

ЭФФЕКТИВНОСТЬ ДЕСТРУКЦИИ КРАСИТЕЛЯ КИСЛОТНОГО ОРАНЖЕВОГО 52 ЭЛЕКТРОКАТАЛИТИЧЕСКИМ МЕТОДОМ

Хуэй Чжао, Хэн Чжун, Лэй Сунь, Донченг Ся, А.В. Невский

Хуэй Чжао, Хэн Чжун, Лэй Сунь, Александр Владимирович Невский*

Кафедра общей химической технологии, Ивановский государственный химико-технологический университет, Шереметевский проспект, 7, Иваново, Российская Федерация, 153000
Факультет Инженерной экологии, Уханьский текстильный университет, ул. ФангЖи, 1, Ухань, Китайская Народная Республика, 430200
E-mail: 771361793@qq.com, zhong359324658@163.com, stylelife@live.com, nevsky@isuct.ru*

Донченг Ся

Факультет Инженерной экологии, Уханьский текстильный университет, ул. ФангЖи, 1, Ухань, Китайская Народная Республика, 430200
E-mail: xds01@163.com

Изучен процесс деструкции красителя кислотного оранжевого 52 в водных растворах электрокаталитическим методом. Кислотный оранжевый 52 был выбран из-за того, что он является типичным представителем семейства азокрасителей и одним из часто используемых кислотных красителей в текстильной промышленности. В электрокаталитическом реакторе в качестве анода использовали титановые пластины с нанесенным слоем катализатора, а пластины из нержавеющей стали работали как катоды. Слои катализатора наносили на титановые пластины электрохимическим методом с последующим прокаливанием. Изучено влияние начальной концентрации красителя ($C_{\text{крас.}}$), природы катализатора на аноде, начального напряжения (U_n), времени электролиза (t), начального значения pH_n раствора и концентрации $NaCl$ на скорость процесса деструкции кислотного оранжевого 52 при протекании электрокаталитического процесса. Установлено, что оптимальными условиями электрокаталитической обработки, в частности, являются: $C_{\text{крас.}} = 100$ мг/л, $U_n = 20$ В, $pH_n = 6$, $t = 50$ мин. Экспериментальные данные свидетельствуют о том, что при обработке в оптимальных условиях модельных сточных вод, содержащих кислотный оранжевый 52, эффективность обработки составляла, соответственно: 95% в видимой области спектра (464 нм) и 38,6% в ультрафиолетовой области (270 нм). Степень снижения величин химического потребления кислорода (ХПК) и общего органического углерода (ООУ) составила 23,5% и 47,7% соответственно. Обнаружено, что электрокаталитический процесс может обеспечить высокую степень обесцвечивания кислотного оранжевого 52. Однако, невысокие значения снижения величины ХПК свидетельствуют о том, что в процессе обработки, вероятно, не происходило существенного разрушения больших фрагментов структуры красителя, таких как бензольное кольцо.

Ключевые слова: электрокаталитическое окисление, краситель кислотный оранжевый 52, деструкция красителя

ACID ORANGE 52 DYE DEGRADATION EFFICIENCY BY ELECTROCATALYTIC METHOD

Hui Zhao, Heng Zhong, Lei Sun, Dongsheng Xia, A.V. Nevsky

Hui Zhao, Heng Zhong, Lei Sun, Alexander V. Nevsky*

General Chemical Engineering Department, Ivanovo State University of Chemistry and Technology, Sheremetevskiy ave., 7, Ivanovo, 153000, Russia
School of Environmental Engineering, Wuhan Textile University, 1 FangZhi Road, Wuhan, P. R. China, 430200
E-mail: 771361793@qq.com, zhong359324658@163.com, stylelife@live.com, nevsky@isuct.ru*

Dongsheng Xia

School of Environmental Engineering, Wuhan Textile University, 1 FangZhi Road, Wuhan, 430200,
P. R. China

