

Study on decolorization of dyeing wastewater by electrochemical treatment

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Abstract: In view of the decolorization of dyeing wastewater, three different kinds of simulated dyeing wastewater were treated by electrochemical method. The effects of current density, initial pH, electrolyte concentration and initial concentration of dye on the treatment effect were investigated, and the decolorization mechanism and color reversion were studied. The experimental results show that the decolorization rate of the three kinds of dyeing wastewater is more than 90% after 60min treatment. And the decolorization process is mainly chromogenic groups gradually destroyed, the dye molecules are gradually degraded. Moreover, in the natural conditions, aeration conditions, heating conditions, almost no phenomenon of color reversion occurred.

1. Introduction

Printing and dyeing wastewater is produced from the processing of cotton, linen, chemical fiber and its blended products. It mainly includes desulfurization wastewater, boiled wastewater, bleaching wastewater, mercerized wastewater, dyeing wastewater, printing wastewater, finishing process wastewater and alkali reduction wastewater, which has large water consumption, high organic pollutant content, chromaticity, alkalescence, quickly changes in water quality and other characteristics.

Decolorization has always been a difficult problem in dyeing wastewater treatment. Many scholars have studied it by adsorption, oxidation and biochemistry [1]. Natarajan E et al. [2] used red mud to derived biologically synthesized iron nanoparticles (bRMINP) and chemically synthesized iron nanoparticles (cRMINP), both immobilized in barium alginate beads. Under the optimal conditions the RB235 dye removal rate by bRMINP and cRMINP was 98.75% and 88.88%, respectively. Hui H P et al. [3] synthesized diatomite composites with two different morphologies (nanowires and nanosheets) by hydrothermal method. The removal rate of methyl orange was 82.36% and 93.50% respectively after 10 min reaction at pH 3, respectively. And the results show that the composites have the potential to remove anionic dyes in wastewater treatment.

As the preparation of the materials is more complex, so some scholars have studied biosorption. Lu T et al. [4] preparation of self-immobilized mycelium pellets using fungal *Aspergillus niger* ZJUBE-1 in order to improve the effective decolorization of dye-containing water by biosorbents and to understand the mechanism of biosorption, and to select azo dyes congo red of the batch decolorization efficiency. Dye adsorption results showed that in the 6 batches of continuous decolorization operation, the mycelia had an effective decolorizing ability (>98.5%). The UV-Vis spectral indicating that the decolorization process may also include biodegradation. Chaibakhsh N et al. [5] used the natural



coagulant to remove the neutral red dye, and the decolorization rate was 92% at 50min, pH 6.5 and 297.6 mg/L.

The actual dyeing wastewater components are complex, adsorption method is often more difficult to have the ideal decolorization effect, so oxidation, biochemical application is necessary. Cai M Q et al. [6] used the bimetallic oxide CuFeO_2 as the heterogeneous catalyst to enhance the decolorization effect of the Fenton-like reaction on the orange G. And 99.9% of the orange G was removed. The study shows that the use of CuFeO_2 microwave enhanced Fenton-like reaction has the potential application of rapid decolorization of dye effluents. Weng C H et al. [7] studied the decolorization of azo dyes RGY-active orange 107 by oxidizing activated persulfate with Fe^0 aggregation. Ghoreishian S M et al. [8] used $\text{UV}/\text{H}_2\text{O}_2/\text{ZnO}$, $\text{UV}/\text{H}_2\text{O}_2/\text{TiO}_2$ and $\text{UV}/\text{H}_2\text{O}_2/\text{ZnO}:\text{TiO}_2$ to photocatalytic decolorization and mineralization of active black B. Sathian S et al. [9] used SBR to treat dyeing wastewater while performing biodegradation and adsorption.

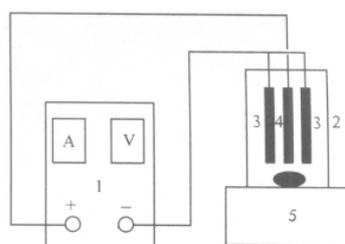
The above studies include physical adsorption, oxidation and biodegradation, in which the loss of the adsorbent used for physical adsorption is unavoidable, and the regeneration of the adsorbent is also very expensive; oxidation requires a large amount of chemicals; biodegradation generally requires a larger space for microbial adaptation Longer period. Moreover, the above research is a simple study of decolorization and removal effect, focusing on material synthesis, bacteria screening, so this paper use electrochemical method to study the decolorization of dye wastewater and its color back phenomenon.

