

Photoelectrochemical advanced oxidation processes for removal of azo dye from water: emerging aspects and oxidation products

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1 **Photoelectrochemical advanced oxidation processes for removal of azo dye from water:**
2 **emerging aspects and oxidation products**

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13
14 **Abstract**

15 Azo dyes are one of the large classes of water soluble synthetic dyes with a wide range of
16 colors and can be released into the environment when used. Azo dyes belong to one of the most
17 numerous groups of synthetic dyes and are characterized by the presence of an azo group (-N=N-
18) with two or more symmetrical or asymmetrical aromatic radicals. Processes of photoelectro-
19 chemical oxidation using various approaches have been developed for the removal of azo dyes
20 from wastewater. The fundamentals of different photoelectrochemical oxidation processes for azo
21 dyes, such as photoelectrocatalytic oxidation (PEC), photoelectro-Fenton (PEF), and solar photo-
22 electro-Fenton (SPEF) processes, are discussed. The use of different semiconductor materials as
23 electrode materials in photoelectrocatalysis and PEF for azo dye removal, the influence of different
24 parameters on the removal of azo dyes from wastewater, reactor design, combined photoelectro-
25 chemical oxidation, including the use of fuel cells, are also considered. The anodic, electrochemi-
26 cal, and photoelectrochemical oxidation processes for azo dye removal is compared. Also shows
27 what products are mainly formed during photoelectrochemical oxidation of azo dyes and how
28 photoelectrochemical oxidation affects the toxicity of azo dye solutions under different conditions.

29 Key words: Photoelectrochemical, advanced oxidation processes, azo dye, removal,
30 wastewater, photoelectrocatalytic, photoelectro-Fenton, solar photoelectro-Fenton.

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1. Introduction

The color of wastewater is one of the regulated parameters for discharge into the environment. The presence of organic dyes gives wastewater an increased coloration (Bilińska and Gmurek 2021). Synthetic dyes are characteristic of wastewater from their production and from technological processes of dyeing various materials, particularly in textile industry, dry cleaning, etc. (Castillo-Cabrera et al. 2022). The textile industry is the most water-intensive and consumes a large amount of water resources. Therefore, the creation of closed-loop water supply systems for the textile industry is one of the acute problems.

Synthetic dyes contained in wastewater from the textile industry are biologically resistant compounds and pose a threat to natural ecosystems and humans due to their potential bio-toxicity. Therefore, a large number of technologies are being developed and implemented for removing synthetic dyes from wastewater, including chemical, electrochemical, photochemical, and photoelectrochemical technologies (de Queiroz et al. 2017; Ganiyu et al. 2018). Advanced oxidation processes (AOP) have great potential, and compared to other methods (e.g., coagulation and adsorption) has high efficiency for removing synthetic dyes and does not cause secondary pollution (Ma et al. 2021). AOP is considered an environmentally safe method since organic dyes can be completely mineralized by oxidation with hydroxyl radicals ($\bullet\text{OH}$). The high standard oxidation-reduction potential ($E^\circ=2.80\text{ V (vs. NHE)}$) of the hydroxyl radical provides its ability to oxidize most organic pollutants (Nidheesh et al. 2018; Brillas 2020). Recently, electrochemical oxidation processes have attracted attention because they allow for continuous and on-site generation of oxidants under mild conditions, which avoids the addition of various chemicals for dye oxidation (Oturán 2014; Mousset and Dionysiou 2020; Ganiyu et al. 2021; García-Espinoza et al. 2021). Electrochemically generated oxidants, particularly $\bullet\text{OH}$, is complete mineralization of organic dyes (Brillas and Martínez-Huitle 2015). Electrochemical methods include heterogeneous processes such as anodic oxidation and photoelectrocatalysis, in which $\bullet\text{OH}$ is formed on the surface of the anode either electrochemically or photochemically, and homogeneous processes such as electro-Fenton, photo-electro-Fenton, and sono-electrolysis, in which $\bullet\text{OH}$ is formed mainly in the solution (Sirés et al. 2014a; Brillas 2020). In recent years, photoelectrocatalytic oxidation methods have been intensively developed for dye removal because their use increases the efficiency of oxidation due to the synergistic effect of combined photochemical reactions and electrolysis reactions (Laghrib et al. 2021). The photoelectrocatalytic removal of synthetic dyes has certain advantages compared to photocatalysis and electrocatalysis. The main advantages include high charge separation efficiency compared to photocatalytic dye removal and low energy consumption compared to electrocatalytic dye removal. In addition, thin film semiconductor electrodes are used

68 for the process of photoelectrocatalytic oxidation of azo dyes, which solves the problem of sepa-
69 ration the catalyst from purified water. The use of solar energy to carry out the photoelectrocata-
70 lytic process with use the high-sensitivity photocatalysts to sunlight is also an obvious advantage
71 (Zhang et al. 2023).

72 The use of photoelectrocatalytic technologies allows for the removal of hard oxidation or-
73 ganic dyes from wastewater (Ochiai and Fujishima 2012). The main electrode material used for
74 photoelectrocatalytic dye removal is titanium dioxide (TiO_2). Over the past years, a wide variety
75 of TiO_2 -based materials have been investigated as it is the most stable, inexpensive, accessible,
76 and effective material for dye oxidation (Karanasios et al.; Of et al. 2009; Ge et al. 2016). The
77 photoelectrocatalytic characteristics of other semiconductor materials, such as ZnO , SnO_2 , WO_3 ,
78 Fe_2O_3 , CdS , and BiOX ($X = \text{Cl, Br, I}$), have also been inten-sively studied for creating dye removal
79 technology using solar energy (visible light) (Zhang et al. 2009; Peleyeju and Arotiba 2018;
80 Orudzhev et al. 2020; Ahmed et al. 2020; Rajput et al. 2021; Castillo-Cabrera et al. 2022).

81 The rapid recombination of photo-generated electrons/holes (e^-/h^+) is the main disad-
82 vantage of using photocatalytic processes (Daghrir et al. 2012; Divyapriya et al. 2021; Yusuf et al.
83 2022). Applying an external potential to the photocatalyst reduces charge recombination (Brillas
84 2020). The combination of electrochemical and photo-catalytic technologies allows for the sepa-
85 ration of photo-generated electrons and holes, prevent-ing their recombination (Ye et al. 2021).
86 The use of photoelectrocatalytic processes increases the efficiency of removing synthetic dyes
87 from wastewater and reduces energy costs when using solar energy (Zhang et al. 2012; Shabanov
88 et al. 2017; Chen et al. 2022b). Therefore, the photoelectrocatalytic method is currently considered
89 one of the most promising methods for removing organic compounds from wastewater. The use
90 of such hybrid processes increases the efficiency of the process due to a synergistic effect (Yuan
91 et al. 2021).

92 This article provides a review of studies dedicated to the photoelectrocatalytic oxidation of
93 azo dyes, one of the largest classes of synthetic dyes. The widespread use of azo dyes is due to
94 their ease of application, diverse properties, wide range of colors from yellow to black, high light-
95 fastness, and use in various industries such as textile, paint, and printing for coloring differ-ent
96 products. Azo dyes can color most types of natural, artificial, and synthetic fibers, including
97 leather, plastic, rubber, and more. Most azo dyes are soluble in water, coloring of different mate-
98 rials and therefore generate a large amount of wastewater (Bafana et al. 2011). The focus is on the
99 use of photoelectro-catalysis, photoelectro-Fenton, and solar photoe-lectro-Fenton processes for
100 removing azo dyes. Particular attention is paid to materials and heterostructures as photoelectro-
101 catalysts with high efficiency in the use of light and the separation of photogenerated charges,
102 which increases their redox characteristics and leads to higher rates of neutralization of azo dyes.

103 The toxicity of azo dye solutions and their inter-mediate after treatment are briefly discussed to
 104 understand issues related to preventing water pollution using the latest developments in photoe-
 105 lectrocatalytic removal of various classes of azo dyes.

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2. Theoretical aspects of photoelectrocatalysis

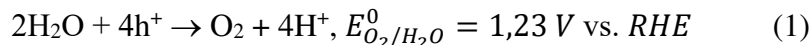
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109 The photocatalysis process was first used for water decomposition using TiO₂ as a photo-
 110 catalyst (Fujishima and Honda 1972). For photocatalytic water decomposition, a minimum
 111 bandgap energy of 1.23 eV is required, which corresponds to the redox potentials of H⁺/H₂ and
 112 O₂/H₂O pairs (Lu et al. 2016). However, to ensure electron transfer and subsequent hydrogen evo-
 113 lution reactions, a larger bandgap (> 2.0 eV) is often required. At the same time, the photocatalyst
 114 should have a small enough bandgap for efficient use of solar energy (E_g <3.0 eV) (Qu and Duan
 115 2013). Compared to photocatalytic processes using powdered photocatalysts, photoelectrocata-
 116 lytic processes promote the separation of electrons and holes (Ma et al. 2020).

116

117 When semiconductors are irradiated with UV or sunlight, n-type material is used as a pho-
 118 toanode, and it generates electron vacancies, which release oxygen (Equation 1). The generated
 119 electrons move to the photocathode, where hydrogen evolution reaction occurs (Equation 2) (Fig.

120

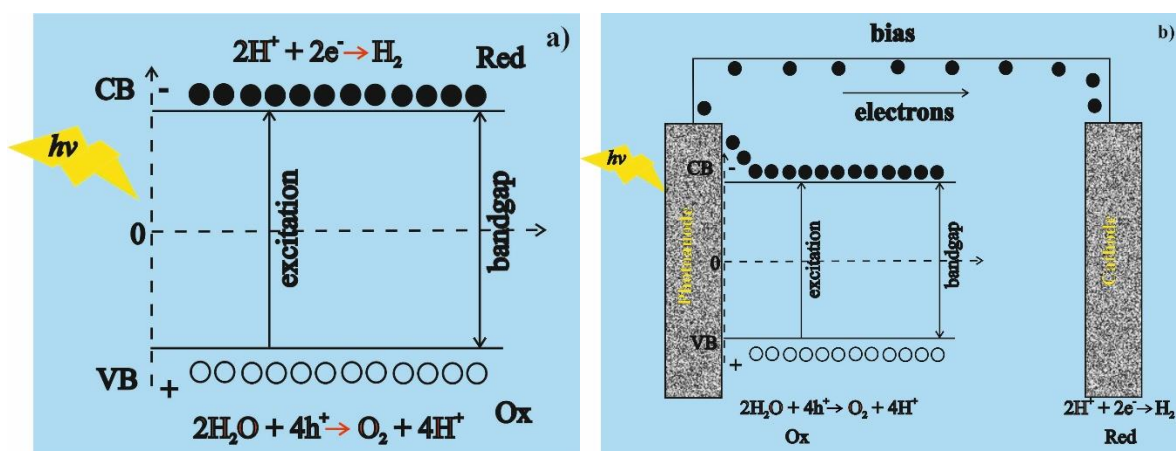


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122

123 The oxygen evolution reaction has thermodynamic limitations, where the minimum con-
 124 duction band of the semiconductor should be more negative than the energy level of H⁺/H₂, while
 125 the maximum valence band should be more positive than the energy level of O₂/H₂O (Qu and
 126 Duan 2013).