E-mail: xds01@163.com

The degradation process of Acid Orange 52 dye in aqueous solutions by electrocatalytic technique has been studied. Acid Orange 52 was chosen as a representative compound of azo dyes and one of the often used acid dyes in the textile industry. In the electrocatalytic reactor, the titanium plates with catalyst layer were used as anode, and the stainless steel plates worked as cathodes. The layers of catalyst were coated on titanium plates by electrochemical method followed by calcination. The effect of dye initial concentration (C_{dye}), catalyst nature on anode, initial voltage (U_{in}), electrolysis time (t), initial solution pH_{in} and NaCl concentration on the rate of Acid Orange 52 degradation process was studied in the electrocatalytic process. It was determined that the optimal conditions of electrocatalytic treatment, in particular are: $C_{dye}=100$ mg/l, $U_{in}=20$ V, $pH_{in} = 6$, $t = 50$ min. The experimental results show that when Acid Orange 52 simulated dye wastewater was treated under the optimal conditions, the treatment effect was 95 % in visible part of light spectrum (464 nm) and 38.6 % in ultraviolet part (270nm), respectively. The removal rate of chemical oxygen demand (COD) and total organic carbon (TOC) were 23.5 % and 47.7 %, respectively. It was found that electrocatalytic process can provide an effective decolorization rate of Acid Orange 52. However, not high values of COD removal rate most likely witness that there was no significant destruction of large fragments of the dye structure, such as the benzene ring.

Key words: electrocatalytic oxidation, Acid Orange 52 dye, dye degradation

Для цитирования:

Хуэй Чжао, Хэн Чжун, Лэй Сунь, Донченг Ся, Невский А.В. Эффективность деструкции красителя кислотного оранжевого 52 электрокаталитическим методом. *Изв. вузов. Химия и хим. технология.* 2018. Т. 61. Вып. 3. С. 64–69

For citation:

Hui Zhao, Heng Zhong, Lei Sun, Dongsheng Xia, Nevsky A.V. Acid Orange 52 dye degradation efficiency by electrocatalytic method. *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.* 2018. V. 61. N 3. P. 64–69

INTRODUCTION

The dye wastewater which is characterized by large amounts of discharge, high concentration, complicated composition and high chroma is a kind of industrial wastewater which is difficult to be treated [1-2]. It accounts for about 10% of the total amount of industrial waste water. Azo dyes are the most variety and the largest number of synthetic organic dyes [3]. The vast majority of azo dyes are coupled from aromatic amines after diazotization and phenols, aromatic amines which have active methylene compounds. Azo dyes wastewater direct discharge has great harm to environment and organism [4-6].

Advanced oxidation processes (AOPs) are one of the most effective methods to degrade organic contaminants. Among AOPs, electrochemical oxidation method has good application prospects. Electrochemical oxidation method requiring a little or even no chemical reagent is a clean and effective wastewater treatment method [7]. There are two processes to destroy the pollutants in the electrochemical process, direct or indirect oxidation process. In direct anodic ox-

idation process, the pollutants are adsorbed on the anode surface at first and then destroyed by the anodic electron transfer reaction. In indirect oxidation process, strong oxidants such as hypochlorite/chlorine, ozone, hydrogen peroxide are electrochemically generated. The pollutants are then destroyed in the bulk solution by oxidation reaction of the generated oxidant. All the oxidants are generated in situ and are utilized immediately [8-10].

As a representative compound of Azo dyes and one of the often used acid dyes in the textile industry, Acid Orange 52 was selected for this study. The objective was to investigate the enhancement of the degradation efficiency of Acid Orange 52 in the electrocatalytic technique. And this study was specifically focused at: the effect of catalyst on anode, initial voltage, electrolysis time, initial solution pH and salt concentration on the rate of Acid Orange 52.

EXPERIMENTAL

Materials

Acid Orange 52 ($C_{14}H_{14}N_3SO_3Na$) was purchased from Sinopharm Chemical Reagent Co., Ltd.

Fig. 1 shows that there are two characteristic absorption wavelengths, 270 nm and 464 nm, respectively. The 270 nm is the absorption peak of benzene ring, and the 464 nm is the absorption peak of the conjugated system of the two benzene rings and $-N=N-$.