Compared with other methods, electrochemical way has the advantages of no secondary pollution, strong controllability, mild condition, simple equipment and small footprint. Electrochemical method has effects of flocculation, flotation, oxidation and micro-electrolysis, in the wastewater treatment of electric flocculation, electrical floatation and electro-oxidation process is often carried out at the same time. Soluble anode iron or aluminum continuously lost electrons, Fe^{2+} or Al^{3+} into the solution to form $\text{Fe}(\text{OH})_2$ or $\text{Al}(\text{OH})_3$ with higher adsorption flocculation activity, which can effectively remove the dye colloidal particles and impurities. Under the action of current, some of the organic matter in the wastewater may decompose into low molecular organic matter, and may be directly oxidized to CO_2 and H_2O . In recent years, electrochemical research is more extensive in dealing with high concentrations of wastewater such as drug waste water [10-11], food waste water [12-13], phenol wastewater [14-15], heavy metal wastewater [16] and paint wastewater [17]. It is a very promising high concentration of organic wastewater treatment methods.

2. Materials and methods

Reactive red 2(Industrial grade), Acid red 66(Industrial grade), Direct red 80(Industrial grade), Na_2SO_4 (A.R.), 10% NaOH , 5% H_2SO_4 (used to adjust the pH).PHS-3C precision pH meter, DDS-11A digital conductivity meter, MS305D DC power supply, FA2004 type electronic balance, CJJ78-1 magnetic heating stirrer, L5S UV Visible Spectrophotometer.

(1)Preparation of a certain concentration of dye solution, under different conditions of electrochemical reaction;(2)Calculate the decolorization rate, decolorization rate = $(A_0-A)/A_0 \times 100\%$;(3) To explore its reaction mechanism and back color phenomenon.The experimental device is shown in Figure 1.



1.DC power supply 2. Beaker 3. Cathode 4. Anode 5. Magnetic stirrer

Figure 1. Electrochemical treatment diagram

3. Results and discussion

3.1. Effect of pH value

Figure 2 shows the change tendency of decolorization rate of reactive red 2, acid red 66 and direct red 80 with different pH (3,5,7,9,10). It can be seen from the figure that the change in pH has different effects on the decolorization rate of the three dyes: a. When the pH is less than 10, the decolorization rate is almost the same, the decolorization rate is obviously lower than that of other pH conditions at pH 10. The reason may be that the stronger the acidity condition is, the stronger the hydroxyl radical is, the higher the oxygen evolution potential is, and the degradation effect of acidic condition is better than the alkaline; On the other hand, the presence of a large amount of OH⁻ in alkaline conditions favors the formation of hydroxyl radicals, which together contribute to the effect of pH on the decolorization rate [18]. In addition, pH10 becomes a "different point" and may be related to the degradation mode pathway, which is different from the rest of the pH. b&c. The decolorization rate of alkaline condition is higher than the acid neutral condition. It is possible that the organic matter is more likely to oxidize on the surface of the metal anode under alkaline conditions, so that the degradation of the alkaline conditions is better [19].

