

DECOLOURIZATION OF WASTEWATER FROM THE PRODUCTION AND APPLICATION OF ACID BLUE 62

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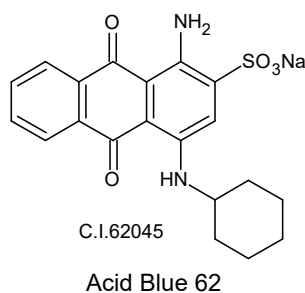
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Abstract: The aim of this work was to evaluate the possibility of bleaching effluents containing aminoanthraquinone dyes Acid Blue 62 selected by indirect electrochemical oxidation of single-chamber laboratory electrolyzers. To evaluate the effectiveness of model solution decolorized wastewater containing Acid Blue 62, UV-VIS spectroscopy was chosen as a suitable method. During electrochemical oxidation velocity changes were measured in model bleach solutions depending on the amount of supporting electrolyte, which was sodium chloride. Furthermore, decolourization rate was observed depending on the voltage of electrodes, which remained constant during the measurement. The samples were taken at various time intervals corresponding to chromaticity change of the electrolyzed solution. For the analysis of samples, (TOC, COD_{Cr}, AOX) and GC-MS (gas chromatography with mass spectrometer assigned) and liquid chromatography were used as auxiliary methods. The results of GC-MS established reaction mechanism of Acid Blue 62.

Key Words: Acid Blue 62, decolourization of wastewater, indirect oxidation

1 INTRODUCTION

Anthraquinone dyes constitute the second largest class of reactive dyes after azo dyes and have been extensively used in the textile industry not only to colour cotton, but also wool and polyamine fibres due to their wide variety of colour shades and ease of application [1]. In previous publications [2], we have described oxidizing agents on chlorine base for wastewater treatment by the method of indirect electrochemical oxidation. In this study, we report on the indirect oxidation of the anthraquinonic dye Acid Blue 62, (sodium 1-amino-4-(cyclohexylamino)-9,10-dihydro-9,10-ioxoanthracene-2-sulfonate), in model wastewaters in presence of sodium chloride.



During electrochemical oxidation, the inorganic or organic pollutant is not oxidized directly on the surface of the anode, but via an oxidant which is continuously generated by the anode. Consequently, the oxidizing agent is generated in-situ. The most commonly used oxidizing agent is chlorine, but it depends on pH medium, that organic pollutant is attacked by chlorine, respectively hypochlorous acid or perchlorate, Figure 1 [3-6].

1.1 Forms of active chlorine

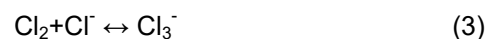
- generation of chlorine on the anode



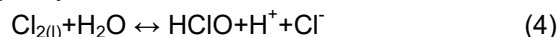
- dissolution of chlorine in water



- formation of trichloride



- hydrolysis of chlorine



- dissociation of hypochlorous acid

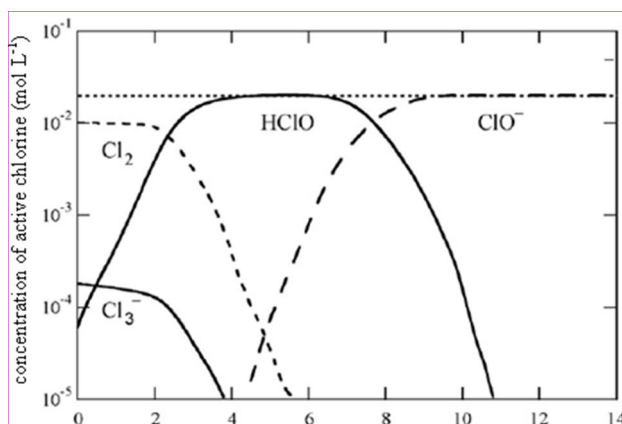


Figure 1 Diagram describing concentration dependence of chlorine-based active agents depending on pH during electrooxidation at concentration of 1.10^{-4} mol.L⁻¹. Active agents were generated in-situ via electrolysis of 0.1 mol.L⁻¹ solution of NaCl in a non-divided single-chamber electrolytic cell at the temperature 25°C [7]

2 EXPERIMENTAL

2.1 Materials

The athraquinone dye AB 62 (the commercial name is Midlon Blue 2R) was supplied by Synthesia a.s. and it was used without further treatment. Sodium hydroxide and 0.1 M hydrochloric acid were of the highest purity available.

