Electrochemical degradation of Amaranth aqueous solution on ACF

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Abstract

The degradation of Amaranth, a kind of azo dye, has been studied under galvanostatic model with activated carbon fiber (ACF) electrode in aqueous solution with electrochemical method. The ACF was used as anode and cathode, respectively for the decolorization process. The onset oxidation potential and reduction potential for Amaranth on ACF were respectively ascertained at 0.6 and -0.4 V. During the range of -1.1 to 0.50 mA cm^{-2}, the decolorization was clarified into three processes as electroreduction, adsorption and electrooxidation. There were little contributions to the color and COD removals for the process of adsorption. The color removal can be up to 99% when the current density was 0.50 mA cm^{-2}. The maximum COD removal was 52% for the process of electrooxidation. Hundred percent color removal was obtained when the current density of -1.0 mA cm^{-2} was applied. The maximum COD removal was 62% for the electroreduction. The COD removal results from the adsorption of products for the decolorization process of electrooxidation or electroreduction.
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1. Introduction

The treatment of wastewater has long been a concern of the textile industry. Textile dyeing and finishing wastewater is known to contain strong color and difficult to be biodegradable [1]. The removal of dyes is really a challenge to both the textile industry and the wastewater treatment facilities.

Electrochemical technique would be an option to treat dyeing wastewater since it is friendly to the environment without secondary pollution. Naumczyk et al. [2] investigated the process of electrochemical treatment of wastewater containing dyes in the presence of high concentration of chlorides. It was proved that Ti/RuO$_2$, Ti/Pt, Ti/Pt/Ir electrodes were very effective in direct or indirect oxidation of textile wastewater. Yang et al. [3] investigated the hypochlorite generation on Ru–Pt for dye wastewater treatment. Scott [4] suggested that in the presence of chloride oxidation of azo dyes happened mainly through the formation of 'active' chlorine. Chen et al. [5] studied the mineralization of orange II and 16 reactive dyes with Ti/boron-doped diamond (BDD) and found that the electrode was much more active than Ti/Sb$_2$O$_5$–SnO$_2$. Cerón-Rivera et al. [6] tested four different electrode materials, BDD, aluminium, copper and iron–zinc alloy electrodes, by applying different potentials with basic yellow 28 and reactive black 5 being the model dyes. Dávila-Jiménez et al. [7] used Pt, Ti and BDD respectively as working electrodes for dyeing water treatment and found that electrochemical treatment using a BDD electrode is an effective method for the study of decomposition of textile dyes of different nature. Shen et al. [8] used Pt/C gas diffusion electrode(GDE) as cathode and graphite electrode as anode to treat Acid Red B. Fe(II) was added into the solution for the process of electro/Fenton. It was found that the model dye was oxidized into small organic acids in both anode and cathode regions. Twenty intermediates formed during the degradation with the detection of GC-MS and IR spectrum.

To improve the treatment efficiency of electrochemical system, the selection of electrode material is one of the key factors. Traditional plate electrode cannot meet the need of the development of electrochemical technology. Activated carbon fiber (ACF), which has large surface area, is attractive to achieve

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high electrochemical efficiency. ACF is a comparatively modern form of porous carbon material with a number of significant advantages over the more traditional powder or granular forms. Moreover, the functional groups on the surface of ACF also have strong reactivities [9]. Jia et al. [10] and Shen et al. [11] studied the decolorization of more than 25 dyes including azo and anthraquinone dyes. They used ACF and Fe as anode and ACF as cathode. Almost all dye solutions tested were decolorized effectively in the electrochemical system. In their study, however, only one compartment cell was used. That is to say, it is difficult to make sure which electrode is responsible in the reaction. Hence no specific conclusion was obtained for the treatment on ACF or Fe. On the other hand, DC power source was used to provide cell voltage for the electrolysis. The effect of potential and current density, the key parameters for electrochemical process, were not considered. Besides, Fe^{2+} can be produced when a proper voltage was applied, leading to possible electrocoagulation in the decolorization, TOC and COD removal [12]. Lin et al. [13] have confirmed that using cast iron as cathode and anode can treat textile wastewater successfully. ACF is considered to be a promising, three-dimensional electrode material. Hence it is necessary to pinpoint the pure effect of ACF from a well-defined experimental process.