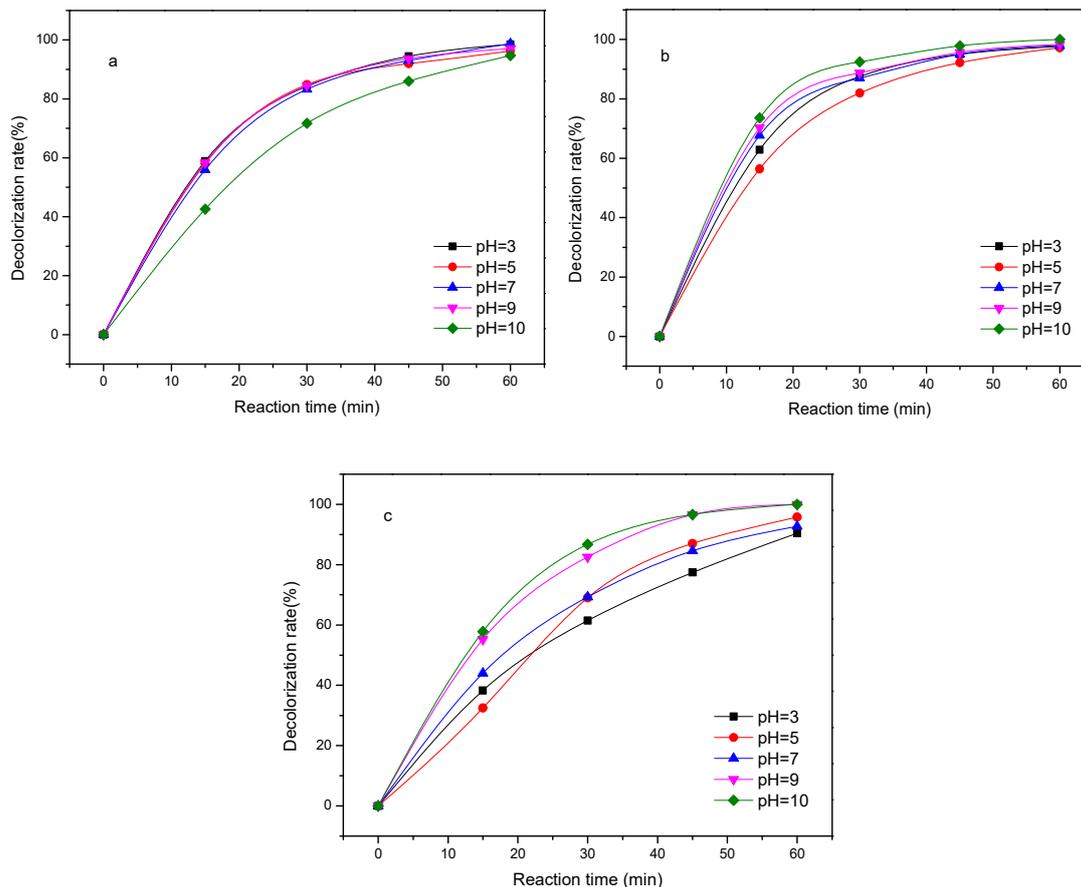


Figure 2. Decolorization rate of three kind of dyes at different pH. a. Reactive red 2, b. Acid red 66, c. Direct red 80 ($c(\text{Na}_2\text{SO}_4)=15\text{g/L}$, $d=0.5\text{cm}$, current density= 10 mA/cm^2)

3.2. Effect of initial concentration

Figure 3 shows the trend of decolorization of the three dyes at different initial concentrations over time. The lower the initial concentration is, the higher the decolorization rate is. This is because, as the amount of dye material increases, the amount of unit electrode treatment increases. However, more

organic molecules cover the anode surface is not conducive to the production of $\cdot\text{OH}$, so the degradation efficiency will be reduced [20].