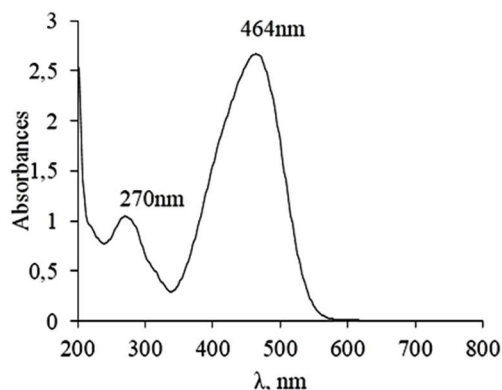


Fig. 1. Characteristic absorption wavelengths
Рис. 1. Характерные длины волн поглощения

All chemicals were of analytical grade if not noticed otherwise and were obtained from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as received without further purification. The sample solutions were prepared using deionized water (Aqua-pro, USA) throughout the experiments.

Anodic titanium plate was purchased from Baoji Honghang Titanium Industry Co., Ltd. The total titanium content of titanium plate is more than 99.8%.

Electrolytic cell

In the electrocatalytic tank, the titanium plates was anode plate, and the stainless steel plates was cathode plate. A layer of catalyst A was coated on titanium plates by electrochemical method and calcination method. Fig. 2 shows the scheme of experimental facility for electrocatalytic degradation study.

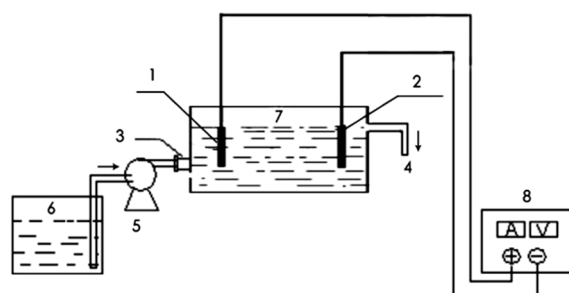


Fig. 2. The experimental setup for electrocatalytic degradation study: 1 - titanium anode; 2 - stainless steel cathode; 3 - input of dye's wastewater; 4 - output of solution; 5 - peristaltic pump; 6 - initial dye's wastewater solution tank; 7 - electrocatalytic reactor; 8 - DC power source

Рис. 2. Экспериментальная установка для исследования электрокаталитической деградации: 1 - титановый анод; 2 - катод из нержавеющей стали; 3 - вход сточных вод красителя; 4 - выход раствора; 5 - перистальтический насос; 6 - резервуар для исходного раствора сточных вод красителя; 7 - электрокаталитический реактор; 8 - источник питания постоянного тока

Electro-catalytic degradation procedures

The experimental setup employed in this study is shown in Fig. 2. The simulated dye wastewater was filled into the electrolytic cell and then began to be treated. The initial COD of the simulated dye wastewater was about 59 mg/L. During the treatment, the above Acid Orange 52 simulated dye wastewater was continuously fed into the electrolytic cell by means of a BT100-1L model peristaltic pump (Nanji Bo-Xin Biological Technology Co., Ltd.) with a constant flow velocity. The electrolysis was carried out under a constant current supplied by a DC power source (KXN-6020D, Shenzhen trillion source Electronic Technology Co., Ltd.). The treated solution was collected from the exit 4 (Fig. 2).

In electrolysis experiments, the effects of initial voltage (U , V), electrolysis time (T , min), pH, and salt concentration on the degradation efficiency were investigated.

Analysis

UV-VIS absorption spectra

To monitor the degradation process of Acid Orange 52, solution samples were taken out at predetermined time intervals and measured immediately on a UV-1201 spectrophotometer (Beijing Rayleigh Analytical Instrument Co., Ltd.) under the characteristic absorption wavelength (270 nm, 464 nm) to record the temporal UV-VIS spectral variations of the dye. The related reaction progress was monitored using the UV-VIS absorption spectra of Acid Orange 52, which was calculated from the following equation (percentage of decolorization):

$$A\% = (A_0 - A_t)/A_0 \cdot 100\% \quad (1)$$

Where A_t is the absorbance at 270 nm and 464 nm for Acid Orange 52 at reaction time t and A_0 is the related initial absorbance.