The objective of the research was to evaluate the electrochemical decolorization processes on pure ACF. Galvanostatic model was applied to evaluate the effect of current density on dyeing solution decolorization process. Amaranth azo dye was chosen as the model organic compound. The decolorization kinetics of Amaranth azo dye was investigated on ACF. The onset oxidation potential and onset reduction potential of the dye on ACF were obtained by following the decolorization and changes of potential with different current densities under galvanostatic model. COD removal was also investigated.

2. Materials and methods

2.1. Experimental facility

The experimental set-up employed in this study was a three-electrode cell as shown in Fig. 1.The working electrode was
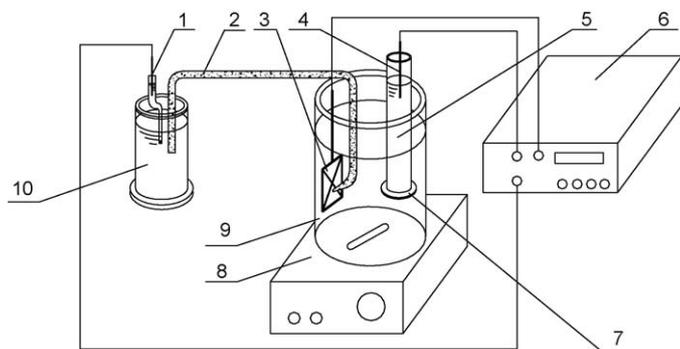

Fig. 1. Experimental set-up for electrochemical decolorization of Amaranth. (1) Reference electrode, (2) salt bridge, (3) working electrode (ACF), (4) counter electrode (Pt wire), (5) counter electrode compartment, (6) galvanostat/potentiostat, (7) cation selective membrane, (8) magnetic stirrer, (9) working electrode compartment, and (10) reference electrode compartment.
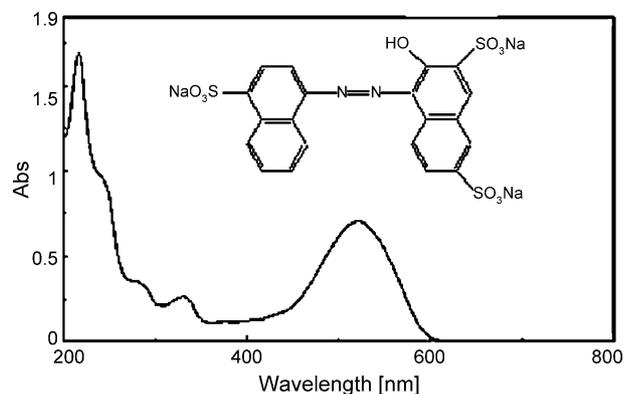

Fig. 2. UV–vis spectrum of initial Amaranth solution and molecular structure of Amaranth (the initial dye solution was diluted three times. Scan rate: 400 nm min^{-1}).

a weighed piece of ACF held by a short Pt wire. The counter electrode was a Pt wire. A saturated calomel electrode (SCE) was used as the reference electrode. The cell was divided into two compartments with a cation selective membrane. The solution was stirred by a magnetic bar. A potentiostat/galvanostat (Shanghai REX Instrument Factory, China) was used in controlling the current density. The UV–vis spectra before and after treatment for the dyeing water were analyzed with an UV–vis spectrophotometer (Jasco V-560, MHT-344, Japan). COD value of all samples was determined according to standard method for the examination of water and wastewater [14].

2.2. Reagents and supplies

The Amaranth was used as model compound whose structure and spectrum are shown in Fig. 2. This azo dye was purchased from Huizhou Fond Food Additives Co. Ltd., Guangdong, China and used as received. All other chemicals used were of analytical grade. $0.1 \, mol \, L^{-1} Na_2SO_4$ was used as the supporting electrolyte. HPO_4^{2-} ($3.533 \, g \, L^{-1}$) and $H_2PO_4^{-}$ ($3.388 \, g \, L^{-1}$) were used as buffer solution of pH about 7. As can be seen from Fig. 2, the maximum absorption for the dye in the visible region was at 521 nm and there is also characteristic absorption peaks at the wavelength of 280 and 330 nm in the ultraviolet region.