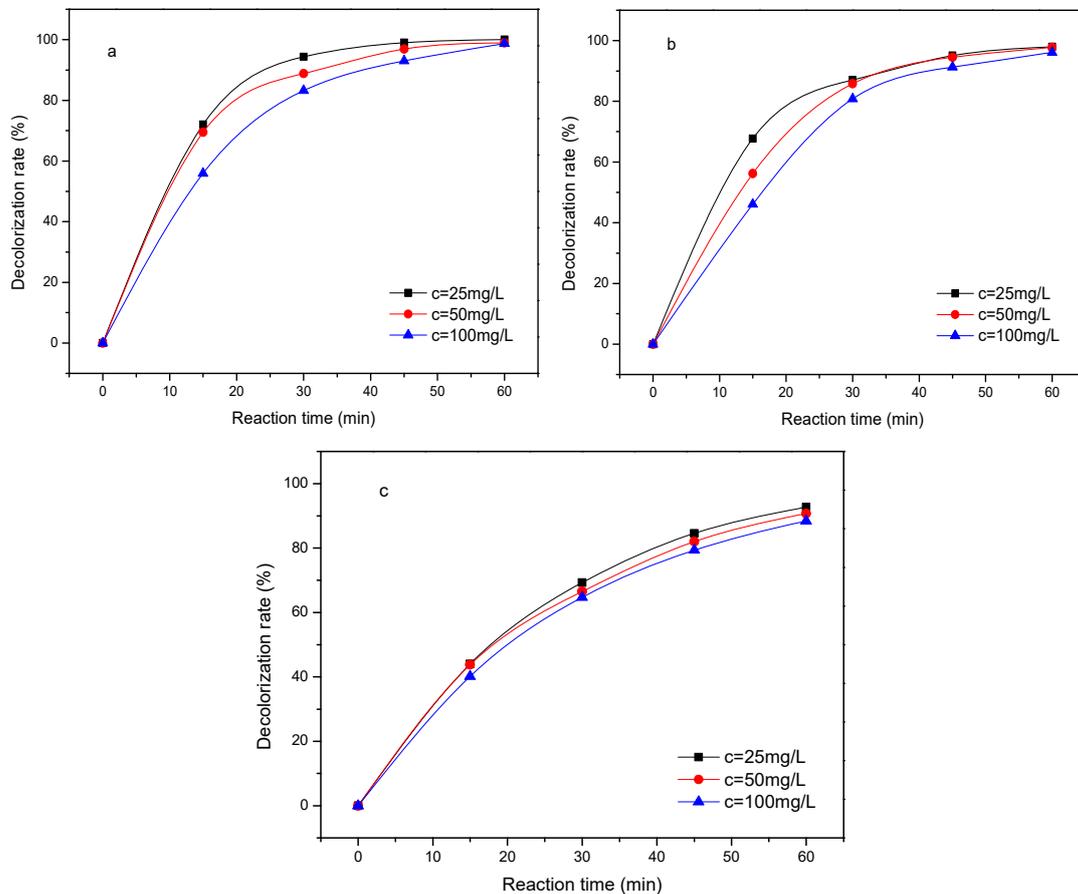


Figure 3. Decolorization rates at different initial concentrations. a. Reactive red 2, b. Acid red 66, c. Direct red 80 (pH=7, $c(\text{Na}_2\text{SO}_4) = 15\text{g/L}$, $d=0.5\text{cm}$, current density= 10 mA/cm^2)

3.3. Effect of electrolyte concentration

Figure 4 shows the trend of decolorization rate over time at different electrolyte concentrations. It can be seen from a and b that as the concentration of the electrolyte increases, the decolorization rate decreases, while c is increased first and then lower. It is consistent with Ding X H's research [21]. Electrochemical oxidation process by adding electrolyte can enhance the treatment effect, but when concentration of Na_2SO_4 is too high, adsorption of SO_4^{2-} on the electrode surface, which hindered the generation of hydroxyl radical and decreased decolorization efficiency.