COD/TOC

To monitor the properties of biodegradable of Acid Orange 52, solution samples were taken out at predetermined time intervals and measured immediately using the relevant standard methods of People's Republic of China (COD:HJ/T399-2007; TOC:HJ/T104-2003) on the COD digestion instrument (Lovibond ET125SC, Qingdao Xu-Yu Environmental Technology Co. Ltd.) and the Total organic carbon (TOC) analyzer (Multi N/C 2100, Germany Jena Analytical Instrument Co., Ltd.). The related removal efficiency was calculated from the following equation:

$$\text{COD}\% = (\text{COD}_0 - \text{COD}_t)/\text{COD}_0 \cdot 100\% \quad (2)$$

$$\text{TOC}\% = (\text{TOC}_0 - \text{TOC}_t)/\text{TOC}_0 \cdot 100\% \quad (3)$$

Where COD_t and TOC_t are the monitoring data under different reaction conditions for Acid Orange 52, COD_0 and TOC_0 are the related initial data.

RESULTS AND DISCUSSION

Degradation efficiency of Acid Orange 52 under different systems

In this experiment, the effect of the catalyst A which was coated on the titanium plate on the degradation of the dye was investigated. The anode of a set of experimental electrolytic tank is titanium plates, and the cathode is stainless steel plates; the anode of the other set of experimental electrolytic cell is titanium plates coated with the catalyst A, and the cathode is stainless steel plates.

Experimental conditions: $C_{\text{dye}} = 100 \text{ mg/L}$, $U_{\text{in}} = 20 \text{ V}$, $\text{pH}_{\text{in}} = 6$, $t = 50 \text{ min}$. The results are shown in Fig. 3.

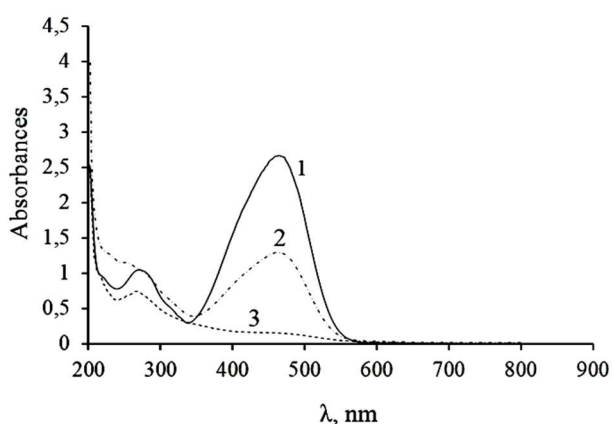


Fig. 3. Effect of catalyst A coated on titanium plate on the dye's degradation efficiency: 1 - simulated dye's wastewater which is untreated; 2 - titanium plate without catalyst A; 3 - titanium plate coated with the catalyst A

Рис. 3. Влияние катализатора А, нанесенного на титановую пластину, на эффективность деструкции красителя: 1 - не обработанная модельная сточная вода, содержащая краситель; 2 - титановая пластина без катализатора А; 3 - титановая пластина, покрытая катализатором А

Because the catalyst A was coated on the anode titanium plate, and then calcined, the degradation effect of the Acid Orange 52 was improved. The removal efficiency of visible light (464 nm) was increased from 51.4% to 95%, while the ultraviolet part (270 nm) increased from 0.0% to 38.6%. The addition of catalyst A to the reaction system enhances the oxidation performance of the system, which is beneficial to improve the decolorization rate of the visible part of the dye. The catalyst A was coated on the anode titanium plate in the following experiments.

Effect of electrolysis time

Experimental conditions were $C_{\text{dye}} = 100 \text{ mg/L}$, $\text{pH}_{\text{in}} = 6$. The results are shown in Fig. 4.