The ACF used in this study was provided by Anshan Activated Carbon Fiber Company, Liaoning, China, with a specific area of about $1180 \, m^2 \, g^{-1}$. Pt wire ($\geq 99.95\%$ in purity) was provided by Shanghai Chemical Reagent Company, China National Pharmaceutical Group. The ACF was first washed with double boiled deionized water. Then it was dried under vacuum at 120 °C for 2 h and cooled in a desiccator for the usages. The ACF was cut in desired dimensions, weighed accurately and attached to the Pt wire before dipping into the reaction cell.

2.3. Experimental

The initial concentration of dye solution was $80 \, mg \, L^{-1}$. The processes of electrochemical polarization were examined at positive and negative polarization, respectively. The ranges were from -1.1 to $0 \, mA \, cm^{-2}$ and from 0 to $0.50 \, mA \, cm^{-2}$ including

open circuit condition. Each test lasted 8 h with 0.5 mL sample taken out every 1 h for absorbency values analysis. The COD and UV–vis spectra were analyzed for the solution at the end of each batch of test. Temperature was maintained at 20 °C and the solution was stirred with the same speed of 240 rpm.

The color, COD removal ratios were calculated as

$$R = \frac{X - Y}{X} \times 100\% \tag{1}$$

where, X is the initial absorbency value at the wavelength of 521 nm or initial COD of the dye solution, Y is the absorbency value at the wavelength of 521 nm after treatment or final COD of the dye solution, respectively.

The ratio of normalized absorbency values were calculated as

$$Z\left(\frac{521}{X}\right) = \frac{A'_{521}/A_{521}}{A'_x/A_x} \tag{2}$$

where, $Z(521/x)$ is the ratio of normalized absorbency values, x is 280 or 330 nm

A_{521}, A_x is the initial absorbency value of the dye solution; A'_{521}, A'_x the absorbency value of the dye solution after treatment.

3. Results and discussion

The polarization curves of Amaranth and blank solution at quasi-steady-state on Pt wire and ACF held by Pt wire were shown in Figs. 3 and 4. For the positive polarization (Fig. 3), it can be seen that the Pt wire in the blank or dye solution does not show any difference. So Pt wire has little effect on the reaction in the positive potential range and only provide even potential for the ACF. It is interesting to note that in blank solution the current on ACF started to increase since 0.6 V and almost kept at the platform of 1.7 V. When dye is used, the increase of current started almost at the same potential and an anodic peak at about 1.0 V can be seen clearly with the current of 4.5 mA. Oxygen evolution is responsible for the steep rise in
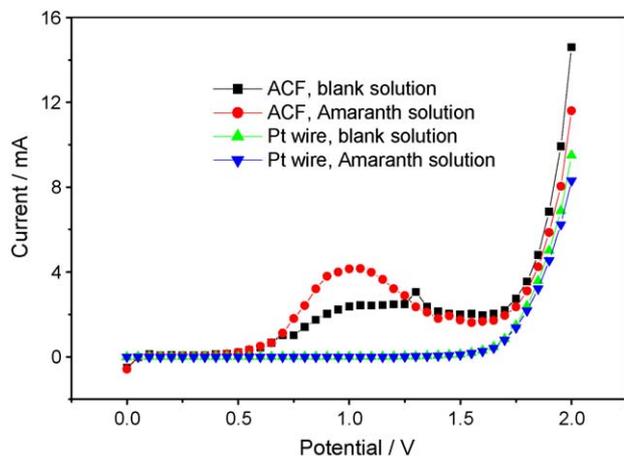

Fig. 3. Quasi-steady-state positive polarization curves for Amaranth on Pt and ACF electrodes.
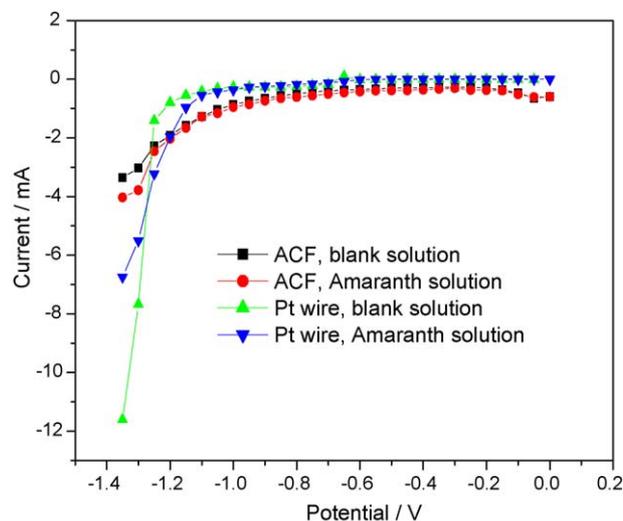