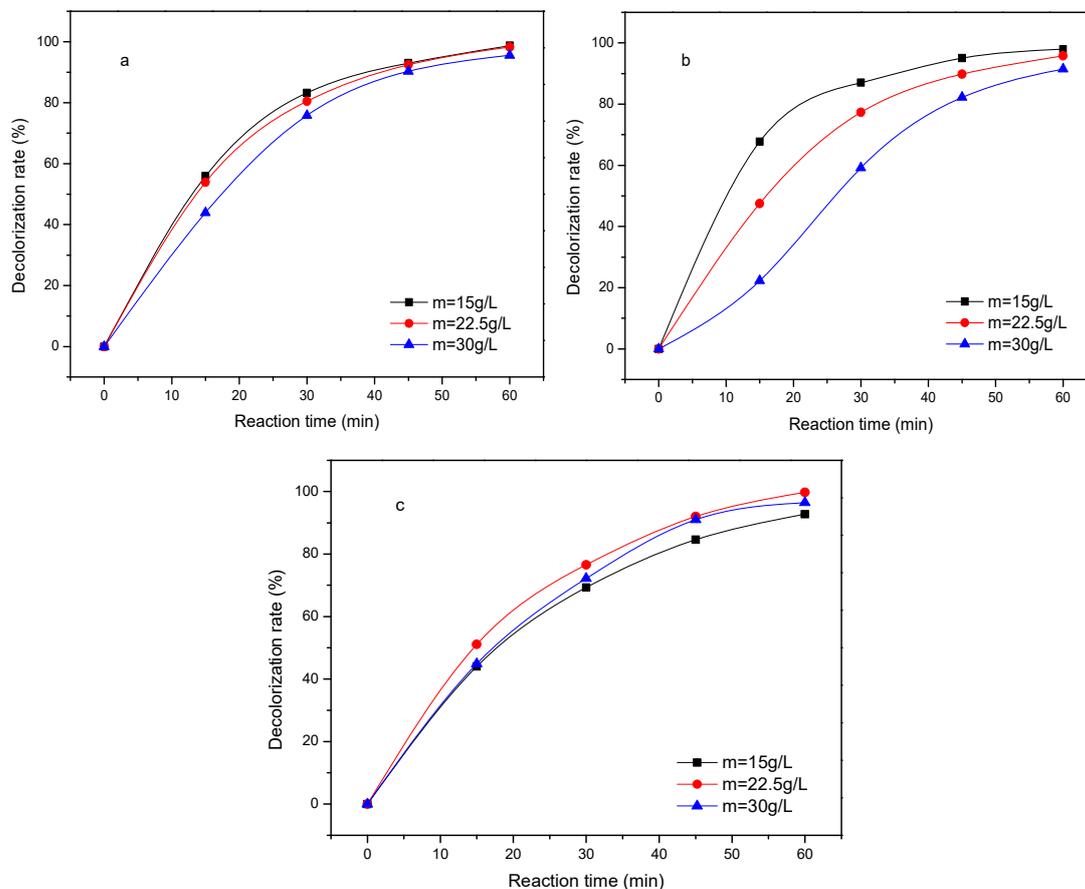


Figure 4. Decolorization rate at different electrolyte concentrations. a. Reactive red 2, b. Acid red 66, c. Direct red 80 (pH=7, d=0.5cm, current density=10 mA/cm²)

3.4. Effect of dyes

As shown in Figure 5, different dye degradation rates are different. And the decolorization rate of the three kinds of dyes can reach more than 90% after electrolysis for 60 min, indicating that the electrochemical method has a significant effect on the degradation of dyes.

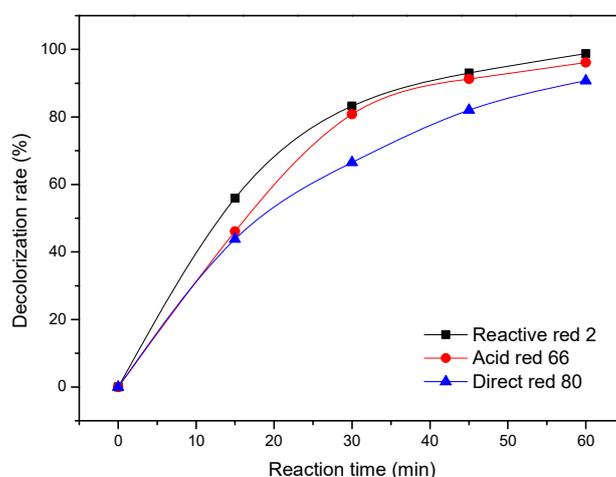


Figure 5. The decolorization rate of different dyes (Initial concentration=100 mg/L, pH=7, c(Na₂SO₄)=15g/L, d=0.5cm, current density=10 mA/cm²)

3.5. Degradation mechanism

Figure 6 is a full-wavelength scan of the three dyes at 0 min, 15 min, 30 min, 45 min, 60 min under optimal reaction conditions. It can be seen that the absorption peak decreases as the reaction time increases. And the absorption peak at 500-600nm is more obvious, namely, the chromophore group is gradually destroyed, the dye molecules are gradually degraded. From figure b, the degradation of the solution during the degradation process at 250nm and 400nm does not coincide with the wavelength sweep of the initial solution, and a new structure may be produced during the degradation process, that is, the degradation of macromolecules into small molecules.

