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Treatment of real printing wastewater with an electrocatalytic process

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ABSTRACT

Many chemicals used in modern printing processes are either toxic or difficult to decompose, which results in the production of complicated and refractory printing wastewater. In this study, an electrocatalytic technology with different catalytic electrodes was employed to treat a real printing wastewater, and the production rates of hydroxyl radicals were determined. The results indicate that under a voltage gradient of 11 V cm^{-1} , the production concentration of hydroxyl radicals by various electrodes followed a decreasing order of $\text{TiO}_2 > \text{DSA}$ (dimensional sustainable anode with IrO_2) $>$ graphite, with the values of 8.21×10^{-3} , 5.24×10^{-3} , and $0.86 \times 10^{-3} \text{ M}$, respectively. A lower wastewater conductivity could lead to a greater electric voltage thus contributing to a higher removal efficiency of TOC and chroma. At a current density of 50 mA cm^{-2} and using one pair of electrodes ($\text{IrO}_2 + \text{stainless steel}$), the TOC and chroma removal efficiencies reached 71% and 53% after 60 min treatment. Under the same operation conditions but using two pairs of electrodes, the removal efficiencies of TOC and chroma were increased to 75% and 82%, respectively. The removal efficiencies of TOC and chroma could be further raised to 90% and 92% if the electrocatalytic effluent was polished by powder activated carbon absorption.

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1. Introduction

The printing process is not only used for the printing of books and newspapers, but also often used for other applications such as clothing, electrical appliances, and circuit boards. After the printing process is completed, the cleaning procedure must be conducted by using various chemicals such as ethers, alcohols, phenols, aldehydes, ketones, benzene, and esters, so that the wastewater often contains a variety of solvents, surfactants, dyes, and other chemicals, thus greatly increasing the difficulty of wastewater treatment. The traditional treatment technologies for printing wastewater include chemical coagulation and bio-degradation. For chemical coagulation, a large amount of sludge will be generated, which leads to not only a lot of follow-up costs, but also secondary pollution if not handled properly. As for the bio-degradation treatment, it will take a longtime because many toxic pollutants present in the wastewater will inhibit the microbial activity. Accordingly, an innovative and efficient treatment technology for printing wastewater is highly expected.

The electrocatalytic technology is promising for biorefractory organics degradation because of the generation of hydroxyl radicals ($\cdot\text{OH}$). The $\cdot\text{OH}$ has a high oxidation potential (2.8 V) [1] with a strong and non-selective oxidation capability, thus it is the crucial substance capable of rapid degradation of organics. The electrocatalytic technology, which combines electric and catalytic processes together, has a high potential for refractory wastewater treatment. The electrocatalytic technology applies an electrical energy higher than the energy gap of a catalytic electrode so that the electrons in the valence band are excited and jumped to the conduction band to form electron-hole pairs. The electrical holes can then generate hydroxyl radicals through reactions with water molecules and hydroxide ions.

Various types of wastewater have been treated by the electrocatalytic process such as dyeing wastewater [2,3], surfactant wastewater [4], and olive oil mill wastewater [5]. According to Panizza and Martinez-Huitle [15], when the boron-doped diamond (BDD) was used as electrode, the generated hydroxyl radicals and activated chloride ions could completely remove the COD, chroma, and ammonia in the landfill wastewater [6]. Ai et al. [17] found that the combination of ultrasonication with electrocatalytic technology could achieve discoloring of an azo dye (Rhodamine B) wastewater within a short time, and also worked for other azo dyes such as methylene blue, reactive brilliant red X-3B, and methyl orange [7]. Radha et al. [5] used NaCl as electrolyte and achieved 96% of chroma removal under a current density of 28 mA cm^{-2} [8].