Fig. 4. Quasi-steady-state negative polarization curves for Armaranth on Pt and ACF electrodes.

current at about 1.5 V. In the region of 0.6–1.4 V, some surface changes maybe took place to make electrochemical degradation as seen in the subsequent section. By analyzing this curve, the dye was probably oxidized since 0.6 V on ACF. For the negative polarization (Fig. 4), there is not any peak detected and almost no difference for ACF in blank or dye solution. Maybe the cathodic process is too slow to be inspected so that no characterized peaks are obtained. What is the potential for the dye on ACF at which electochemical reaction could be triggered? That will be discussed with bulk electrolysis in the following part.

The process of dye decolorization with different galvanostatic current densities was clarified based on the final ration of normalized absorbency values. If the ratio of normalized absorbency values were equal to 1.0, then the dye structure was taken as intact. Otherwise, the dye structure was destroyed through electrochemical reaction [15]. From Table 1 shown in the supplemental part, a conclusion could be made that no chemical reaction took place in the range of −0.18 to 0.063 mA cm^{-2}, since the ratio was equal to 1. The small decolorization noted in this region results from adsorption [16,17]. Electrooxidation leads to the decolorization as seen in the range of 0.13–0.50 mA cm^{-2}. Similarly, electroreduction in the region of −1.1 to −0.84 mA cm^{-2} can also achieve decolorization.

Some UV–vis spectra of different current densities were shown in Figs. 5 and 6. From Fig. 5 it can be seen that at current density of −0.81 mA cm^{-2}, there is only a little decrease in the absorbency values during the whole scan range. However, when the current density was over −0.84 mA cm^{-2}, the absorption peaks at 521 and 280 nm were decreased sharply. The shoulder peak at 330 nm was shifted to around 320 nm with a low absorption value. However the absorbency value of shoulder at 250 nm increased. Yasuki et al. [18] reported similar result with a Pt-modified palladized Pd sheet electrode. From Fig. 6, it can be seen that at 0.063 mA cm^{-2}, the absorption values in the whole region decreased insignificantly. Starting from 0.13 mA cm^{-2}, the shape of the spectra changed gradually until their disap-
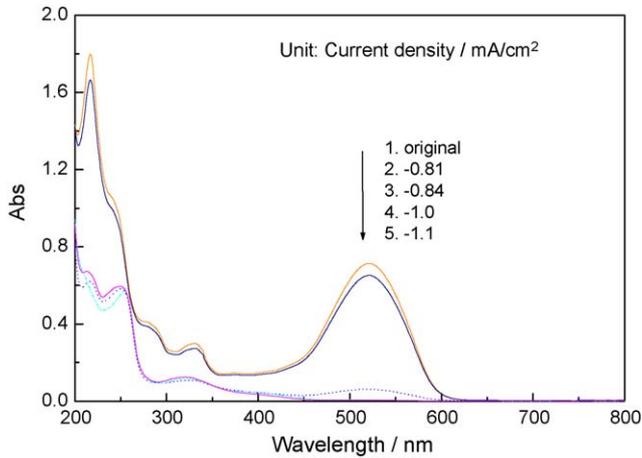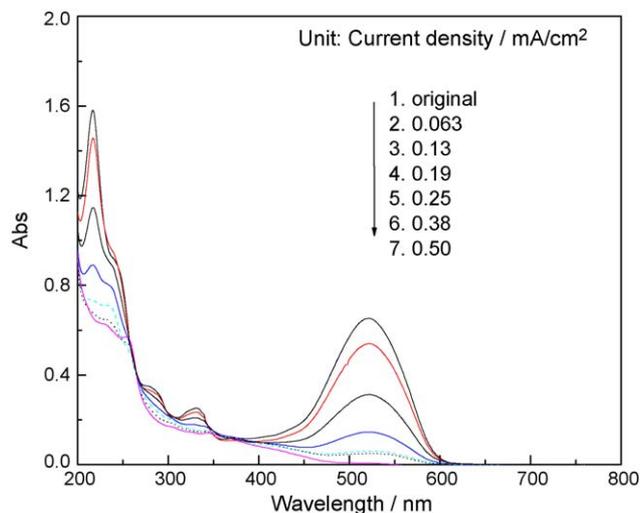
Fig. 5. UV–vis spectra of Amaranth solution at different negative current densities.