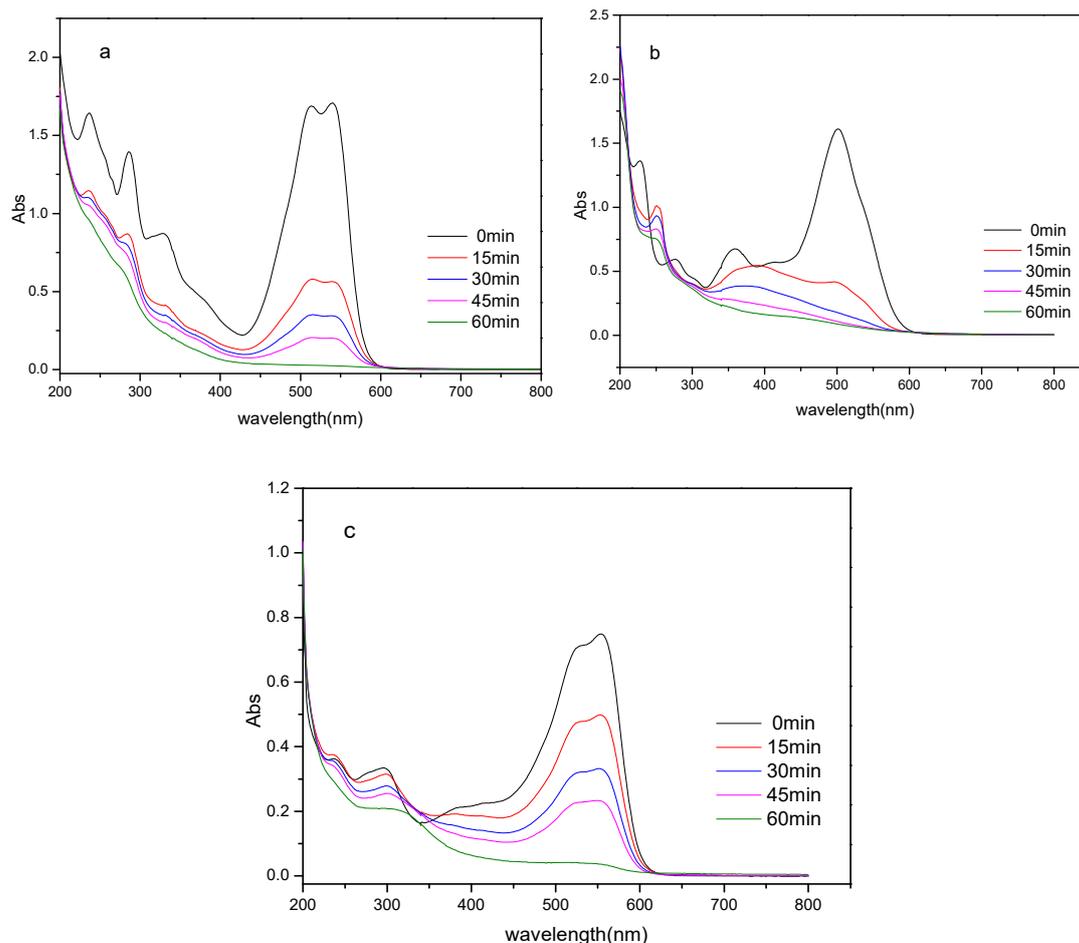


Figure 6. Full-wavelength scanning, a. Reactive red 2, b. Acid red 66, c. Direct red 80 (Initial concentration=100 mg/L, pH=7, $c(\text{Na}_2\text{SO}_4) = 15\text{g/L}$, $d=0.5\text{cm}$, current density=10 mA/cm²)

3.6. Study of color reversion

Dye wastewater in the reuse process may exist in the phenomenon of color reversion in some degree, so the phenomenon of color reversion of electrolytic dye wastewater in the natural conditions, oxygenation aeration conditions and heating conditions was studied. From Figure 7, there is almost no color regaining phenomenon. In the color groups within the band, under the three conditions of wastewater and electrolysis finished wastewater absorption is almost the same. However, there is a little change in the ultraviolet band. It may be a reaction that oxidizes the organic matter which was not fully mineralized.