Fig. 4 shows that the longer the reaction time, the higher the degradation rate between 10 and 60 min. When the reaction time was 60 min, the visible light

(464 nm) is 95.1%, and the ultraviolet part (270 nm) is 39.8%. Compared with the reaction time 50 min, the removal efficiency of visible light was increased by 0.1%, and the ultraviolet part was improved by 1.2%. So, the reaction time in the following experiments is 50 min.

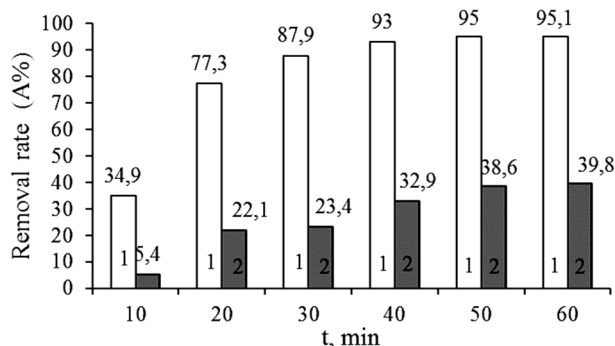


Fig. 4. Effect of electrolysis time: 1 - 464 nm, 2 - 270 nm
Рис. 4. Влияние времени электролиза: 1 - 464 нм, 2 - 270 нм

Effect of initial voltage of DC power source

Experimental conditions were $C_{\text{dye}} = 100 \text{ mg/L}$, $\text{pH}_{\text{in}} = 6$, $t = 50 \text{ min}$. The results are shown in Fig. 5.

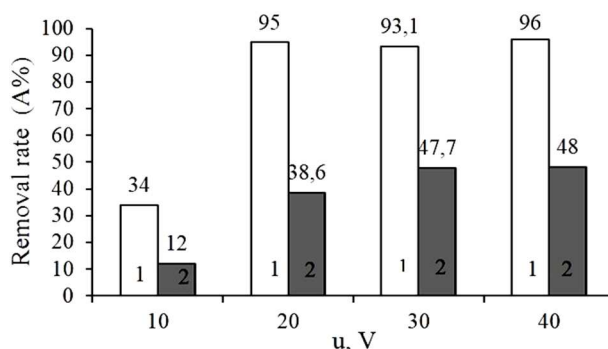


Fig. 5. Effect of initial voltage of DC power source: 1 - 464 nm, 2 - 270 nm

Рис. 5. Влияние начального напряжения источника питания постоянного тока: 1 - 464 нм, 2 - 270 нм

Fig. 5 shows that the higher the voltage, the higher the degradation rate between 10 V and 40 V. When the initial voltage was 40 V, the visible light (464 nm) is 96%, and the ultraviolet part (270 nm) is 48%. Compared with the initial voltage of 20 V, the removal efficiency of visible light was increased by 1%, and the ultraviolet part was improved by 9.4%. However, the increase of the initial voltage means that the energy consumption increases during the operation. Based on cost considerations, the initial voltage selection in the following experiments is 20 V.

Effect of initial pH of Acid Orange 52 solution

The effects of initial pH value ($\text{pH}=4$, $\text{pH}=6$ and $\text{pH}=8$) on the degradation of dyes were investigated in the study. Results are shown in Fig. 6. Experimental conditions were $C_{\text{dye}} = 100 \text{ mg/L}$, $U_{\text{in}} = 20 \text{ V}$, $t = 50 \text{ min}$.

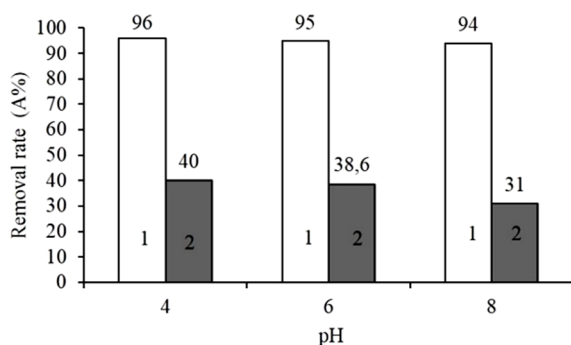


Fig. 6. Effect of initial pH of Acid Orange 52 solution:
1 – 464 nm, 2 – 270 nm; 1 – 464 nm, 2 – 270 nm