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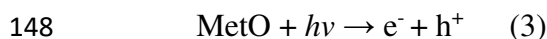
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Fig. 1. a – Scheme of electron and hole pair generation on semiconductors by irradiation UV or sunlight; b – Photoelectrochemical separation of charges with the formation of electrons and holes.

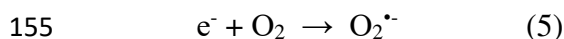
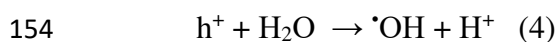
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131 For photoelectrocatalytic oxidation of organic compounds, photocathodes made of semi-
 132 conductors deposited to various substrates and capable of reacting to UV or solar light are used,
 133 which are irradiated with light with energy equal to or greater than the bandgap with simultaneous
 134 application of external potential (Cao et al. 2017; Kusmierek 2020). Absorption of a quantum of
 135 light by the semiconductor photocathode with energy greater than its bandgap results in the sepa-
 136 ration of charges with the formation of electrons (e^-) in the conduction band and holes in the va-
 137 lence band (Fig. 2b) (Rajput et al. 2021). Under the influence of an externally applied potential,
 138 photo-generated e^- can be moved to the counter electrode, leading to redox reactions on the elec-
 139 trode surfaces (Cao et al. 2017). Simultaneously with the electrolysis process, direct oxidation
 140 reactions of azo dyes and the formation of highly active oxygencontaining particles occur on the
 141 photocatalyst surface (Feng et al. 2021). The combination of electrocatalytic and photocatalytic
 142 processes decrease the rate of electron-hole pair recombination and increasing hole lifetime. How-
 143 ever, photo-generated electrons and holes can also recombine and release heat, reducing quantum
 144 efficiency (Zarei and Ojani 2016).

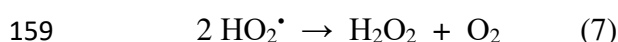
145 In order for a photocatalytic process to proceed on a semiconductor electrode, it must be
 146 irradiated with energy greater than its bandgap energy, leading to the generation of a pair of e^-/h^+
 147 (Garcia-Segura and Brillas 2017):



149 The generated holes act as oxidizers, while electrons act as reducers. The resulting h^+ has
 150 strong oxidizing ability and can migrate to the surface for direct interaction with organic sub-
 151 stances or interact with $\text{H}_2\text{O}/\text{OH}^-$ to form hydroxyl radicals, which also oxidize organic pollu-
 152 tants. Photogenerated electrons can react with dissolved oxygen to form active oxygencontaining parti-
 153 cles according to reaction (5) (Garcia-Segura and Brillas 2017).



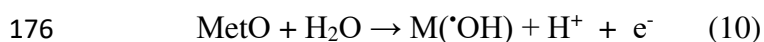
156 Other oxygencontaining particles, such as hydroperoxyl radical HO_2^{\cdot} and hydrogen perox-
 157 ide, can be formed during reactions (6) and (7):



160 The electrons and holes generated by the photocatalytic process are unstable and can to
 161 return to their base state or through reaction with adsorbed $\cdot\text{OH}$ according (6) or predominantly
 162 through recombination with unreacted h^+ (7) (Bessegato et al. 2015; Meng et al. 2015).



165 In addition to photocatalytic processes on the metal oxide semiconductors, electrochemical
 166 oxidation of organic compounds can also occur. Anodic oxidation of organics can occur through
 167 direct electron transfer to the anode surface and hydroxyl radicals formed on the anode surface
 168 during water oxidation. The efficiency of hydroxyl radical formation and, consequently, the oxi-
 169 dation of azo dyes depends on the anode material. Since the process of forming $\bullet\text{OH}$ is a hetero-
 170 geneous process, the use of active metallic and metal oxide anodes leads to chemisorption of prod-
 171 ucts of azo dye oxidation on the electrode surface and their low activity in oxidation process
 172 (Panizza and Cerisola 2009). Anodes with high oxygen evolution overpotential, such as boron-
 173 doped diamond (BDD), PbO_2 , and others, contribute to the formation of hydroxyl radicals (Peralta-
 174 Hernández et al. 2012; Alimirzaeva et al. 2019; He et al. 2019; Karim et al. 2021). This is due to
 175 the oxidation of water to an adsorbed hydroxyl radical $\text{Met}(\bullet\text{OH})$:



177 The low conductivity of the oxide semiconductor materials used in the photoelectrocata-
 178 lytic process allows only small values of anodic current density to be applied (no more than 10
 179 mA/cm^2), which is characterized by a low rate of hydroxyl radical formation. The use of high
 180 anodic potentials leads to a loss of photocatalyst characteristics (Garcia-Segura and Brillas 2017).

181

182 **3. Photoelectrocatalytic oxidation**

183 The efficiency of photoelectrocatalytic oxidation of azo dyes depends on the type of back-
 184 ground electrolyte, pH, electrode potential, semiconductor electrode material and type of irradiation
 185 source used, as well as the initial concentration of the pollutant, photoanode surface morphol-
 186 ogy, and reactor design. TiO_2 , WO_3 , SnO_2 , ZnO , CdS , BDD, etc. are mainly used as electrode
 187 materials in the photoelectrocatalytic oxidation of azo dyes (Hepel and Hazelton 2005; Isaev et al.
 188 2012; Orudzhev et al. 2019).

189 In the photoelectrocatalytic oxidation of azo dyes on metal oxide electrodes, first of all, the
 190 nitrogen-nitrogen bond ($-\text{N}=\text{N}-$) breaks, which leads to discoloration of the solution (Subba Rao
 191 et al. 2017). When comparing electrocatalytic and photoelectrocatalytic oxidation of azo dyes, the
 192 efficiency for the photoelectrocatalysis process is much higher. For example, when using SnO_2 -
 193 Sb_2O_4 as an anode, a decrease in color up to 88% was achieved at 240 min of electrolysis, while
 194 in photoelectrolysis, the decrease in color was 93%. Deposition on SnO_2 - Sb_2O_4 of WO_3 resulted
 195 in an increase in both color and COD removal efficiency. It was found that the percentage of COD
 196 removal using the SnO_2 - Sb_2O_4 - WO_3 electrode is 78 and 84%, respectively, under the conditions
 197 of electrocatalysis and photoelectrocatalysis (Subba Rao et al. 2017).

198 TiO_2 obtained using various approaches, was used as a photoanode in the photoelectrocata-
 199 lytic oxidation of azo dyes. Larbi K.H. et al. (Larbi et al. 2021) reported on TiO_2 films synthesized

200 from TiCl_3 on conductive glass substrates (ITO) using direct and pulsed electrodeposition for the
201 oxidation of methyl orange (MO). Thin films of TiO_2 deposited on FTO-coated glass substrates
202 using the method of sputtering onto a heated substrate were used for the photoelectrocatalytic
203 oxidation of azo dyes in aqueous solutions of Active Red 152 (AR152) (Ali et al. 2018) and Acid
204 Orange 7 (AO7) (Shinde et al. 2009). The efficiency of oxidation of AR152 was 70% when illu-
205 minated with ultraviolet light after 120 minutes of photoelectrocatalysis (Ali et al. 2018). The TiO_2
206 film obtained using the sol gel technology also exhibits good catalytic activity in the oxidation of
207 a mixture of Reactive Orange 16 (orange), Reactive Black 5 (RB5) (black), and Reactive Red RB
208 133 (red) azo dyes (Cervantes et al. 2013).

209 The use of TiO_2 nanotubes obtained by electrochemical anodization for the oxidation of
210 various azo dyes has great interest. During the oxidation of azo dyes Disperse Red 1, Disperse Red
211 13, and Disperse Orange 1 on Ti/TiO_2 nanotubes, the decrease in total organic carbon (TOC) was
212 $\geq 87\%$ after 240 minutes of treatment (Ferraz et al. 2013). Arrays of TiO_2 nanotubes have a larger
213 specific surface area than a film of TiO_2 particles, which leads to an increase in their adsorption
214 capacity and charge transfer rate (Qiu et al. 2018). An increase in the rate of MO oxidation on
215 arrays of TiO_2 nanotubes compared to a TiO_2 film obtained by the sol-gel technology was ob-
216 served Zhao Q. et al. (Zhao et al. 2009). At the same time, the use of TiO_2 obtained by plasma
217 electrolytic oxidation leads to an increase in the efficiency of oxidation of the azo dye Drimaren
218 Red 243 X6BNB compared to TiO_2 obtained by titanium anodization (Franz et al. 2015).

219 Various approaches are used to increase the efficiency of photoelectrocatalytic oxidation
220 of azo dyes. In particular, to increase the efficiency of the oxidation of azo dyes by increasing the
221 activity of TiO_2 due to doping with various metals and non-metals are used. The use as doping
222 elements of metal atoms leads to the excitation of TiO_2 under visible light irradiation (Zhang et al.
223 2013). Boron-doped TiO_2 was used for photoelectrocatalytic oxidation of acid red 151 Acid Red
224 151 (AR151) in 0.01 mol/l Na_2SO_4 as an electrolyte. Complete discoloration of the solution was
225 observed within 30 minutes, and complete mineralization was achieved after 90 min of photoelec-
226 trocatalysis (Bessegato et al. 2019). On tellurium-doped TiO_2 , a complete decolorization of a so-
227 lution of reactive yellow 105 was achieved within 60 minutes under visible light irradiation
228 (Nurdin et al. 2022). For another azo dye, such as reactive orange 84 with an initial concentration
229 of 0.5 ppm, a 98% discoloration of the solution was achieved within 60 min during photoelec-
230 trocatalytic oxidation on selenium-doped TiO_2/Ti under sunlight irradiation (Tian et al. 2021).

231 On lanthanum doped TiO_2 nanoparticles electrode the efficiency of photoelectrocatalytic
232 oxidation of MO with a concentration of 15 mg/L under UV light irradiation was more than 90%
233 at 140 minutes. At the same time, compared with pure TiO_2 nanoparticles, the efficiency of oxi-
234 dation of azo dye on La doped TiO_2 was 26.17% higher (Xing et al. 2013). For the same dye,

235 copper-modified TiO₂ showed a higher efficiency. There, 92.88% MO discoloration was achieved
236 in a solution with a concentration of 0.5 ppm at 60 minutes when irradiated with visible light
237 (Nurdin et al. 2021). A photoanode based on a TiO₂ film doped with Fe and fabricated by the sol-
238 gel method, when UV light irradiated at 3 hours, showed a degree of discoloration of the MO
239 solution of 85% (Tang et al. 2014).