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Samet et al. [18] used BDD as the anode for chlorpyrifos degradation, and reported that chlorpyrifos could be completely degraded after 6 h of operation [9]. In addition to aforementioned researches, the electrocatalytic technology has also been used for the treatment of other pollutants which are more toxic and difficult to handle [10–13]. In addition to the above broad applications, there are several advantages of the electrocatalytic technology, such as simple equipment, easy operation, high removal efficiency, and little sludge generation [14,15].

Among many kinds of electrocatalytic materials, titanium dioxide (TiO_2) is relatively cheap and popular compared to the BDD. Our research team has applied TiO_2 electrode to treat two types of wastewater. One was methyl orange wastewater, which was treated with a nano- TiO_2 electrode fabricated by chemical vapor deposition, where the chroma and TOC removal efficiencies reached 97% and 56% after 160-min treatment, respectively [13]. The other was municipal wastewater treatment, where the COD removal efficiency could be as high as 90% after 60-min treatment. The wastewater pH was slightly increased and then stabilized, and the DO concentration was greatly enhanced [4]. According to our previous results, TiO_2 was selected as one kind of electrode material in this study. However, during the electrocatalytic treatment process, the anode material may be depleted due to the long-term usage and the complicated properties of wastewater (such as extreme pH and corrosive conditions). Hence, in this study the DSA (containing iridium dioxide, IrO_2) with acid/alkaline resistance, corrosion resistance, and high chemical stability was selected as another catalytic electrode as well [18,19].

This work was to investigate the TOC and chroma removal efficiencies of real printing wastewater treated by various kinds of catalytic electrodes such as TiO_2 , DSA and graphite. In contrast to other researches that used only synthetic wastewater, the experimental results obtained from the real printing wastewater treatment can provide practical information to environmental engineers. In addition, this work also discussed the production rate of hydroxyl radicals on the above different catalytic electrodes, which helped to clarify the degradation mechanism.

2. Materials and methods

2.1. Experimental system for hydroxyl radical test

The experimental system for hydroxyl radical test is shown in Fig. 1, which consisted of a cylindrical reaction tank (15 cm

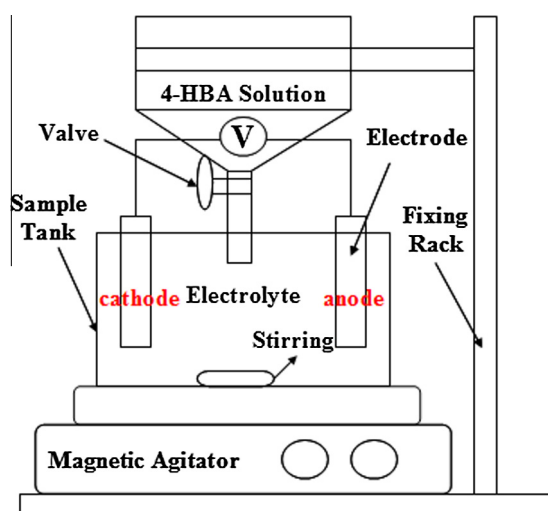


Fig. 1. Experimental system used to generate and capture hydroxyl radicals.

diameter \times 7.5 cm height), an electromagnetic stirrer, a reagent injector, and a commercially available catalytic anode such as TiO_2 , DSA and graphite (5.5 cm length \times 5 cm width \times 0.5 cm height). The cathode for all tests was a graphite plate. The spacing between two electrodes was 7 cm. The electrolysis was conducted based on an external electric field provided by a direct current (DC) power supply. The electrolyte solution was 0.01 M Na_2SO_4 , and the reagent injector filled with 4-hydroxybenzoic acid (4-HBA) solution was installed above the reaction tank. When hydroxyl radicals were generated during the experiment, the scavenger (i.e., 4-HBA) was added by the injector, and the electromagnetic stirrer was turned on to mix the scavenger solution to fully react with the hydroxyl radicals for 1 min to form 3,4-dihydroxybenzoic acid (3,4-DHBA). Then, high performance liquid chromatography (HPLC) was used to measure the concentration of 3,4-DHBA in the water sample, and six replicate analyses were conducted to minimize potential analytical errors.