Fig. 7. Dependence of potential on the adsorption time with different current densities.

pearance ($0.38 \, \text{mA cm}^{-2}$) whereas the absorption region below 250 nm increased as a defined peak and an absorption shoulder.

Thus the decolorization processes can be divided into three parts: adsorption (-0.81 to $0.063 \, \text{mA cm}^{-2}$), electroreduction ($-1.1$ to $-0.84 \, \text{mA cm}^{-2}$) and electrooxidation ($0.13$ to $0.50 \, \text{mA cm}^{-2}$).

3.1. Process of adsorption

In order to estimate the contribution of pure adsorption, open circuit experiment was investigated first. It was found that the color removal was only 5.7% at an initial concentration of $80 \, \text{mg L}^{-1}$ for the open circuit. The color removal ratio fluctuates around 5% and is below 15% if the current density is in the range of -0.81 to $0.063 \, \text{mA cm}^{-2}$. Thus adsorption made little effect on the decolorization of the dye. This may result from the microporous structure [19] of the ACF, which is smaller than the size of the dye molecule.

It is interesting to find that when the current density was over $0.13 \, \text{mA cm}^{-2}$, the potential was about 0.6 V. However when

the current density was up to $-0.81 \, \text{mA cm}^{-2}$, the potential was still lower than $-0.2 \, \text{V}$ (Fig. 7). That is to say the negative polarization has much more capacity. It may result from the higher quasi-capacity because of different functional groups on ACF.

3.2. Process of electrooxidation

Fig. 8 shows the result of color removals increase with current densities in the range of electrooxidation. When the current density was $0.13 \, \text{mA cm}^{-2}$, the color removal at the eighth hour was about 25%, almost five times of that under $0.063 \, \text{mA cm}^{-2}$. When the current density was $0.50 \, \text{mA cm}^{-2}$, the color removal reached 99% at the eighth hour.

The relationship between the color removal and the potential was shown in Fig. 9. There is also an inflexion at 0.6 V and the increase of color removal was mainly from 0.6 to 0.9 V. It is supposed to be similar to the process of electroreduction discussed previously. ACF is a kind of material with high capacitance. In the early period for the polarization, the potential increased

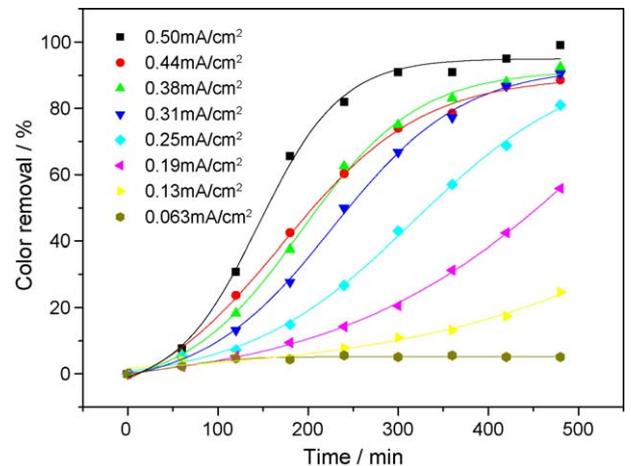Fig. 6. UV–vis spectra of Amaranth solution at different positive current densities.