240 TiO₂ based heterostructures show good efficiency of the oxidation of azo dyes. This can
241 be explained by the synergistic effect associated with the formation of a p-n-heterojunction be-
242 tween a p-type and n-type semiconductors, which increases the photogenerated electron transfer
243 rate, which improving the photocatalytic properties of semiconductors and a decrease of the pho-
244 togenerated electron-hole pairs recombination rate due to voltage application during photoelec-
245 trolysis (Isaev et al. 2022). Photoelectrocatalytic oxidation of X-3B azo dye (CI Reactive red 2)
246 (X-3B) using the cerium doped TiO₂ nanoparticles deposited on a film of BDD showed that the
247 degradation rate during photoelectrocatalysis was higher than the sum of photocatalysis and elec-
248 trooxidation processes (Wang et al. 2011). The same effect was also demonstrated for an electrode
249 made of a graphene-TiO₂ (D-P25) composite film prepared by dipping. The percentage degrada-
250 tion of X-3B during photoelectrolysis on a D-P25 sample containing 1% graphene after 25 minutes
251 of the process increased from 36.4% to 71.8% with increasing applied potential from 0 to 2.0. V
252 (relative to saturated Ag/AgCl), and for samples containing 2 and 3% graphene - 41.6–78.7% and
253 38.3–73.8%, respectively (Wang et al. 2012). The oxidation efficiency of Acid Red 33 (AR33)
254 azo dye on a titanium electrode coated of multi-walled carbon nanotubes and titanium dioxide
255 composite (MWNT–TiO₂/Ti) was 98% solution discoloration and 41.66% mineralization after 60
256 min of treatment at a current density of 7.5 mA cm⁻² and pH = 5.2 (Nabizadeh Chianeh and Basiri
257 Parsa 2015).

258 Photoelectrocatalytic oxidation of MO using TiO₂ nanotube (NT) heterostructures was
259 demonstrated in works (Deng et al. 2018; Zeng et al. 2021). The results of the studies showed that
260 heterostructures exhibit higher activity during electrocatalysis (EC), photocatalysis (PC), and pho-
261 toelectrocatalysis (PEC) than the initial TiO₂ NTs. Comparison of the electrocatalytic, photocata-
262 lytic and photoelectrocatalytic processes of azo dyes oxidation for all heterostructures showed that
263 the efficiency of oxidation increases in the range: EC<PC<PEC. For example, when MO oxidation
264 on TiO₂ NTs under optimal conditions showed 16.1% mineralization with EC, 39.4% with PC,
265 and 78.0% with PEC at 60 min under irradiation of a 350 W xenon lamp. Under the same condi-
266 tions, the mineralization efficiency of MO on CeO₂/TiO₂ NT is 23.2%, 56.5%, and 98.1%, respec-
267 tively, which is mainly due to good absorption of visible light and a higher efficiency of charge
268 carrier separation (Fig. 2) (Deng et al. 2018).

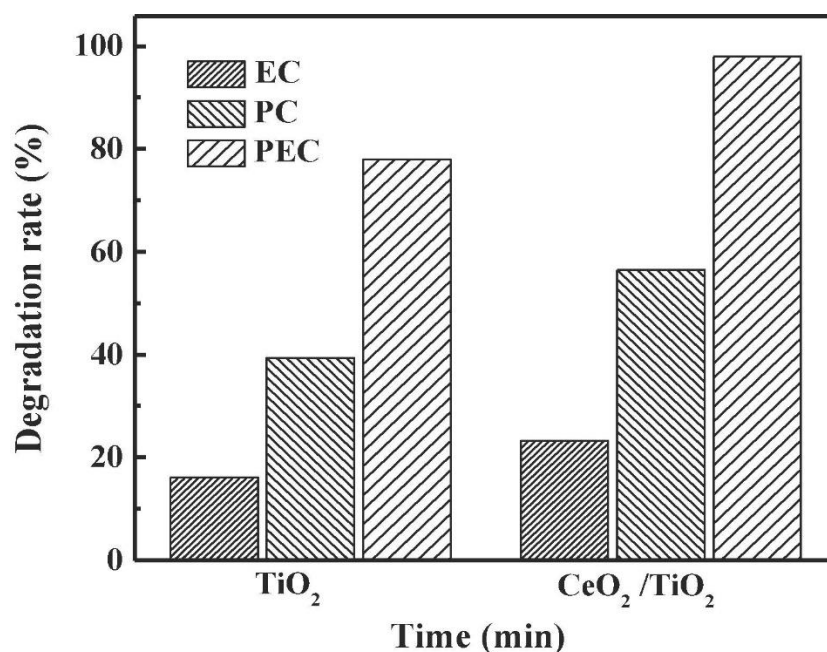


Fig. 2. Efficiency of MO degradation on TiO₂ NT and CeO₂/TiO₂ NT photoelectrodes under simulated solar irradiation. Reprinted by permission from (Deng et al. 2018). Copyright 2018, Elsevier.

The MO photoelectrocatalytic oxidation on a ZnO/TiO₂ electrode under UV light irradiation, complete removal of the dye was achieved after 90 min, while in the photocatalytic process at the same time only 39.6% MO removal was obtained (Zhang et al. 2008). Compared to the TiO₂ NT electrode, the efficiency of MO oxidation on CdS/TiO₂ NT increased from 78% to 99.2% under UV light at 2 h and from 14% to 99.2% at 3 h under visible light irradiation (Jiang et al. 2011). A higher MO oxidation rate is observed when using TiO₂-SiO₂ ceramic nanostructures formed by anodization of the Ti surface using sodium hexafluorosilicate electrolyte. Complete discoloration of MO 100% was observed after 70 min of photoelectrolysis (Mumjitha and Raj 2015). This is due with use of NaCl as an electrolyte and the generation of active chlorine, but, unfortunately, the authors did not indicate which light source was used for irradiation. Complete removal of another azo dye of AO7 by photoelectrocatalytic oxidation under optimal conditions and irradiation with visible light requires 180 min, and a complete reduction of COD is achieved after 270 min (Ghalebizade and Ayati 2016).

WO₃ based photoanodes have also been used for photoelectrocatalytic oxidation of azo dyes. Discoloration of the MO solution on WO₃ obtained by electrochemical anodization of tungsten foil was shown in (Zheng and Lee 2014). As TiO₂, the WO₃ is characterized by a higher efficiency in decolorization of an azo dye solution by photoelectrocatalysis than photocatalysis or electrocatalysis. On WO₃ based composite photoanodes, such as W/WO₃/TiO₂, the efficiency of TOC removal during the oxidation of azo dye basic red 51 using UV and visible light irradiation

293 is 94 and 88%, respectively (Fraga et al. 2013). WO₃/TiO₂ heterostructures with layered structure,
294 high crystallinity, a large specific surface area, and strong light absorption in the solar spectrum
295 visible region, is show the high activity of the photoelectrocatalytic oxidation of active red 152
296 (Hunge et al. 2018). Kusmierek E. et al. (Kusmierek and Chrzescijanska 2015) conclude that it is
297 possible to use the WO₃ modified TiO₂-RuO₂/Ti electrodes for the photoelectrocatalytic oxidation
298 of azo dyes not only under UV irradiation, but also under visible light irradiation, for example,
299 sunlight or room lighting lamps.

300 Heterostructures based on Fe₂O₃ were also used as electrode materials to the photoelectro-
301 catalytic oxidation of azo dyes. For example, an α -Fe₂O₃/TiO₂/activated carbon (α -
302 Fe₂O₃/TiO₂/ACP) nanocomposite obtained by electrophoretic deposition was used as an electrode
303 for decolorization of azo dye active yellow 39 under the visible light irradiations. The results
304 showed that the decolorization efficiency the visible light photoelectrocatalytic process using the
305 α -Fe₂O₃/TiO₂/ACP nanocomposite was higher (94%) compared to those for TiO₂/ACP (45%) and
306 α -Fe₂O₃/ACP (60.26%) under optimal conditions (Ayoubi-Feiz et al. 2014). The Fe₂O₃/TiO₂ nano-
307 tube electrode exhibited a higher photoelectrocatalytic activity to MO degradation in an acidic me-
308 dium. At an initial pH 3, the rate of MO solution discoloration reach 91.7% under UV-light irra-
309 diation at 5 min (Cong et al. 2012). The thin-film Sn₃O₄/TiO₂/Ti electrode showed high efficiency
310 the mono-azo dye Acid Yellow 17 (AY17) oxidation under visible light and achiev 95% color
311 removal after 60 minutes at pH 2. At low potentials (0.5 V), the efficiency of photoelectrocatalytic
312 color removal increased to 97.% and TOC removal 83% with rate almost 3 times higher than with
313 photocatalysis (Huda et al. 2019). The use of the TiO₂ NT/Bi₂MoO₆ composite leads to complete
314 discoloration of the MO solution under sunlight irradiation at 3 hours, which is mainly associated
315 with the formation of a type II heterojunction between TiO₂ and Bi₂MoO₆ [76]. The type II het-
316 erojunction not only enhances the efficiency of visible light absorption, but also increase the trans-
317 fer of photogenerated charge carriers and limits the recombination of electron-hole pairs by use
318 of an internal electric field [59]. The same efficiency at the level of 95% at the oxidation of active
319 green 19 under visible light irradiation is shown by the TiO₂/Ti electrode decorated with FeTiO₃
320 (Azis et al. 2021).

321 Other semiconductors and heterostructures based have been studied at the photoelec-
322 tatalytic oxidation of azo dyes. The YFeO₃/Carbon fiber composite electrode provides high pho-
323 toelectrocatalytic activity by the removal of RB5 with visible light irradiation and efficiency of
324 99% after a 60-minute treatment (Liu et al. 2021). The Orange II oxidation efficiency on bismuth
325 ferrite (BFO) and 10% La-BFO photoanodes was 55.3% and 84.2%, respectively (Nkwachukwu
326 et al. 2021). Electrodes SnO₂-Sb₂O₄-WO₃ during photoelectrolysis for 120 min showed complete
327 discoloration of the trypan blue dye solution with 84% COD removal at the same time (Subba Rao

328 et al. 2017). The use of a Ti/Pt/PbO₂ electrode as a photoanode at the oxidation of direct red 80
329 (DR80) leads to increase the process efficiency compared to other electrode materials. Complete
330 discoloration of the Direct Red 80 solution was achieved after 4 hours of treatment at an initial
331 dye concentration of 25.0 mg/l and a current of 50 mA (Florêncio et al. 2013). A composite of
332 exfoliated graphite and bismuth vanadate was used as a photoanode to the oxidation of AO7 and
333 the dye removal efficiency was 88% at 90 minutes (Orimolade and Arotiba 2019). The high effi-
334 ciency of photoelectrocatalytic oxidation of acid red 1 was achieved on the Ni@ZnO/MoS₂ com-
335 posite. The presence of MoS₂ improves the catalytic properties of the composite, which is mainly
336 associated with the formation of p-n junctions between ZnO and MoS₂ (Fei et al. 2020).