Рис. 6. Влияние начальной величины pH раствора кислотного оранжевого 52: 1 – 464 нм, 2 – 270 нм

Fig. 6 shows that in the different acid-base condition, the removal effect of Acid Orange 52 in the visible light is about 95%. And in the ultraviolet part, Acid Orange 52 has better removal effect in the acid condition, 40%. Compared with pH6 of simulated wastewater, the removal efficiency of ultraviolet part was improved by 1.4%. And in alkaline conditions, the removal rate decreased significantly.

The change of pH value can change the nature of Acid Orange 52, affect the electrode reaction and the surface characteristics of the catalyst which was coated on the anode titanium plate. Under the acidic condition, the anode showed strong oxidation.

Effect of NaCl concentration on treatment efficiency

The effects of NaCl concentration on the degradation of dyes were investigated in the study. Results are shown in Fig. 7. Experimental conditions were $C_{\text{dye}} = 100 \text{ mg/L}$, $\text{pH}_{\text{in}} = 6$, $U_{\text{in}} = 20 \text{ V}$, $t = 50 \text{ min}$.

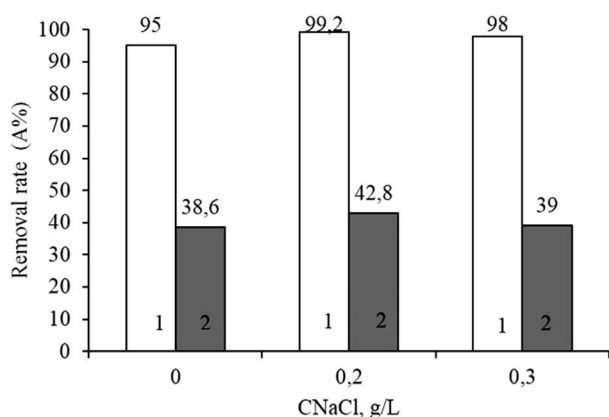


Fig. 7. Effect of NaCl concentration on treatment efficiency:
1 – 464 nm, 2 – 270 nm

Рис. 7. Влияние концентрации NaCl на эффективность обработки: 1 – 464 нм, 2 – 270 нм

As shown in Fig. 7, the presence of NaCl salt has a small effect on the treatment efficiency. But it was observed in this experiment that the addition of salt leads to current growth.

Changes of COD/TOC removal in degradation

Experimental conditions were $C_{\text{dye}} = 100 \text{ mg/L}$, $U_{\text{in}} = 20 \text{ V}$, $t = 50 \text{ min}$, $\text{pH}_{\text{in}} = 6$. Results are shown in Fig. 8.

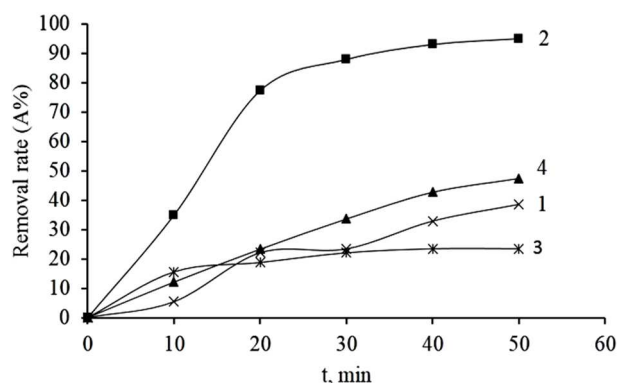


Fig. 8. Changes of COD/TOC ratio in degradation process:
1 – 270 nm; 2 – 464 nm; 3 – COD; 4 – TOC. $C_{\text{dye}} = 100 \text{ mg/L}$;
 $U_{\text{in}} = 20 \text{ V}$; $t = 50 \text{ min}$; $\text{pH}_{\text{in}} = 6$