2.2. Properties of the printing wastewater

Real printing wastewater, collected from a printing factory located in Taichung City of Taiwan, was used for the electrocatalytic oxidation experiments. The wastewater was discharged during the cleaning procedure (to remove ink and surfactants) after the completion of the printing process, which contained a high concentration of organics and chroma. This wastewater was characterized with a high pH (around 13), a high conductivity (60–700 mS cm^{-1}) and a high TOC concentration (28,000–30,000 mg L^{-1}). A TOC analyzer (O.L. Analytical, Auroramodel 1030W) and a spectrophotometer (Yi-Hung Inc., U-2001) were used for TOC and chroma measurements, respectively. In terms of chroma analysis, the wastewater sample was first subjected to full wavelength scanning to obtain the maximum absorption wavelength (i.e., 360 nm), and then the chroma variation was monitored at this wavelength.

2.3. Experimental system for electrocatalytic treatment of wastewater

The experimental system for the electrocatalytic treatment of real printing wastewater is illustrated in Fig. 2, where a cylindrical tank was used as the reactor (17 cm diameter \times 16 cm height). An electromagnetic stirrer was placed beneath the tank to completely mix the reaction solution during operation. Three electrocatalytic

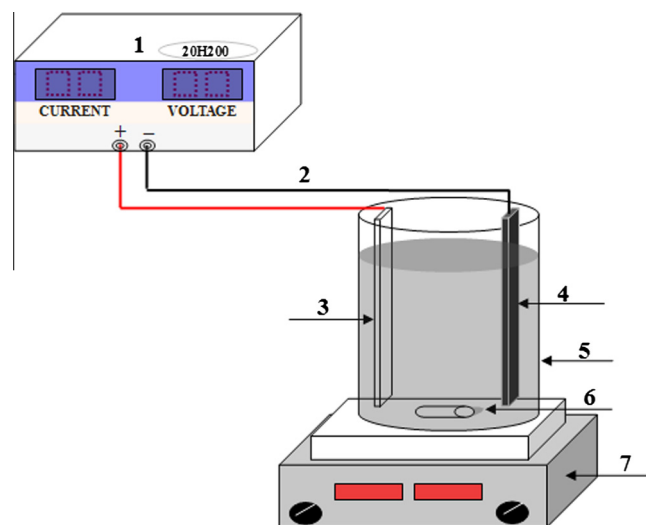


Fig. 2. Experimental system for the electrocatalytic treatment of real printing wastewater (1. DC power supply, 2. copper wire, 3. anode, 4. cathode, 5. electrolysis reactor, 6. magnetic bar, 7. electromagnetic stirrer).

Table 1

The operation conditions for the printing wastewater treatment.

Anode	Iridium dioxide (IrO ₂)
Cathode	Stainless steel
NaCl	0.25 M
Volume	3.0 L
Conductivity	5–20 mS cm ⁻¹ (via dilution)
Current density	10–50 mA cm ⁻²
Catalytic electrodes	1 or 2 pairs
Treatment time	60 min

materials as mentioned above (TiO₂, DSA, and graphite) were served individually as the anode, and the cathode plate was made of stainless steel. Both anode and cathode had a dimension of 12 cm (length) × 9 cm (width) × 0.3 cm (thickness), and a spacing of 7 cm.

Table 1 listed the operation conditions for the printing wastewater treatment. The wastewater volume for each batch experiment was 3.0 L, and the pH was pre-adjusted to 9.0 by HNO₃ solution. The IrO₂ catalytic electrode was used as anode due to its high catalytic ability and corrosion resistance. Our previous study had shown that the addition of 0.25 M NaCl into tea wastewater treated by electrocatalytic technology could increase chroma removal by 25%. As a result, 0.25 M NaCl was also added in this study. Different operating conditions were tested to clarify their impacts on the removal efficiencies of TOC and chroma, including the wastewater conductivity (5–20 mS cm⁻¹), current density (10–50 mA cm⁻²), and number of electrode pairs (1–2 pairs). The operation time of each test lasted for 60 min, and wastewater sample was collected once every 20 min for TOC and chroma measurements. The variation of wastewater pH and conductivity was monitored simultaneously during the electrocatalytic treatment process. Afterwards, the electrocatalytically-treated wastewater was mixed with a certain amount of powder activated carbon for 60 min to further improve the effluent quality.