337 The electrolyte type also affects the efficiency of the photoelectrocatalytic oxidation of azo
338 dyes. A comparison of the photoelectrocatalytic oxidation of AO7 on nanocrystalline TiO₂ films
339 in NaCl and Na₂SO₄ solutions showed that the oxidation of the azo dye in NaCl solution occurs
340 mainly due to the electrochemical generation of active chlorine (Tantis et al. 2015). The presence
341 of ammonium persulfate ((NH₄)₂S₂O₈) in solution significantly increases the efficiency of removal
342 due to the formation of SO₄^{•-} radicals, which was demonstrated in (Thabet and El-Zomrawy 2016)
343 during the oxidation of the azo dye acid red 17. Non-radical (NH₄)₂S₂O₈ activation mechanism
344 demonstrated at the use of the visible-light-sensitive ternary structure TiO₂-graphene oxide-
345 phthalocyanine Zn nanosheets (TiO₂ @GONS@ZnPc) for the photoelectrochemical degradation
346 of azo dye Orange G (Nwahara et al. 2021).

347 Another advantage of the photoelectrocatalytic process is the use of carbon-based cathode
348 materials for the generation of hydrogen peroxide due to the cathodic reduction of oxygen, which
349 leads to an increase in the efficiency of the photoelectrocatalytic process (Ghalebizade and Ayati
350 2016). An increase in the aeration rate leads to an increase the solubility of oxygen with a corre-
351 sponding increase to the yield of hydrogen peroxide [89, 90]. To increase the yield of hydrogen
352 peroxide during the photo-electrochemical oxidation of the direct black dye 22 are shown in works
353 (Isaev et al. 2013; Isaev et al. 2018), photoelectrolysis is carried out at elevated oxygen pressures
354 of 0.1 to 0.7 MPa.

355 Table 1 shows the comparative characteristics of various materials used as photoanodes at
356 the oxidation of azo dyes.

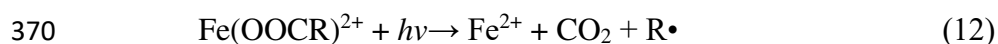
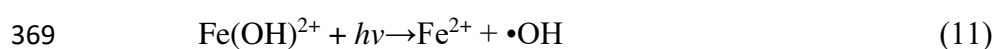
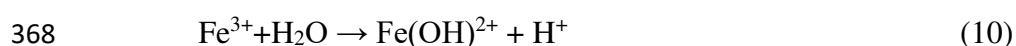
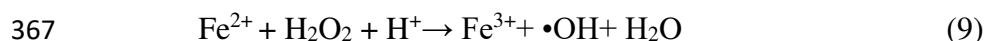
Table 1. Comparative characteristics of various materials used as photoanodes at the photoelectrocatalytic oxidation of azo dyes

Photoanode	Synthesis method	Azo dye	Process parameters	Light source	Discoloration	Ref
TiO ₂ -RuO ₂ /Ti electrodes modified with WO ₃	thermal decomposition	Acid Orange 7	0.1 mol/l Na ₂ SO ₄ [Dye] ₀ = 200mg/l 2h at 0.01 Acm ²	UV and Vis irradiation	98.63	(Kusmierek and Chrzescijanska 2015)
Fe-doped TiO ₂	sol-gel method.	Methyl orange	2 V [Dye] ₀ = 10 mg/L 3 h	300 W Xenon arc lamp	85%	(Tang et al. 2014)
Cu ²⁺ -doped TiO ₂	sol-gel method, using dip-coating as the coating way	Methyl orange	1 h 1.0 V	two UV lamps (?max = 365 nm, 8 W		(Zhang et al. 2013)
TiO ₂ NT	anodization	Methyl orange	0.1 M Na ₂ SO ₄ light intensity = 2.0 mW/cm ² 0.6 V [Dye] ₀ = 20 mg/l 5 h	200 W high-pressure mercury lamp	90.6	(Zhao et al. 2009)

multiwall carbon nano-tubes- TiO ₂ /Ti	electrophoretic deposition	Acid Red 33 (AR33)	7.5 mA/cm ² 60 min pH = 5.2	UV light source (280–400 nm)	98	(Nabizadeh Chianeh and Basiri Parsa 2015)
Cu-TiO ₂	anodizing and electrodeposition	Methyl orange	0.5 V [Dye] ₀ = 3.0 ppm 10 min	UV and Vis irradiation	92.88	(Nurdin et al. 2021)

4. Photoelectro-Fenton and Solar Photoelectro-Fenton

359
360 Photoelectro-Fenton is a modernization of the EF process by irradiation with UV or sun-
361 light, or photoexcitation with visible light of Fe³⁺ complexes with carboxylic acids formed in the
362 Fenton reaction (equation (9) for the regeneration of Fe²⁺ with the formation of •OH (equations
363 (11) and (12)), thus increasing the amount and regeneration of •OH, as well as the efficiency of
364 the process (Vasudevan and Oturan 2014; Sirés et al. 2014b; Brillas and Martínez-Huitle 2015;
365 Nidheesh et al. 2018; Brillas 2020). The photogenerated Fe²⁺ ion can subsequently catalyzed the
366 Fenton reaction with the formation of Fe³⁺ and ring closure (equation (9)).



371 The high oxidation effect in the PEF is due to the action of hydroxyl radicals generated in
372 situ under UV or solar irradiation in wastewater (Salazar et al. 2019a). This process is more effec-
373 tive for the complete mineralization of synthetic azo dyes and treatment of real wastewater (Wang
374 et al. 2008; Almeida et al. 2012; Bedolla-Guzman et al. 2016).

375 The PEF has shown high efficiency to removal of azo dyes from wastewater. In the PEF
376 and SPEF oxidation of azo dyes, hydrogen peroxide H₂O₂ is formed in dye solutions due to two-
377 electron reduction of O₂ on cathode materials. The presence of small amounts of Fe²⁺ leads to an
378 increase the oxidation of azo dyes due to the formation of •OH and Fe³⁺ in the bulk solution ac-
379 cording to the Fenton reaction at the optimum pH ~ 3 (Sirés et al. 2014b). The use of sunlight in
380 the PEF makes this technology inexpensive compared to the process using UV light. UV light
381 contributes to the photoreduction of Fe(OH)²⁺ according to reaction (11) with the regeneration of
382 Fe²⁺ and additional formation of •OH and the occurrence of the destruction reaction of Fe(III)-
383 carboxylate intermediates (12), which are are resistant to various oxidative processes (Brillas
384 2020).

385 Various groups of researchers have investigated the effectiveness of both the PEF and the
386 SPEF for the removal of azo dyes. The comparative study of the destruction of the azo dye active
387 yellow 160 (RY160) due to anodic oxidation with the simultaneous generation of H₂O₂ (AO-
388 H₂O₂), EF, PEF was carried out (Bedolla-Guzman et al. 2016). BDD as an anode and an air-diffu-
389 sion cathode to produce H₂O₂ with the addition of 0.50 mmol/dm³ Fe²⁺ were used. The minerali-
390 zation efficiency of the processes increases in the range AO-H₂O₂ < EF < FEF (Márquez et al.
391 2020). This trend is explained by the predominant formation of hydroxyl radicals on the anode
392 surface as a result of water oxidation and in the volume as a result of the Fenton reaction (Medrano-
393 Rodríguez et al. 2020). When using PEF, 94% mineralization of the azo dye active yellow 160

394 was achieved after 360 minutes at 100 mA/cm² at an initial concentration of 0.167 mmol/dm³
395 (Bedolla-Guzman et al. 2016). The discoloration and mineralization of 290 mg/l azo dye Sunset
396 Yellow FCF (SY) under analogous conditions was studied (Moreira et al. 2013). The same com-
397 parison of the efficiency of oxidation processes was carried out when removing acid blue 29 with
398 a concentration of 118 mg/l with BDD, Pt and Ti/RuO₂ anodes, where the highest efficiency of
399 azo dye oxidation due to the SPEF was also observed in comparison with electrochemical oxida-
400 tion with simultaneous generation of H₂O₂ and EF process. After 15 min with the current density
401 of 33.3 mA/cm², almost complete degradation of acid blue 29 was achieved, regardless of the
402 anode used, and after 285 min, complete mineralization according to TOC was achieved (Fajardo
403 et al. 2019). The combination of a gas-diffusion cathode and a DBA under sunlight irradiation
404 leads to the same effect of removing azo dyes as when using UV light, which makes the use of the
405 SPEF economically advantageous (Paz et al. 2020).

406 In some cases, SPEF can be supplemented by a process of continuous electrochemical gen-
407 eration of hypochlorous acid (HClO) and photoregeneration of Fe(II) with the formation of hy-
408 droxyl radicals. The presence of chloride ions in the electrolyte and the use of DSA anodes leads
409 to the formation of HClO, which is involved in the oxidation of azo dyes (Murrieta et al. 2020).
410 The use of anodes (DSA type) and an air-diffusion cathode connected to a solar photoreactor made
411 it possible to completely mineralize the Acid Blue 29 dye using SPEF (Salazar et al. 2019b). Com-
412 parison of the efficiency of the SPEF process for processing solutions of acid red 1 in an electrolyte
413 containing chlorides showed that in the PEF process a faster removal of color occurs compared to
414 the process with the generation of HClO. The simultaneous implementation of both processes leads
415 to a slightly faster discoloration than at the PEF (Titchou et al. 2022).

416 Congo red diazo dye under these conditions at 100 mA/cm² is completely mineralized at
417 240 minutes with a current efficiency of about 49% and 0.45 kWh/(g DOC) energy consumption
418 (Solano et al. 2015). Azo dyes are removed mainly by the OH formed at the anode as a result of
419 water oxidation and in the bulk solution as a result of the Fenton reaction between Fe²⁺ and H₂O₂
420 generated at the cathode, as well as as a result of photolysis of Fe(OH)²⁺ particles by light (Moreira
421 et al. 2013). When Fe²⁺ is added with the simultaneous generation of hydrogen peroxide at the
422 cathode, the pH of the solution under optimal conditions should correspond to acidic values. This
423 conclusion was made by the authors of works (Almeida et al. 2015; Elumalai et al. 2022), where
424 the oxidation of active yellow 186 and orange G azo dyes was studied. The kinetics of the photo-
425 electro-Fenton oxidation of azo dyes corresponds to the pseudo-first order (Brillas and Garcia-
426 Segura 2016).