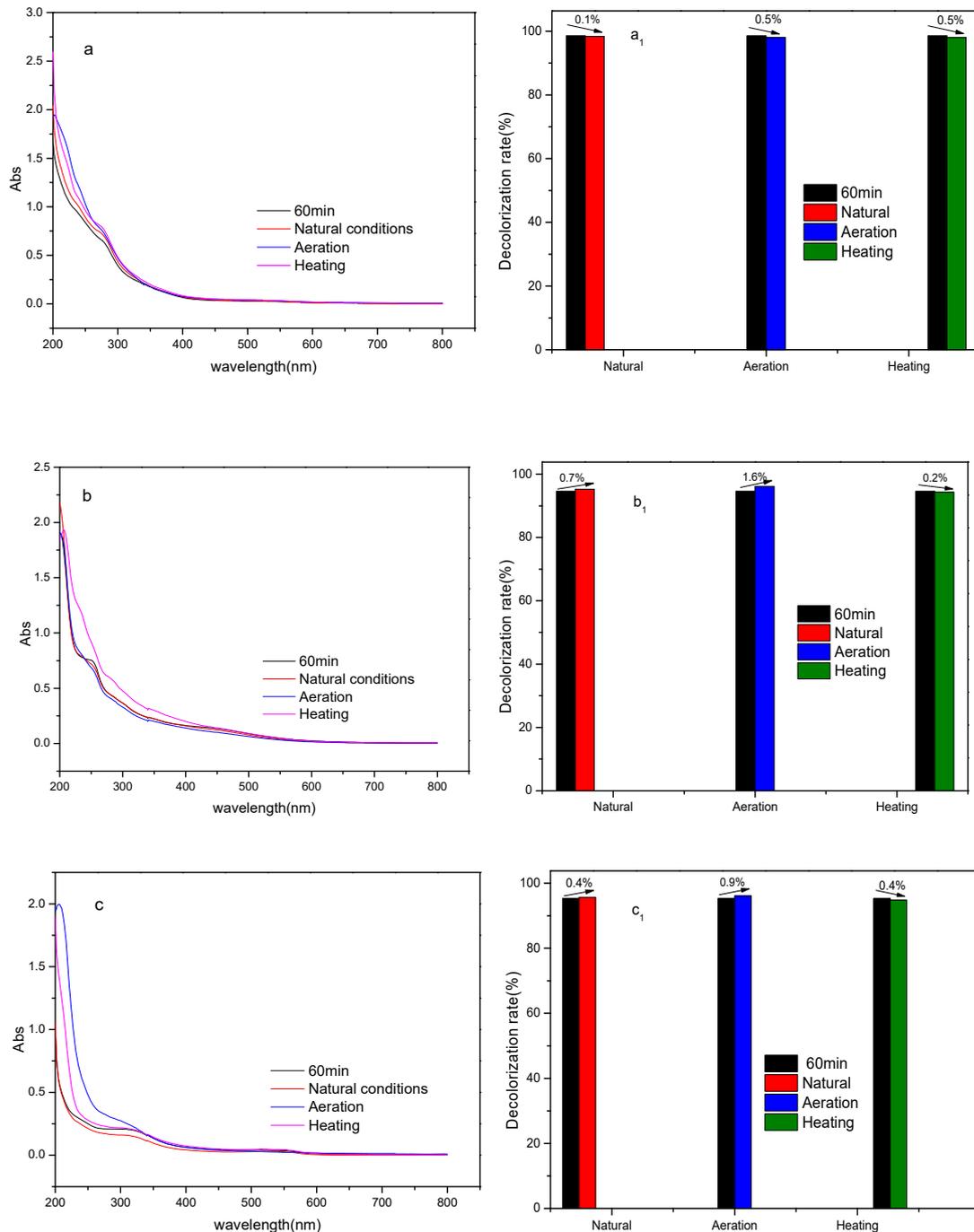


Figure 7. Comparison of electrocatalytic 60 min and natural conditions, oxygenation aeration, heating conditions, full-wavelength scan-a. Reactive red, b. Acid red, c. Direct red; decolorization rate-a₁. Reactive red, b₁. Acid red, c₁. Direct red

4. Conclusion

In this paper, the influence factors of reactive red, acid red and direct red dyestuffs were studied, and the decolorization mechanism and color reversion were discussed. The following conclusions were obtained.

(1) At the same conditions, pH has little effect on the decolorization rate of Reactive Red, except that pH 10 is low; acid red and direct red are alkaline conditions > acidic conditions.

(2) Under the same conditions, the lower the initial concentration of dye wastewater, the higher the decolorization rate; the higher the concentration of the additive electrolyte, the better the effect is, but the effect is reduced after reaching a certain limit.

(3) After the treatment of three kinds of dye wastewater for 60min, the decolorization rate reached more than 90%.

(4) Decolorization process is mainly chromogenic groups gradually destroyed, the dye molecules are gradually degraded.

(5) In the natural conditions, aeration conditions, heating conditions are almost no color back phenomenon.

(6) Electrochemical method has a good effect in the decolorization of dyeing wastewater, and has a certain potential in its reuse process.

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