Рис. 8. Изменения отношения ХПК/ОУУ в процессе электрокаталитической деструкции: 1 – 270 нм; 2 – 464 нм; 3 – ХПК; 4 – ОУУ. $C_{\text{крас}} = 100 \text{ мг/л}$; $U_{\text{н}} = 20 \text{ В}$; $t = 50 \text{ мин}$; $\text{pH}_{\text{н}} = 6$

As shown in Fig. 8, with the extension of the reaction time, the removal rate is increasing. After 50 min of reaction, the removal rates of COD and TOC were 23.5% and 47.4%, respectively. And the treatment effect of the characteristic absorption wavelength were 95% (464 nm) and 38.6% (270 nm). So, the electrocatalytic process not only damages the large coloring structures (chromophore groups) in the dye molecule, but also improves partially the biodegradability of the dye water solution.

CONCLUSION

Acid Orange 52 degradation process was studied in the electrocatalytic process. It was determined that the optimal conditions of electrocatalytic treatment, in particular are: $C_{\text{dye}} = 100 \text{ mg/L}$, $U_{\text{in}} = 20 \text{ V}$, $\text{pH}_{\text{in}} = 6$, $t = 50 \text{ min}$.

The experimental results show that when Acid Orange 52 simulated dye wastewater was treated under the optimal conditions, the treatment effect was 95% in visible part of light spectrum (464 nm) and 38.6% in ultraviolet part (270 nm), respectively. The removal rate of chemical oxygen demand (COD) and total organic carbon (TOC) were 23.5% and 47.7%, respectively.

It was found that electrocatalytic process can provide an effective decolorization rate of Acid Orange 52. However, not high values of COD removal rate most likely witness that there was no significant destruction of large fragments of the dye structure, such as the benzene ring.

REFERENCES

ЛИТЕРАТУРА

1. **Yan J.X., Cheng Q.L.** A review on the treatment technology of dyeing wastewater. *Dyestuffs Coloration*. 2007. V. 44. P. 48–51.
2. **Du B., Chen X.Y.** Research on photochemical catalytic oxidation technology. *Inner Mongolian Environmental Sciences*. 2007. V. 19. N 2. P. 52-54.
3. **Li Z., Zeng G.M., Gao X.Z.** Study on the treatment process Technique of Wastewater from Azo Dye Production. *Res. Environm. Sci.* 2001. V. 14. N 3. P. 29-32.
4. **Huang Y.** Methods and development of azo dye wastewater treatment. *J. Yi bin University*. 2007. V. 6. P. 54-57.
5. **Novotný Č., Dias N., Kapanen A., Malachová K., Vádrovcová M., Itävaara M., Lima N.** Comparative use of bacterial, algal and protozoan tests to study toxicity of azo and anthraquinone dyes. *Chemosphere*. 2006. V. 63. P. 1436-1442. DOI: 10.1016/j.chemosphere.2005.10.002.
6. **All'egre C., Moulin P., Maisseu M., Charbit F.** Treatment and reuse of reactive dyeing effluents. *J. Membr. Sci.* 2006. V. 269. P. 15-34. DOI: 10.1016/j.memsci.2005.06.014.
7. **Yi F.Y., Chen S.X., Yuan C.E.** Effect of activated carbon fiber anode structure and electrolysis conditions on electrochemical degradation of dye wastewater. *J. Hazard. Materials*. 2008. V. 157. P. 79–87. DOI: 10.1016/j.jhazmat.2007.12.093.
8. **Rajeshwar K., Ibanez J.G., Swain G.M.** Electrochemistry and the environment. *J. Appl. Electrochem.* 1994. P. 24. DOI: 10.1007/BF00241305.
9. **Teng H.K., Xie C.X., Zhao H.** A photoelectric integration unit for catalytic oxidation of organic wastewater. China. 00910235353.9. P. 2010-04-07.
10. **Ying C.Y.** Research progress of electrocatalytic oxidation technology. *Chem. Eng. Equip.* 2010. N 8. P. 140-142.

Поступила в редакцию 16.10.2017
Принята к опубликованию 26.01.2018

Received 16.10.2017
Accepted 26.01.2018