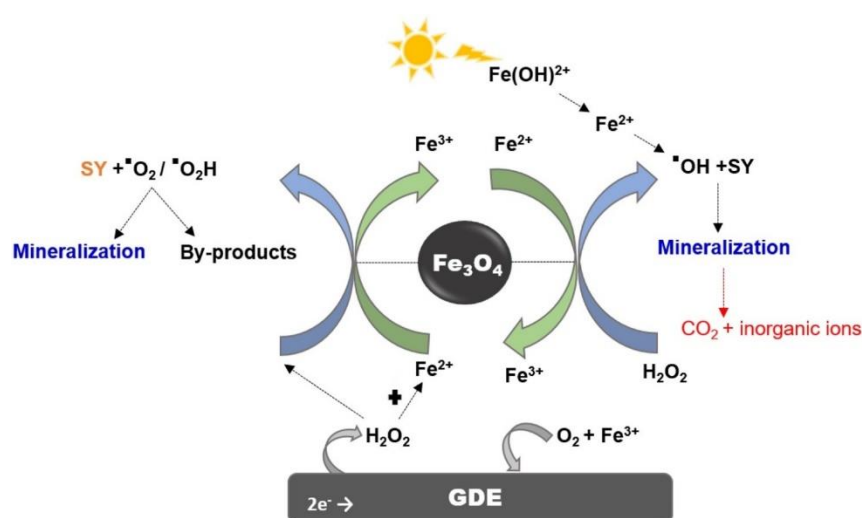
427 In the case of using iron electrodes for the oxidation of azo dyes, the generation of Fe^{2+} and
428 H_2O_2 occurs directly during the PEF (Moradi et al. 2015). In this case, a combination of electro-
429 coagulation and PEF to remove azo dyes is the most appropriate option. Oxidation of Acid Blue
430 29 (AB 29) in an electrochemical filter press reactor equipped with a Ti|Ir-Sn-Sb oxide anode and
431 stainless steel cathode plates achieved 62% discolouration and 84% COD removal (Márquez et al.
432 2022a). The combination of the electrocoagulation process makes it possible to treat highly con-
433 centrated azo dyes wastewater. The main part of the dye is removed due to the electrocoagulation
434 process, and the dye remaining in the solution can be oxidized to CO_2 due to the PEF (Márquez et
435 al. 2022b). The mineralization of the azo dyes Acid Violet 7 (AV7) and RB5 was studied using a
436 photoelectro-Fenton process using a glassy carbon mesh electrode (cathode) and a steel mesh as
437 anode (Salazar and Ureta-Zañartu 2012). Simultaneous generation of hydroxyl radicals on a
438 TiO_2/Ti photocatalyst and in situ generation of Fenton's reagent on a stainless steel electrode sig-
439 nificantly increases the efficiency of the removal of azo dyes, for example, orange G (Liu et al.
440 2019a). It should be noted that the hybrid process of electrocoagulation with PEF can be an alter-
441 native to conventional PEF in solutions containing a significant amount of chloride ions (Márquez
442 et al. 2022b).

443 The mineralization of the azo dye Acid Red 14 was studied using the PEF in a single-
444 chamber electrochemical reactor with a RuO_2/Ti anode and an activated carbon fiber cathode to
445 generation of H_2O_2 electrochemically. Research results have shown that the EF process yields
446 about 60–70% mineralization of AR14, while the PEF can mineralize AR14 more efficiently (re-
447 moval of more than 94% TOC) even at low current densities after 6 hours of electrolysis (Wang
448 et al. 2008). The combination of a photocatalytic process on TiO_2 nanoparticles with PEF during
449 the oxidation of CI Basic Red 46 (BR46) and CI Acid Red 17 (AR17), as well as a mixture of azo
450 dyes, leads to their complete mineralization according to TOC (Khataee et al. 2010a, 2012; Zarei
451 et al. 2010). At the same time, the efficiency of mineralization decreases in the range
452 $\text{PEF}/\text{TiO}_2 > \text{PEF} > \text{EF} > \text{UV}/\text{TiO}_2$. The use of additional sonication makes it possible to further in-
453 crease the rate of oxidation of azo dyes (Mahmoudi et al. 2022).

454 The presence of Fe^{2+} ions is necessary for the oxidation of azo dyes in the PEF process. To
455 avoid the use of iron salts as precursors for the homogeneous Fenton process, it is proposed to add
456 iron compounds to the solution of azo dyes or to precipitate zero-valent iron on various substrate.
457 The addition of heterogeneous catalysts containing iron compounds to the solution of azo dyes
458 during the PEF leads to additional occurrence of heterogeneous Fenton-like processes (Isaev and
459 Magomedova 2022). The results of studies to the removal of SY due to the SPEF showed that the
460 discoloration of the solution is 98.7%, and the removal of TOC is 71% in 90 min of photoelectrol-
461 ysis (Pinheiro et al. 2020). The mechanism of azo dye oxidation is shown on Fig. 3. The deposition

462 of zero-valent iron on various substrate with a large specific surface, which can be used as cathode
 463 materials, in particular, on activated carbon, promotes an additional occurrence of a heterogeneous
 464 photo-Fenton process during the oxidation of azo dyes (Ramírez et al. 2010; Bañuelos et al. 2015).
 465 Iron oxalates can also be used as catalysts for the decomposition of H_2O_2 during the oxidation of
 466 azo dyes in PEF (Khataee et al. 2010b). Comparison of the rate of oxidation of active red 195
 467 showed that the removal of the color of the solution follows in descending order: PEF/oxalate >
 468 PEF > EF (Djafarzadeh et al. 2013).

469
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 471



472
 473
 474

475 Fig. 3. The mechanism of oxidation of the SY dye due to the solar photoelectro-Fenton
 476 process in the presence of Fe_3O_4 . Reprinted by permission from (Pinheiro et al. 2020). Copyright
 477 2020, Elsevier.

478

479 The efficiency of oxidation of azo dyes by the PEF process is affected by such operating
 480 parameters as current density, solution pH, flow rate, initial Fe^{2+} concentration, initial dye concen-
 481 tration, etc. (Zhang et al. 2011; Ruiz et al. 2011b; Khataee et al. 2013; Aveiro et al. 2018). The
 482 material of the anode and cathode also play an important role in the oxidation of azo dyes by the
 483 PEF process (Pereira et al. 2016; Wang et al. 2022). For example, Paz E.C. et al. (Paz et al. 2018)
 484 a new catalyst for the efficient generation of hydrogen peroxide using tungsten oxide as an additive
 485 was proposed, which was used in the oxidation of orange II and which showed high H_2O_2 current
 486 efficiency and low energy consumption. The rate of oxidation of azo dyes in PEF depends on the
 487 number of azo bonds in the molecule. Comparison of the oxidation rate of AO7 monoazo dye, acid

488 red 151 diazo, and dispersed blue 71 triazo dye using SPEF showed that the mineralization rate
489 decreased in the following order AO7>DS71>KK151. For AO7, mineralization up to 97% was
490 achieved, while short-line carboxylic acids remained in the final solution. For two other azo dyes,
491 a mineralization of 90–92% was achieved, and their final solutions contained undetected products
492 that were more stable than carboxylic acids (Garcia-Segura and Brillas 2016). Mahmoudi N. et al.
493 (Mahmoudi et al. 2022) studied the discoloration of two widely used textile dyes, acid black 172
494 and dispersed black 56, of the combined sonophotocatalytic-Fenton process. A dye oxidation effi-
495 ciency of 95.5% and a COD removal efficiency of 91.6% for Disperse Black 56 were obtained
496 under optimal conditions pH 3, current density 2 mA/cm², dye concentration 200 ppm, and a treat-
497 ment time of 30 min, and in the case of acid black 172, the treatment time was 50 minutes to
498 achieve the same performance.

499 Recently, researchers have great attention to the removal of food azo dyes. This is because
500 some food azo dyes can reason hyperactivity and allergies in children. These food azo dyes include
501 food additives E122 (Carmoisine, CI 14720), E124 (Ponceau 4R, CI 16255), and E129 (Allura
502 Red AC, CI 16035) (Thiam et al. 2015a). The decomposition of a mixture of food azo dyes E122,
503 E124 and E129 was studied by the PEP under UV light irradiation using BDD (or Pt) as an anode
504 and an air diffusion cathode. In a sulfate medium, all azo dyes showed rapid discoloration, but
505 almost complete mineralization was achieved faster in PEF with BDD. At the presence of chloride
506 ions in solution, the formation of stable chlorine derivatives slowed down the oxidation process
507 (Thiam et al. 2015a). Comparative oxidation of the food monoazo dye tartrazine due to various
508 electrochemical processes was shown in (dos Santos et al. 2018). For a better understanding of the
509 role of oxidizing agents, comparative tests of anodic oxidation and electrogenerated H₂O₂ (AO-
510 H₂O₂), EF and PEF were carried out. Anodic oxidation with generation of H₂O₂ showed a small
511 rate of oxidizing power. EF led to partial mineralization due to the formation of molecules resistant
512 to the action of •OH. By-products were destroyed in the SPEF process, which led to complete
513 mineralization of tartrazine (dos Santos et al. 2018).

514 Comparison of the oxidation process of another food coloring Allura Red AC in sulfate
515 medium containing 0.50 mM Fe²⁺ was studied using SPEF and EF. EF treatment resulted in rapid
516 discoloration but poor mineralization as most of the products were slowly degraded by •OH formed
517 from the Fenton reaction between Fe²⁺ and H₂O₂ generated on the air diffusion cathode. During
518 EF, TOC decreased by 39% after 180 min, after which the Allura Red AC oxidation process
519 slowed down and reached only 46% mineralization after 360 min. Almost complete mineralization
520 (96%) was achieved after 240 min of SPEF, which can be explained by the rapid photolysis of
521 non-oxidizing intermediates (Thiam et al. 2015b). The comparison of the oxidation of azo dyes by
522 various Photoelectro-Fenton process are presented in Table 2.