3. Results and discussion

3.1. Impact of electrode materials on hydroxyl radical production

To examine whether there was any signal overlapping or interference from the electrolyte, a water sample containing the ·OH scavenger (4-HBA), its derivative 3,4-DHBA, and the electrolyte (NaNO₃) was prepared and analyzed by HPLC. As shown in Fig. 3,

the peaks of 4-HBA and 3,4-DHBA emerged at 5.0 and 3.7 min, respectively, indicating neither signal overlapping nor electrolyte interference. As a result, the concentration of 3,4-DHBA in the wastewater sample can correspond to the concentration of hydroxyl radical.

Fig. 4 shows the change of ·OH concentration with reaction time for various electrode materials. After 3 min of electrocatalytic treatment, the TiO₂, DSA, and graphite electrodes produced 8.21×10^{-3} , 5.24×10^{-3} , and 0.86×10^{-3} M hydroxyl radicals (accumulative concentration), respectively. This result demonstrated that the catalytic materials (TiO₂ and DSA) could yield much more ·OH than the non-catalytic material (graphite). This big difference in ·OH production also denoted the organic degradation capability of the electrocatalytic electrodes. It is also noted that the ·OH concentration produced by TiO₂ was greater than that by DSA. This was attributed to their differences in specific surface area, energy gap, and surface hydrophobicity. The ·OH concentration for each electrode was maintained in a certain range after 0.5 min, which implies the rapid balance between the production and consumption of ·OH in the electrocatalytic process.

3.2. Impact of wastewater conductivity on TOC and chroma removal

The raw wastewater had a large conductivity, which induced a low voltage and consequently, a low production rate of hydroxyl radicals. The conductivity of the raw wastewater was serially diluted to 5, 10, 15 and 20 mS cm⁻¹ before the electrocatalytic treatment. Our experiments showed that the wastewater pH increased slightly from 9.00 to 9.29, 9.28, 9.36 and 9.37 at the above four different conductivities after 60-min treatment (current density 10 mA cm⁻², IrO₂ anode, and stainless steel cathode). If a sufficient electric energy is applied, the hydroxyl radicals generated by the catalytic electrode can form hydroxide ions, which will result in a high pH [17]. The wastewater conductivity remained stable throughout the electrolytic treatment.

The variation of TOC removal efficiency with reaction time at different conductivities was shown in Fig. 5(A). The results indicate that at a fixed current density of 10 mA cm⁻², the TOC removal efficiency first increased with operating time before 40 min, and maintained almost stable afterwards. At the end of treatment (60 min), the TOC removal efficiencies were 16%, 10%, 7%, and 6% at 5, 10, 15, and 20 mS cm⁻¹, respectively. It is noted that the lowest conductivity (5 mS cm⁻¹) led to the highest voltage under a fixed current density, which was favorable for organic pollutants