Fig. 8. Dependence of color removal on the time of electrooxidation with different current densities.
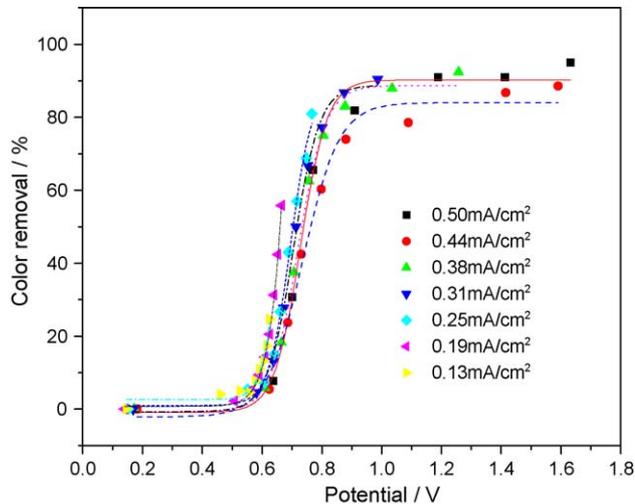
Fig. 9. Plot to the color removal and potential for the process with positive current densities.

Fig. 11. Dependence of color removal on the time of electroreduction with different current densities.

gradually. Once the potential was up to 0.6 V, the dye structure was destroyed and the color decreased rapidly. Fig. 10 shows the trends of normalized absorbency value with the potential detected under different current densities. Also in the range of 0.6–0.9 V, the ratio of normalized absorbency value changed greatly, which double confirms the cleavage of the azo bond.

3.3. Process of electroreduction

Fig. 11 shows the result of color removal at different current densities in the range of electroreduction. The color removal increased with the increase of current density (more negative) The color removal was about 100% at the current density of $-1.0\,\mathrm{mA\,cm^{-2}}$ after 7 h experiment. When the current density was $-1.1\,\mathrm{mA\,cm^{-2}}$, the color removal was up to 100% at the fifth hour with the potential at -0.82 V. There is an inflexion at almost the same potential with different current densities, Fig. 12. It may associate with the over-potential of the ACF electrode. Only when it is up to the over-potential, electroreduction took place with much more decolorization. As can be seen
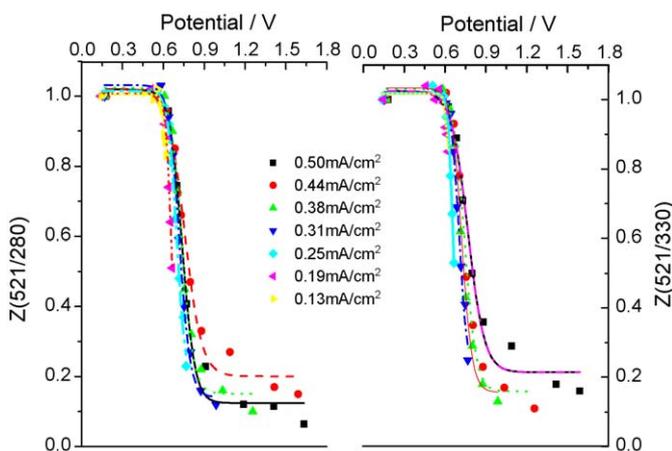
from Fig. 12 in the range of -0.4 to -0.8 V the color removal increased considerably, suggesting the reaction rate in the range be much fast comparing with other potentials. Fig. 13 showed the relationship of the potentials detected and the ratio of normalized absorbency values at different current densities. From it we can see that before the potential was up to -0.4 V, the ratios were almost not changed. However when the potential was over -0.4 V, the ratios decreased rapidly with the potential and changed to be a constant which is nearly zero when the potential was -0.8 V. These results were consistent with those obtained in Fig. 12. The adsorption is probably the dominating stage before the potential was up to -0.4 V. More negative potential triggers the electroreduction.

It is well known that electroreduction cannot remove COD. However the removals of COD in the process of electroreduction were even much more than that in the process of electrooxidation. In order to make sure more how the electroreduction works, a set-up avoiding O_2 entering was designed. The experiment

Fig. 10. Relationship between the ratio of normalized absorbency values and potentials with positive current densities.