Table 2. Comparison of the oxidation of azo dyes by Photoelectro-Fenton process

Photoanode	Type of process	Azo dye	Process parameters	Light source	Discoloration/TOC*	Ref
Ti Ir-Sn-Sb-oxides	electro-coagulation (EC) and active chlorine-based photoelectro-Fenton-like	Acid Blue 113	$u = 24.2 \text{ cm/s}$, $i = 15 \text{ mA/cm}^2$ 0.4 mM Fe^{2+}	UV-A lamp	100	(Márquez et al. 2022b)
	sono-photo-electro-Fenton	Acid Black 172 Disperse Blue 56	$[\text{Dye}]_0 = 125 \text{ mg/l}$, $\text{pH } 5$, $i = 4 \text{ mA/cm}^2$	UV lamp	95.5–97.4%	(Mahmoudi et al. 2022)
BDD	photoelectro-Fenton	Acid Red 1	$[\text{Dye}]_0 = 300 \text{ mg/l}$ $0.05\text{M Na}_2\text{SO}_4$ $\text{pH } 3.0$ 0.50mM Fe^{2+} $i=16.6\text{-}66.6 \text{ mA/cm}^2$	UVA lamp	95.2	(Wang et al. 2022)
BDD	photoelectro-Fenton in chloride and sulfate media	direct red 23	$i=5 \text{ mA/cm}^2$, 6 h, $75\% \text{ Na}_2\text{SO}_4 + 25\% \text{ NaCl}$	UV irradiation	100*	(Titchou et al. 2022)

Ti anode	photo electro-Fenton	Reactive Yellow 186	[Dye] ₀ = 0.05–0.25 g/l, pH 2–9, Fe dosage 0.01–0.03 g/l, H ₂ O ₂ = 0.1–0.5 g/l i = 0.1–0.5 mA/cm ²)	UVA radiation	99 94.82*	(Elumalai et al. 2022)
BDD	UVA photoelectro-Fenton solar photoelectro-Fenton	Erythrosine B	[Dye] ₀ = 100 mg/l i = 20 mA/cm ² ; [Fe ²⁺] = 0.1 mM; pH 3; 50 mM Na ₂ SO ₄ , 2 h	UVA lamp Solar Light	100*	(Clematis and Panizza 2021)
	Solar photoelectro-Fenton process using Fe ₃ O ₄ nanoparticles as a catalyst	Sunset Yellow	0.13 M NaCl 0.1 M Na ₂ SO ₄ pH 3.0 90 min	Solar light	98,7 71*	(Pinheiro et al. 2020)
Ti RuO ₂	photoelectro-Fenton	Methyl Orange	[TOC] ₀ = 30 mg/l 50 mM Na ₂ SO ₄ 0.50 mM Fe ²⁺ pH 3.0 i = 20 mA/cm ²	UVA lamp	100 at 30 min 94* at 240-300 min	(Márquez et al. 2020)

BDD	simulated solar photoelectro-Fenton	Orange II	[Dye] ₀ = 0.26 mM 0.1M K ₂ SO ₄ pH 3.0 150 mA/cm ²	Xe lamp	93*	(Paz et al. 2020)
BDD	solar photoelectro-Fenton	Acid Blue 29	[Dye] ₀ = 118 mg/l 0.05 M Na ₂ SO ₄ pH 3.0 0.5 mM Fe ²⁺ i = 33.3 mA/cm ²	Sun light	100 at 15 min 100* at 285 min	(Fajardo et al. 2019)

5. Combined photoelectrochemical processes and reactors

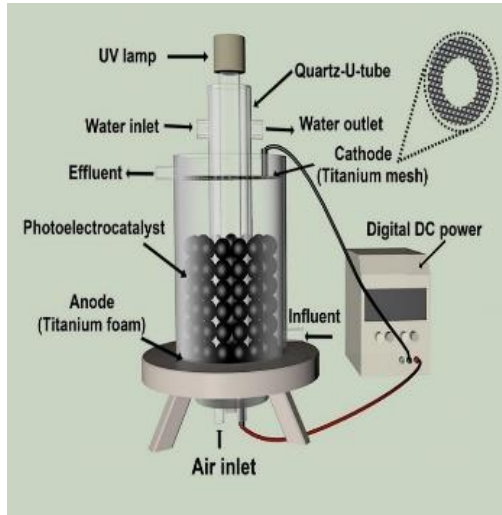
525
526 Great interest in the photoelectrochemical oxidation of azo dyes, caused the appearance of
527 various types of reactor designs for the process (Jaramillo-Gutiérrez et al. 2020) . Photoelectroca-
528 talysis and related reactor designs have already been considered and discussed in some reviews
529 (Meng et al. 2015; McMichael et al. 2021; Divyapriya et al. 2021). In recent years, great efforts
530 have been made to bring the industrial application of photoelectrocatalysis out of its infancy and
531 introduce this technology into production. In this regard, new types of reactors have been proposed
532 based on new materials that are more efficient for oxidation of azo dyes and do not depend on their
533 nomenclature. The main components of the installation for the photoelectrochemical oxidation of
534 azo dyes are the reactor, where the photoelectrochemical reaction takes place, the light source and
535 the power supply.

536 Reactors for photoelectrochemical removal of azo dyes can operate in batch, semi-batch
537 and flow (continuous mode). Basically, all research and reactors that are used to remove azo dyes
538 are currently at the level of laboratory developments. Fig. 4a shows a laboratory operating in a
539 semi-batch mode and consisting of a polymethyl methacrylate tube with a bottom water inlet and
540 a top outlet, a UV source surrounded by a titanium dioxide mesh (anode), and a steel mesh acting
541 as a counter electrode (cathode) (Franz et al. 2015). A modular type reactor equipped with up to 9
542 separate photo-electrochemical cells is shown in Fig. 4b. In an individual cell, a TiO₂ electrode
543 deposited on a conductive glass substrate was used as a photoanode, and a stainless steel plate at
544 a distance of 0.1 cm from the photoanode served as a cathode. The light source was either a UVA
545 lamp placed behind the photoelectrode or sunlight using manual tilt and azimuth tracking (Shinde
546 et al. 2009).

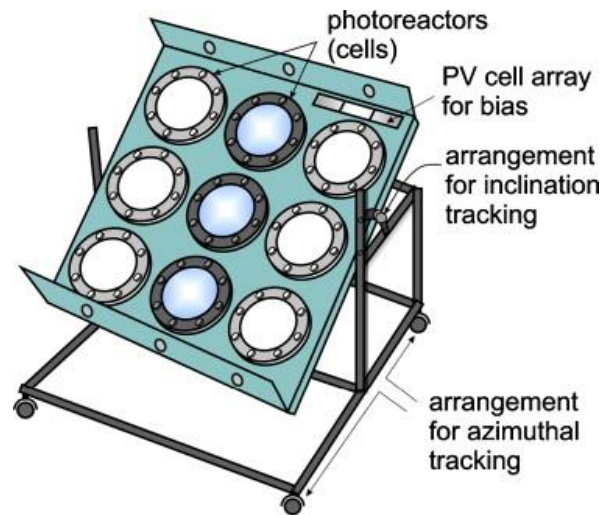
547 A new three-dimensional photoelectrocatalytic reactor (3D-PER) for the removal of dyes
548 from wastewater, the scheme of which is shown in Fig. 4d, is proposed by Meng H.S. et al (Meng
549 et al. 2021) . The outer structure is a cylindrical tank. A titanium plate (diameter 62 mm) fixed at
550 the bottom of the reactor was used as an anode. An annular titanium grid located above the anode
551 served as the cathode. A quartz U-shaped tube was placed in the middle of the reactor, inside which
552 a high-pressure mercury lamp was fixed. Granular carbon was placed in one layer between the
553 cylindrical container and the quartz U-shaped tube. Air was purged from the bottom of the reactor
554 using an aeration pump. The bleaching efficiency of the dye solution was more than 95%; granular
555 carbon showed stable characteristics when processed for 11 continuous cycles (Meng et al. 2021).

556 Blowing oxygen or air through the photoelectrochemical reactor leads to the reduction of
557 oxygen to hydrogen peroxide, which increases the efficiency of removing azo dyes. Using this
558 concept, an industrial prototype was developed with four identical reactors for the implementation
559 of the PEF (Fig. 4c). H₂O₂ is formed electrochemically in the first stage by reduction of dissolved

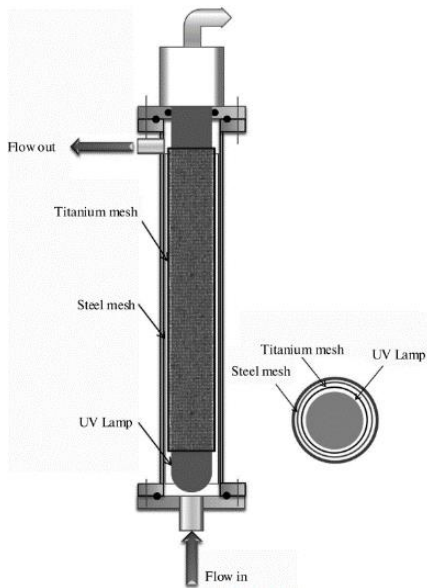
560 oxygen. Then, in a second step, H_2O_2 is passed through an iron-catalyst column irradiated with
 561 UV light to stimulate the formation of hydroxyl radicals, which are added to an aqueous solution
 562 of Orange-II azo dye. The decolorization efficiency of Orange II solution ranged from 75% to 96%
 563 at pH 3-5 (Robles et al. 2017).



a



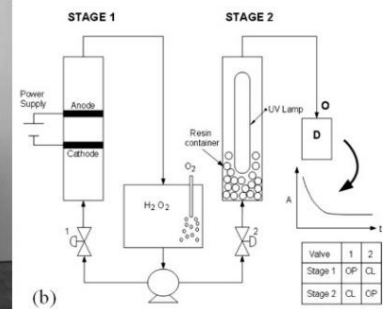
b



c



(a)



d

566

567

568 Fig. 4. a) – Photoelectrochemical semi-batch mode module for azo dye removal. Reprinted
 569 by permission from (Shinde et al. 2009). Copyright 2021, Elsevier; b) – modular type reactor
 570 equipped with up to 9 separate photo-electrochemical cells. Reprinted by permission from (Franz
 571 et al. 2015). Copyright 2009, Elsevier; c) – three-dimensional photoelectrocatalytic reactor
 572 reprinted by permission from (Meng et al. 2021). Copyright 2015, Springer; d) – industrial prototype
 573 for producing an oxidant solution (a) and schematic description of the system, along with a two-
 574 stage process for producing an oxidant-rich aqueous solution (b). Reprinted by permission from
 575 (Robles et al. 2017). Copyright 2017, Elsevier.

576 The classic reactor for photoelectrochemical oxidation of azo dyes is a reservoir with two
577 electrodes, a photoanode and a cathode, a radiation source and a power source, to support the
578 required temperature, the reactor is in some cases equipped with a "jacket" around the reactor
579 (Huda et al. 2019). A reactor with two electrodes is most often performed with undivided anode
580 and cathode spaces. Photoanodes based on TiO_2 (Turolla et al. 2018; De Vidales et al. 2022; Chen
581 et al. 2022a), BDD (Espinoza et al. 2016) are used as anodes, and carbon-based materials are used
582 as cathodes. The main function of cathodes is the electrochemical reduction of oxygen to produce
583 H_2O_2 (Chen et al. 2022a). In the case of the implementation of the PEF process, the cathode ma-
584 terial plays a key role in the efficiency of the oxidation of azo dyes. As a cathode, materials with
585 a large specific surface area, such as graphite felt and carbon cloth, are most often used (Thor et
586 al. 2021). Semiconductors can also be used as cathodes. In this case, both electrode processes
587 perform a useful function. A laboratory cell for photoelectrocatalysis using a Cu_2O photocathode
588 and a $\text{WO}_3/\text{BiVO}_4$ photoanode was developed for the simultaneous production of H_2 and decom-
589 position of organic dyes (Thongthep et al. 2021). The efficiency of azo dye oxidation can be in-
590 creased by about 50% due to additional destruction at the cathode, as demonstrated in work (Xu
591 et al. 2013).

