The results obtained from the transformed model showed that the optimum operating
486 conditions for obtaining maximum percentage of dye decolorization were pH of 11.0
487 electrolyte concentration of 0.5 M. The elimination capacity of electrochemical reactor was
488 studied with respect to residence time for the continuous removal of azo dyes. The effect of
489 other process parameters such as mass transport coefficient, dimensionless current density,
490 current efficiency and specific energy were evaluated. The α value given for the process shows
491 that the global kinetics was under mass transport control. Current efficiency (%) increased for
492 dyes with maximum number of azo bonds (irrespective of the initial dye concentration and
493 flow rate) and the condition was vice versa with respect to specific energy calculation. From
494 the kinetic analysis and transport modelling, in case of both the batch and continuous process,

495 it is evident that the percentage of removal efficiency is directly linked to the initial dye
496 concentration, pH, flow rate and number of azo bonds. Thus the model developed in this
497 research work shows a paramount feasibility of using stainless steel electrode for the
498 continuous electrochemical decomposition of textile effluents containing azo dyes. Moreover,
499 the experimental understanding on mass transport coefficient, dimensionless current density,
500 current efficiency and specific energy give interesting information towards the efficiency and
501 the reactor design optimization for upscaling the process. As a next step, since the kinetics
502 seems to be under mass transport control, a further optimization of the reactor design would
503 even increase the current performance, by intensifying the mass transport between the bulk and
504 the surfaces of electrodes.

505

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510

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