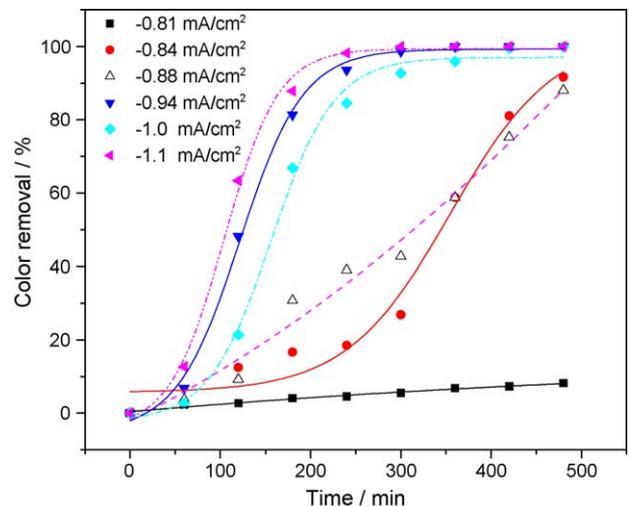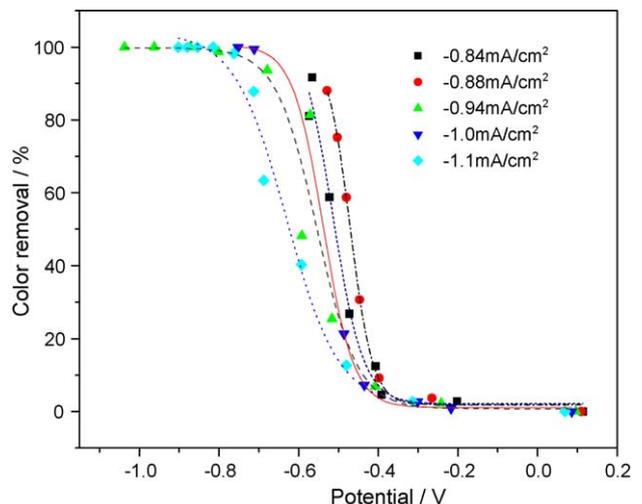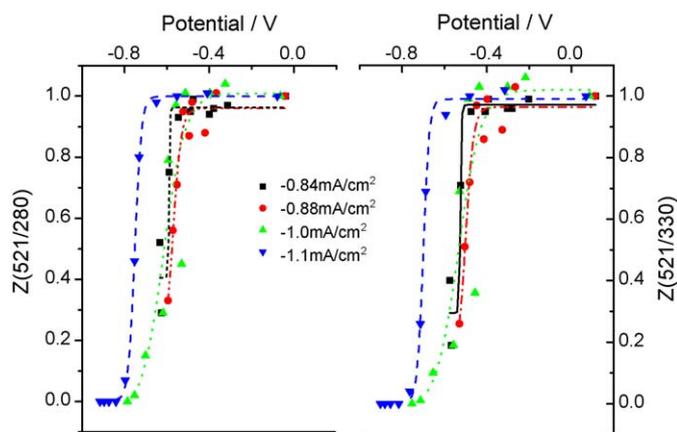Fig. 12. Plot to the color removal and potential for the process with negative current densities.

Fig. 13. Relationship between the ratio of normalized absorbency values and potentials with negative current densities.

Fig. 15. Changes of COD removals with current densities.

of electroreduction of Amaranth aqueous solution on ACF was made with N_2 during the reaction. It is known that -0.5 and -0.6 V are the preferred potential for H_2O_2 to be produced. So the two potentials were tested with N_2. In this condition, there is no O_2 exited and H_2O_2 could not be produced. The result of color removal and COD removal was shown in Fig. 14 and supplemental Table 2. From it we can see that the results for the COD removal with or without N_2 were almost the same. So the decolorization did not result from the H_2O_2 production on ACF. A conclusion could be made that the removals of color and COD resulted from the electroreduction of Amaranth and the absorption of the products on the ACF. Besides, surface polymerization of dye molecules might help to remove color and COD.