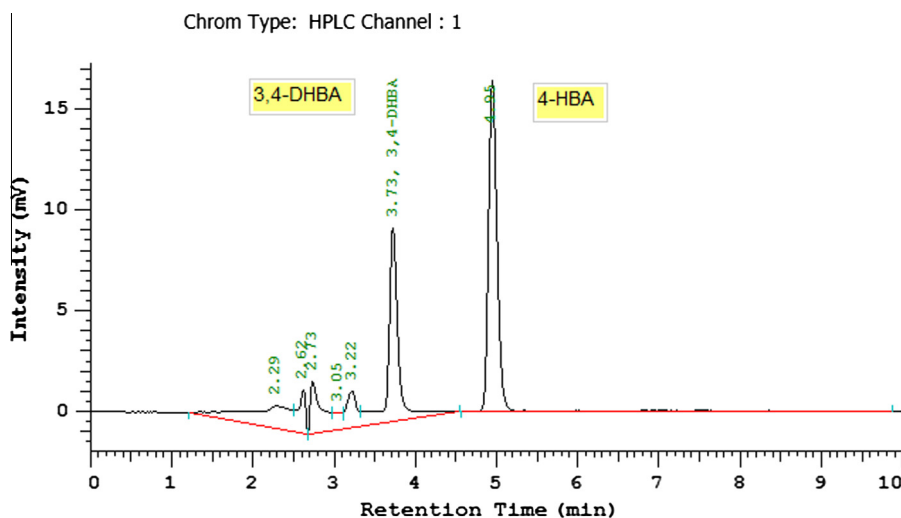


Fig. 3. HPLC spectrum of 4-HBA and 3,4-DHBA.

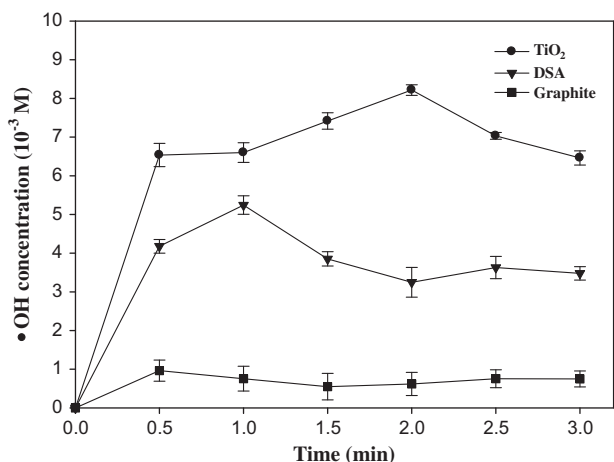


Fig. 4. The change of $\cdot\text{OH}$ concentration with reaction time for various electrode materials (0.01 M NaNO_3 , 11 V cm^{-1} , Cathode: graphite).

degradation by hydroxyl radicals produced on the catalytic electrode. Besides hydroxyl radicals, other strong oxidants, such as OCl^- and HOCl , could be produced as well when NaCl was added as an additional electrolyte [20,21], which further enhanced the decomposition of organic pollutants. The wastewater conductivity played a key role in treating printing wastewater since a high conductivity resulted in an insufficient production of these oxidants.