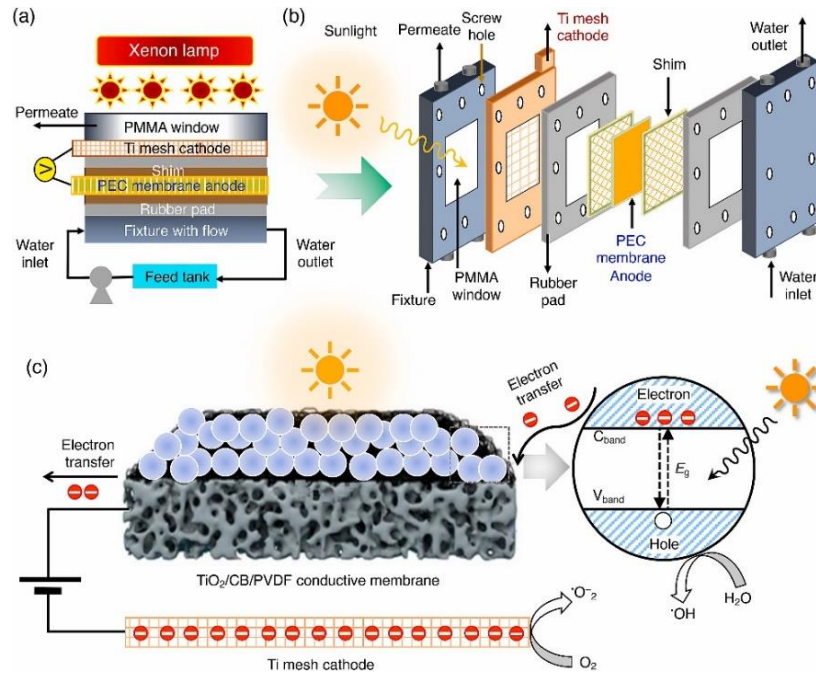
592 In some cases, it is proposed to use a two-chamber electrolyzer. Lian Z. et al. (Lian et al.
593 2020) used a laboratory reactor made of quartz glass and divided into two chambers by a Nafion
594 cation-exchange membrane to oxidize MO. Basically, two-chamber electrolyzers are used for la-
595 boratory studies in determining the magnitude of the applied voltage to the photoanode (Diao et
596 al. 2013). Oxidation of active red 106 in a photoelectrocatalytic flow microreactor, where a tubular
597 TiO_2 electrode was used as a partition separating the anode and cathode spaces and which simul-
598 taneously served as a photoanode, with a maximum degree of oxidation in the anode chamber of
599 80% of the initial dye concentration and 63 % dye in the cathode chamber was studied Suhadolnik
600 L. et al (Suhadolnik et al. 2019).

601 An annular reactor with simultaneous air bubbling with a TiO_2 nanotube photoanode was
602 studied Cardoso J.C. et al. (Cardoso et al. 2015) by the course of photoelectrochemical purification
603 of real wastewater containing dyes. To implement the process of photoelectrochemical oxidation
604 of azo dyes in a flow mode, a tubular design of the reactor is mainly used (Jaramillo-Gutiérrez et
605 al. 2020). In the case of using solar energy to implement the photoelectrofenton process, the reac-
606 tors for the oxidation of azo dyes are equipped with solar collectors (Garcia-Segura and Brillas
607 2014).

608 To achieve a more efficient removal of azo dyes, it was proposed to use combined photo-
609 electrocatalysis with adsorption or filtration processes (Zhang et al. 2023). The combination of
610 photoelectrocatalysis and membrane filtration is currently considered an attractive technology for

611 wastewater purification from organic compounds (Cheng and Han 2016). The creation of a reactor
612 in which both filtration and photoelectrocatalysis can occur simultaneously is a rather difficult task
613 due to the need to create a connection between the catalyst and a conductive substrate with effective
614 filtering properties (Martins et al. 2020). In connection with this, research is being carried out
615 on reactors with various membranes for the photoelectrochemical oxidation of dyes. As conducting
616 porous membranes, it is proposed to use stainless steel membranes coated with TiO_2 and ZnO
617 semiconductor oxides (Kumari et al. 2022, 2023). A sandwich membrane consisting of nylon fiber
618 and stainless steel mesh with electro-deposited WO_3 showed high efficiency in photoelectrocatalytic
619 wastewater treatment from active red dye 120. Complete removal of the dye was achieved
620 after 150 min by passing an aqueous solution of active red for 120 s concentration of 10-5 mmol/l,
621 $\text{pH} = 4.0$ and voltage of 1.0 V at a rate of 160 ml/min (Martins et al. 2020). The combination of
622 microfiltration technology and photoelectrocatalysis with a conductive TiO_2 /polyaniline
623 (PANI)/polyvinylidene fluoride (PVDF) membrane, when irradiated with sunlight, significantly
624 improves the decolorization efficiency of the azo dye (Sboui et al. 2022). The transfer of reagent
625 molecules through membrane pores under pressure in the cross-flow filtration mode additionally
626 facilitates the contact of the pollutant with catalytically active centers on and across membrane
627 pores during photoelectrocatalysis (Chin et al. 2011).

628 Membrane fouling in the implementation of combined photoelectrochemical purification
629 with simultaneous filtration is one of the main problems. To solve this problem, it is proposed to
630 use a composite conductive membrane based on PVDF, carbon black, and TiO_2 . The combined
631 process of FEC with microfiltration in the flow mode includes a FEC reactor, an illumination unit
632 with a Xe-lamp, and a constant voltage unit (1.0 V) (Sboui et al. 2023). Schematic diagram of
633 filtration based on TiO_2 /CB/PVDF membrane is shown in Fig. 5.



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Fig. 5. Schematic diagrams of (a) the PEC membrane-based cross-flow filtration system; (b) the configuration of PEC membrane reactor with PEC membrane anode and Ti mesh cathode, and (c) PEC oxidation mechanism over $\text{TiO}_2/\text{CB}/\text{PVDF}$ conductive membrane with electrochemical potential bias and TiO_2 charge transfer. Reprinted by permission from (Sboui et al. 2023). Copyright 2023, Elsevier.

The combination of photoelectrochemical oxidation of azo dyes with a fuel cell under UV or sunlight irradiation makes it possible to simultaneously purify wastewater and generate electricity (Antolini 2019). In this case, the energy generated in the fuel cell can be used to carry out photoelectrolysis. In this regard, the technology of microbial fuel cells (MFC) is proposed, which has the unique ability to convert organic substances in wastewater directly into electricity while treating wastewater (Janicek et al. 2015). In the MFC, electrons generated in the anode chamber by microorganisms due to separation from synthetic azo dyes as components of wastewater are transferred to the anode, and then, under the action of a difference in redox potentials, begin to move to the cathode, on which the reduction reactions proceed. Thus, electricity is produced along with the decomposition of pollutants. One of the ways to increase power generation in MFCs is the formation of a synergistic bioelectrophotochemical system. The recombination of photogenerated electron-hole pairs in such elements can be effectively reduced, resulting in more photogenerated electrons available for cathodic reduction reactions (Antolini 2019). However, a high cathode reduction reaction overvoltage is often the main limiting factor in MFC performance (Wei et al. 2011). A photoelectrocatalytic microbial fuel cell (photo-MFC) consisting of a p-type silicon

656 photocathode modified with Pd nanoparticles and a bioanode demonstrated the possibility of sim-
657 ultaneously generating electrical energy and decomposing the model azo dye MO. When illumi-
658 nated with visible light, the photo-MFC showed an MO removal efficiency of 84.5% and a maxi-
659 mum output power density of 0.119. W/m² for 36 h, which is twice as much as that of a conven-
660 tional MFC with a carbon paper cathode (Han et al. 2017).

661 The cathodic destruction of RB5 with the simultaneous release of energy is effectively
662 carried out in a two-chamber photo-MFC consisting of a bioanode and an AgBr/CuO hybrid pho-
663 to cathode both in bright light and in the dark. The characteristics of the composite are comparable
664 with AgBr, CuO and pure graphite in terms of the specific MFC power, as well as its ability to
665 decompose the ACh5 dye. The maximum efficiency of AF% destruction using an AgBr/CuO pho-
666 to cathode was 55.56% within 72 hours with a maximum power of 61.11 mW/m² (Ahmadpour et
667 al. 2020). When using TiO₂ nanotubes as a photoanode in photo MFC, the reduction in COD was
668 56%, the degree of discoloration was 85% (Long et al. 2017). The use of an array of TiO₂ nano-
669 tubes also increases the generation of electric current from 3.64 ± 0.112 mA to 6.246 ± 0.135 mA
670 (Long et al. 2019). When using MFC, the decomposition of azo dyes occurs mainly due to the
671 reduction of dye molecules and oxidation by free radicals.

672 Another route of using combined methods of photoelectrochemical oxidation of azo dyes
673 is their combination with the production of hydrogen at the cathode. Photoelectrochemical pro-
674 duction of hydrogen and simultaneous destruction of organic compounds is a new route of re-
675 search. On Ti/TiO₂/WO₃ under sunlight irradiation and optimal process conditions, it resulted in
676 satisfactory hydrogen generation efficiency (46%) and dye removal (100% bleaching and 85%
677 TOC reduction) (Guaraldo et al. 2016). The use of a heterostructure based on samarium vanadate
678 (SmVO₄) and sulfur-doped carbon nitride (g-C₃N₄) as a photoanode showed a satisfactory effi-
679 ciency of hydrogen generation with simultaneous photoelectrochemical oxidation of MO. The
680 amount of hydrogen released during irradiation with sunlight was 22618 μ mol/g-1 for 4 h. At the
681 same time, the degree of discoloration for 80 min was 90% (Alkorbi et al. 2022).

682 To assess the profitability and overall performance of any treatment technology, an assess-
683 ment of the energy consumption of the process is necessary. The research results showed that
684 photolytic and photocatalytic processes require much more processing time and energy consump-
685 tion (32 and 24 kWh/m³, respectively) than the photoelectrocatalytic process (Ghasemian et al.
686 2017).