3.4. COD removal

The COD removal at different current densities are shown in Fig. 15. Within the range of current density for adsorption, there is little fluctuation comparing with that under open-circuit about 10% removal ratio, therefore, pure adsorption made almost no contribution to the COD removal.
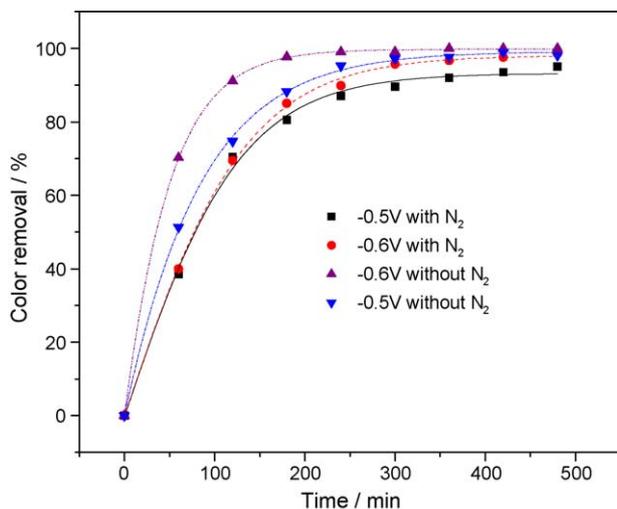

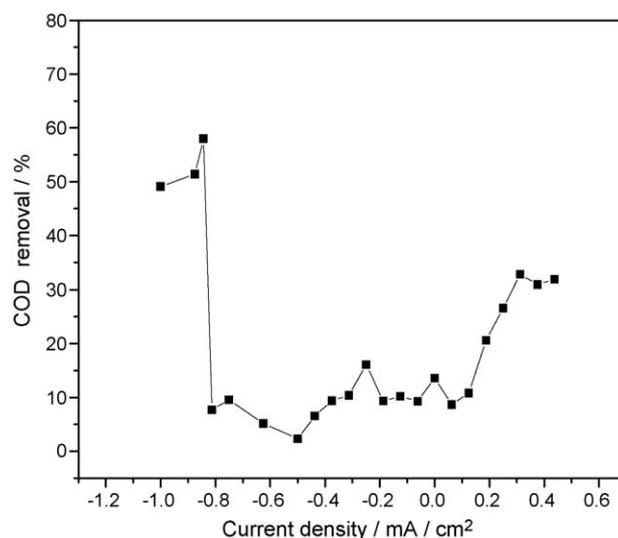Fig. 14. Comparison of color removal at different potentials with and without N_2.

Within the region of electroreduction, COD removal was 48% when the current density was -0.84 mA cm^{-2}, which is around five times than that under open circuit. If the current density was increased to -1.0 mA cm^{-2}, the COD removal was increased to 62%. Further increase in current density does not bring any increase in the COD removal. We supposed that the removal of COD resulted from the adsorption of the products of Amaranth on ACF. Yasuki et al. [18] had tested the products of electroreduction of Amaranth on Pd/Pd black/Pt electrode. Two kinds of naphthylamines were produced, which were much smaller than the dye molecule and easy to be adsorbed. So the COD decreased during the process of electroreduction.

Within the range of electrooxidation, the maximum COD removal was obtained at the current density of 0.38 mA cm^{-2} with 52%. Further increase in the current density leads to insignificant increase in the COD removal. It was suggested that the removal of COD resulted from the carbonization of the dye or the adsorption of the products with much smaller size comparing with the initial dye. Karkmaz et al. [20] reported that Amaranth can be degraded to N_2, CO_2 and SO_4^{2-} with complete photocatalytic oxidation.

Analyzing the COD removal in the whole range, it can be found that, the process of electroreduction was superior to the process of electrooxidation. In fact, the color removal was also much better in the process of electroreduction in comparison with the process of electrooxidation.

4. Conclusions

The electrochemical decolorization behavior was successfully clarified with the galvanostatic model for the dye solution on ACF. Three different decolorization processes exist: adsorption, electroreduction and electrooxidation. Adsorption makes little contribution to the color and COD removals. Both electroreduction and electrooxidation can decolorize the dye and remove COD. The onset oxidation potential and onset reduction potential are respectively ascertained at 0.6 V and -0.4 V.

The process of electroreduction out performs the process of electrooxidation in color and COD removals though its specific energy consumption was much higher. The color removal may be up to 99.1% at the eighth hour when the current density was $0.50\,\mathrm{mA\,cm^{-2}}$. The maximum COD removal is 52% for the electrooxidation. On the other hand, 100% color removal ratio may be obtained when the current density of $-1.0\,\mathrm{mA\,cm^{-2}}$ was applied. The maximum COD removal is 61% for the electroreduction.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2006.04.008.

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