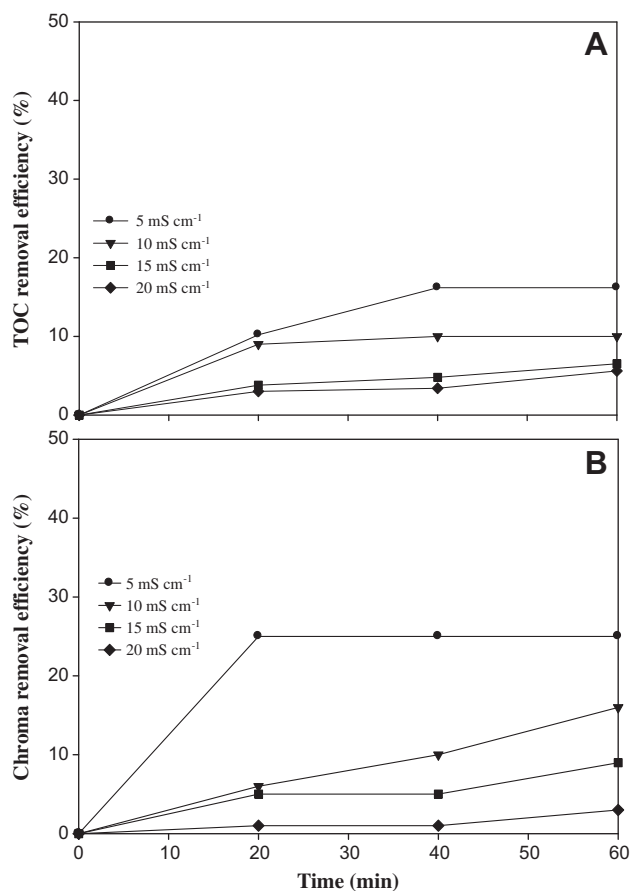


Fig. 5. The TOC(A) and chroma(B) removal efficiency with reaction time at different dilution ratios of conductivity. (Current density: 10 mA cm^{-2} , Anode: IrO_2 , Cathode: Stainless steel.)

The variation of chroma removal efficiency with reaction time at different conductivities was shown in Fig. 5(B). At the end of treatment (60 min), the chroma removal efficiencies at conductivities of 5 , 10 , 15 and 20 mS cm^{-1} were 25% , 15% , 9% and 3% , respectively. Similar to the variation of TOC removal efficiency, a lower wastewater conductivity led to a higher chroma removal efficiency because more hydroxyl radicals were produced.

3.3. Impact of current density on TOC and chroma removal

Fig. 6(A) shows the variation of TOC removal efficiency at different current densities applied. The TOC removal efficiencies were 25% , 25% , 31% , 42% and 53% at current densities of 10 , 20 , 30 , 40 , and 50 mA cm^{-2} , respectively. The mechanisms for organic pollutants decomposition by electrocatalytic system could be divided into the direct oxidation by the anode and the indirect oxidation by secondary oxidants. If a small current density was applied, neither direct oxidation by the anode nor indirect oxidation by the hydroxyl radicals would be important. As a result, the TOC removal efficiency increased with an increasing current density in the applied range from 10 to 50 mA cm^{-2} . The maximum TOC removal efficiency of 53% was achieved at the highest current density of 50 mA cm^{-2} . A similar trend was also found by other researchers [16,21]. This result implies that a high current density can not only promote the direct anodic oxidation of pollutants but also enhance the production of hydroxyl radicals, OCl^- and HOCl .

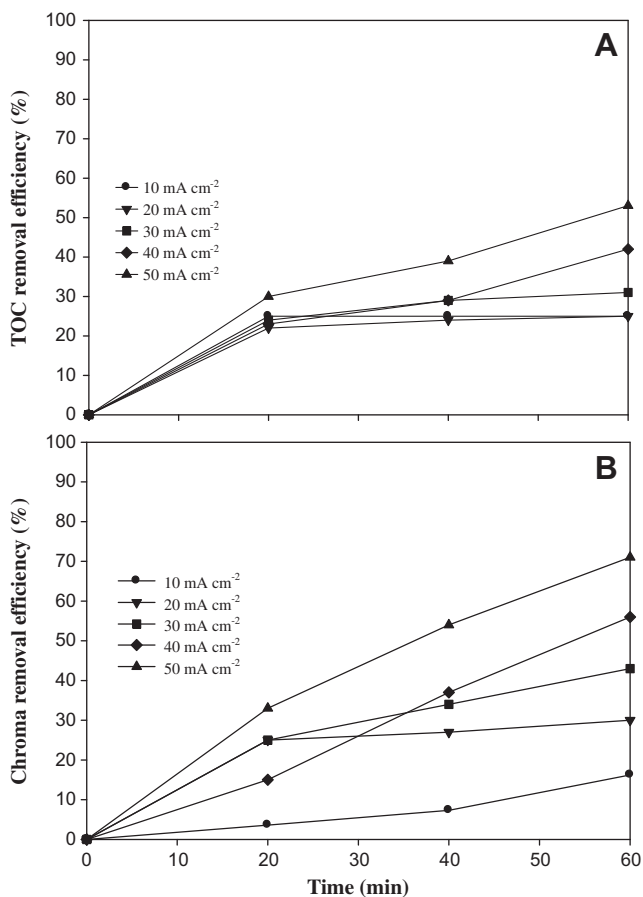


Fig. 6. The TOC(A) and chroma(B) removal efficiency with reaction time at different current densities applied. (Electrolyte: 5 mS cm^{-1} , Anode: IrO_2 , Cathode: Stainless steel.)