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6. Azo dye oxidation products

689 Azo dyes are characterized by the presence of a functional azo group (-N=N-), with two or
690 more symmetrical or asymmetric aromatic radicals (Bafana et al. 2011). The azo group can be

691 associated with benzene rings, naphthalene, aromatic heterocycles, or aliphatic groups, which im-
692 part color to the dye with different shades and intensities (Benkhaya et al. 2020). Currently, most
693 dyes are not controlled for toxicity and are considered non-toxic. However, supposedly non-toxic
694 azo dyes have functional groups that can impart mutagenic and carcinogenic properties when de-
695 graded (for example, compounds such as β -naphthylamine, aniline, triazine, p-phenylenediamine,
696 β -amino- α -naphthol, which are known genotoxicants (Brüschweiler et al. 2014; Rawat et al.
697 2016)). It should also be noted that of the majority of azo dyes studied for toxicity, diazo, triazo,
698 and polyazo dyes turned out to be more toxic (Golka et al. 2004). When assessing the toxicity of
699 azo dyes, their possible destruction under the influence of various environmental factors is not
700 taken into account, paying attention only to a laboratory study of toxicity. In addition, the micro-
701 biota of the animal's organism, including skin or intestinal microflora, can convert non-toxic azo
702 dyes into carcinogenic metabolites (Feng et al. 2012). The formation of toxic decomposition prod-
703 ucts of azo dyes has been shown in many works (Brüschweiler et al. 2014). In particular, the au-
704 thors (Golka et al. 2004) showed the formation of carcinogenic 3,3'-dimethoxybenzidine during
705 the decomposition of the azo dye Direct blue 15 (Gottlieb et al. 2003). Analysis of the chemical
706 structure of azo dyes showed that mutagenicity depends on the nature and position of halogen
707 substituents both to aromatic rings and to the nitrogen atom of the amino group (Carneiro et al.
708 2010). When azo dyes, such as Disperse Blue 291, are oxidation using chlorine in solution, the
709 formation of chlorinated products can occur, which are more toxic than the original dye. However,
710 photoelectrochemical treatment reduces the mutagenicity of a solution containing CI Disperse
711 Blue 291 (Carneiro et al. 2010). Based on this, one of the main tasks of the photoelectrochemical
712 oxidation of azo dyes should be to reduce their toxicological properties.

713 Another problem of dye oxidation is to remove the color of solutions, which affects the
714 biochemical processes in water bodies. In different works, high-performance liquid chromatog-
715 raphy and mass spectrometry were mainly used to identify the products of oxidation of azo dyes
716 (Huda et al. 2019), and for the characterization and genotoxicity, cytotoxicity, and mutagenicity
717 of both initial solutions of azo dyes and solutions after photoelectrochemical treatment used the
718 method of analysis of DNA comets, micronuclei and cytotoxicity in HepG2 cells, as well as anal-
719 ysis of mutagenicity using Salmonella (Ferraz et al. 2013).

720 At the photoelectrochemical oxidation of dyes, the destruction of the chromophore group
721 occurs first, in the case of azo dyes, this is the -N=N- azo bond. Aromatic fragments of the azo dye
722 molecule are formed as bond breaking products. For example, during the oxidation of RB5, frag-
723 ments containing benzene rings and naphthalene structures are formed, and the solution becomes
724 completely colorless, although the COD and TOC values are still at a high level (Liu et al. 2021).
725 The initial nitrogen of the dye is mainly mineralized to the NO_3^- ion and, to a lesser extent, to the

726 NH_4^+ ion, and the initial sulfur is converted to the SO_4^{2-} ion (Solano et al. 2015; Garcia-Segura
727 and Brillas 2016; Wang et al. 2022). Nitrogen contained in the azo dye molecule accumulates in
728 the solution after photoelectrochemical treatment in the oxidation of acid blue 29 mainly in the
729 form of NO_3^- , with an insignificant content of NO_2^- and NH_4^+ (Fajardo et al. 2019).

730 The main products of the oxidation of azo dyes using different approaches are carboxylic
731 acids, such as p-benzoquinone, maleic, fumaric, tartaric, tartaric, acetic, oxalic, oxamic, and formic
732 acids (Almeida et al. 2012; Ghalebizade and Ayati 2016; Subba Rao et al. 2017). At the same time,
733 carboxylic acids are also completely removed during longer processing. Oxalic acid, which accu-
734 mulates in large amounts, is rapidly oxidized during photolysis of Fe(III)–oxalate complexes under
735 UV or sunlight irradiation, while tartronic and oxamic acids are the most stable by-products due
736 to the greater stability of their Fe(III)–oxalate complexes (Almeida et al. 2012). Chloride, sulfate,
737 ammonium ions and, to a lesser extent, nitrate ions are the main mineral products of azo dye oxi-
738 dation, which are released into solution from azo dye heteroatoms (Macedo et al. 2007; Brillas and
739 Garcia-Segura 2016; Bedolla-Guzman et al. 2016).

740 The formation of carboxylic acids during the oxidation of acid blue 29 was studied by
741 HPLC. Chromatograms showed well-defined peaks corresponding to acetic, formic, maleic and
742 oxalic acids (Fajardo et al. 2019). Acetic and maleic acids are formed upon cleavage of the benzene
743 rings of the diazo dye (do Vale-Júnior et al. 2018), and formic and oxalic acids upon the oxidation
744 of longer carboxylic acids with subsequent mineralization to CO_2 and H_2O (de Queiroz et al. 2017).
745 The maximum accumulation of maleic and formic acids was observed after 120 min of treatment
746 with a subsequent decrease in their content (Fajardo et al. 2019).

747 The main intermediates during Acid Red 88 and Direct Yellow 12 oxidation are various
748 aromatic compounds and carboxylic acids (Table 3). The oxidation of the azo dye SY using PEF
749 revealed 14 aromatic products and 34 hydroxylated derivatives, including compounds of benzoic,
750 naphthalic, and phthalic acids. At the same time, carboxylic acids, such as tartronic, oxalic, formic,
751 and oxamic, were also found (Moreira et al. 2013). For another dye, Congo red, the formation of
752 21 aromatic intermediates and 13 hydroxylated derivatives was identified, including compounds
753 of diazo, monoazo, biphenyl, benzene, naphthalene, and phthalic acid (Solano et al. 2015). During
754 PEF, the presence of iron ions leads to the formation of Fe(III)-carboxylate complexes, which are
755 also subject to rapid destruction in the case of photostimulated processes (Ruiz et al. 2011a). After
756 oxidation products of food azo dyes such as E122 (Carmoisine, CI 14720), E124 (Ponceau 4R, CI
757 16255) and E129 (Allura Red AC, CI 16035), 18 aromatic intermediates were identified by GC-
758 MS and 6 short linear carboxylic acids using ion-exclusion HPLC (Thiam et al. 2015a).

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Table 6. Intermediates of azo dye degradation products identified by various methods.

Azo dye	Intermediates	Structure	Process parameters	Detection method	Ref
Acid Red 88	3-Sulfo-benzoic acid		Photoelectrocatalytic degradation under solar light irradiation, pH – 7, bias potential – 1.6 V, 5 mg/l NaCl	HPLC	(Olya et al. 2013)
	4-Hydroxy-phthalic acid				
	Benzene				
	Naphthalene-1-sulfonic acid				
	Naphthalen-2-ol				
Direct Yellow 12	3-Ethoxy benzoic acid		Photoelectro-Fenton combined with photocatalytic process under UV-light irradiation, initial amount of Fe(III) 0.2 mM, initial dye concentration 50 mg/l, reaction time 70 min and applied current 400 mA	GC-MS	(Khataee and Zarei 2011)
	4-Ethoxy phenol				
	Hydroquinone				
	4-Ethoxy benzenamine				
	Ethanedioic acid				
	Butendioic acid				

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7. Conclusions

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Azo dyes are one of the large classes of water-soluble dyes. Some food azo dyes have shown toxicological and health effects in humans. Therefore, there is a need to develop methods for their removal from aqueous solutions. The studies carried out over the past decades on the photoelectrochemical oxidation of azo dyes have shown the potential applicability of this technology for the treatment of wastewater containing azo dyes. Photoelectrochemical methods include the advantages of both electrochemical and photocatalytic oxidation of azo dyes, showing a syn-

771 ergistic effect. The main advantage of photoelectrocatalysis compared to conventional photocatal-
772 ysis is the suppression of the recombination of e-/h+ pairs due to the applied voltage, which leads
773 to an increase in the concentration of charge carriers. Much attention of researchers is currently
774 focused on the synthesis and use of corrosion-resistant semiconductors with a high efficiency of
775 solar light conversion. In the case of photoelectrochemical oxidation of azo dyes, semiconductor
776 materials are used in the form of electrodes, and in this case there is no need to clean the treated
777 wastewater from particles, as in the case of a photocatalytic process. The use of sunlight makes
778 the use of photoelectrochemical methods for the removal of azo dyes economically feasible. In
779 this aspect, the preparation and study of new semiconductor catalysts that absorb daylight in the
780 entire range of the sunlight spectrum is a direction for future research. The most promising for the
781 removal of azo dyes are photo-electro-Fenton methods using solar light, which can be imple-
782 mented at relatively low energy costs and a high rate of COD and TOC removal. In most cases,
783 during the oxidation of azo dyes, carboxylic acids are formed as end products, followed by their
784 mineralization to inorganic compounds. The combination of photoelectrochemical methods with
785 other methods of azo dye removal, such as adsorption, membrane filtration, and fuel cells, is one
786 of the promising areas of research in the field of azo dye removal. In general, most of the studies
787 devoted to the photoelectrochemical removal of azo dyes from aqueous solutions are at the level
788 of laboratory developments. The schemes of reactors given in the works refer to laboratory proto-
789 types. At present, the question of the influence of the structure of azo dye molecules on the effi-
790 ciency of their oxidation using photoelectrochemical methods (photoelectrocatalysis, photo-elec-
791 tro-Fenton, solar photo-electro-Fenton) remains unexplored. Photoelectrochemical oxidation of
792 azo dyes leads only to discoloration of growth solutions with the formation of various aromatic
793 structures. In this regard, there is a more detailed study of the decrease in the toxicological prop-
794 erties of azo dye solutions after photoelectrochemical treatment. Further research should be aimed
795 at developing industrial technologies for treating real wastewater using photoelectrochemical ox-
796 idation using sunlight as an energy source.

797

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801 **Conflicts of interest/Competing interests**

802 The authors declare they have no financial interests.

803

804 **Ethics approval** (include appropriate approvals or waivers)

805 This study does not require ethics approval

806

807 **Availability of data and material** (data transparency)

808 Availability of data and material is not applicable to this article as no new data were created or
809 analyzed in this study.

810

811 **Authors' contributions**

812 A. Isaev, N. Shabanov: Conceptualization, methodology, validation, formal analysis, writing
813 original draft and review, visualization; M. Rabadanov: validation, writing—review and editing,
814 supervision; Zhu Mingshan: conceptualization, methodology, validation, writing—review and
815 editing, supervision.

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