Fig. 7. The change of wastewater color with treatment time of 0, 6, 20, 40, and 60 min (from left to right).

Fig. 6(B) shows the variation of chroma removal efficiency with reaction time at different current densities. The chroma removal efficiencies were 16%, 30%, 43%, 56% and 71% at current densities of 10, 20, 30, 40 and 50 mA cm⁻², respectively. Compared to TOC (Fig. 6(A)), the chroma removal efficiency was more significant. This result implied that the characteristics of wastewater such as the ink and other organic matters might be decomposed to some smaller organic compounds without color, which resulted in the high decolorization but low TOC removal. It was observed that the color of the printing wastewater became nearly invisible at the current density of 50 mA cm⁻² (Fig. 7).

3.4. Influence of the number of electrode pairs and powder activated carbon

Fig. 8 shows the TOC and chroma removal efficiencies of the printing wastewater treated by two pairs of electrodes and followed by powder activated carbon adsorption (100 g/L). The removal efficiencies of TOC and chroma were 75% and 82%, respectively, with two pairs of electrodes used. Two pairs of electrodes increased the contact interface between pollutants and electrodes as compared to one pair of electrodes, where the removal efficiencies of TOC and color were 53% and 71%, respectively. Moreover, the TOC and color removal efficiencies could reach up to 90% and 92% if activated carbon adsorption was used to polish the electrolytic effluent.

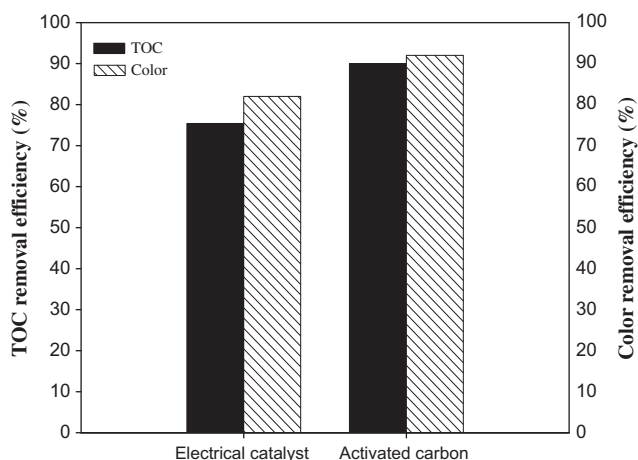


Fig. 8. The removal efficiencies of TOC and color with two pairs of electrodes and activated carbon sorption.

4. Conclusions

Based on the above experimental results, the following conclusions can be drawn:

1. The electrocatalytic process could generate hydroxyl radicals steadily, and the ·OH production rates of various electrodes followed a decreasing order of TiO₂ > DSA > graphite.
2. Under a fixed current density, a lower wastewater conductivity resulted in a high electric voltage, which subsequently enhanced the removal of TOC and chroma.
3. The electrocatalytic process could effectively remove the TOC and chroma of the real printing wastewater. At a current density of 50 mA cm⁻² and with one pair of electrodes (IrO₂ + stainless steel), the TOC and chroma removal efficiencies reached 71.0% and 53.0%, respectively, after 60 min treatment.
4. Under the same operation conditions but using two pairs of electrodes, the removal efficiencies of TOC and chroma were enhanced to 75.0% and 82.0%, respectively. The removal of TOC and chroma could be further improved to 90.0% and 92% if the electrolytic effluent was polished by powder activated carbon adsorption.

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