2.2 Electrochemical decolourization

The electrochemical oxidation was carried out in the single-chamber laboratory electrolytic cell with the volume of 400 mL. The electrolytic cell had a double-case. For measurements the dye solution was tempered to 20°C by thermostat Julabo ED 5. The model wastewater was prepared by mixing distilled water, NaCl and AB62. The initial concentration of electrolyzed solutions was $1\text{--}1.5 \cdot 10^{-4}$ for kinetic measurements and $688 \text{ mg} \cdot \text{L}^{-1}$ ($1.628 \cdot 10^{-3} \text{ mol} \cdot \text{L}^{-1}$) for the analysis TOC, COD and AOX. The anode of the electrolytic cell (dimensions: $25 \times 100 \times 0.4 \text{ mm}$) was made of polished platinum, the cathode was made of austenitic stainless steel AISI – 316 (CSS 17.346, dimensions: $25 \times 100 \times 0.4 \text{ mm}$, composition: C 0.08%, Cr 16-18%, Ni 10-14%, Mn 2%, Mo 2-3%, P 0.045%, S 0.03% and Si 1%) with a declared corrosion resistance in sea water. The active area of electrodes was 13.5 cm^2 at specified conditions. Stabilized DC Power Supply Matrix MPS-3005 L-3 was used for the electrolysis of the solution. The laboratory DC Power Supply provides voltage from 0 to 30 V and current from 0 to 5 A. For kinetic measurements the electrolytic cell was equipped with a closed circulation circuit composed of peristaltic pump PP1B-05, connecting tubes and 1 cm quartz flow cell which was located in the temperate block of UV-VIS spectrophotometer Libra S22. The electrolyzed solutions were stirred by magnetic stirrer Heidolph MR Hei-Tec (300 rpm). During the electrooxidation the actual concentration of dyes was determined using UV-Vis spectrometer Libra S 22 according to Lambert-Beer law at the dye's maximum wavelength ($\lambda_{\text{max}} = 662 \text{ nm}$). The determination of TOC, COD and AOX was carried out by standard analytical methods [8-11].

2.3 TOC analysis

The total organic carbon was measured by Protoc® 300 analyzer. The samples were taken at time intervals 1-48 hours for the analysis.

2.4 Determination of COD

The cuvette tests for determination of chemical oxygen demand (LCK 514, HACH LANGE), thermostat LT 200 (HACH LANGE) and spectrophotometer DR 2800 (HACH LANGE) were used for the determination of COD. The samples were taken at time intervals 1-48 hours for the analysis. The COD value of solution dyes was

established through electrolysis before and after the electrooxidation by the standard method determining the chemical oxygen consumption by potassium dichromate based on oxidation of organic substances by potassium dichromate in strongly acidic conditions of sulfuric acid in 2 hours-boiling at the temperature $148^\circ\text{C} \pm 3^\circ\text{C}$.

2.5 AOX analysis

Adsorbable organohalogenic compounds were determined by AOX/TOX multi X® 2500 analyzer. The samples were taken at time intervals 1-48 hours for the analysis. The sample was acidified with HNO_3 . The adsorption of organic compounds was carried out by batch system on activated carbon (Analytik Jena, particle size 30-63 μm). The inorganic chlorides were removed by NaNO_3 washing. Then the activated carbon was burned in oxygen atmosphere at the temperature of 950°C . Incurred halohydrogens were determined by argentometry.

2.6 GC/MS analysis

The degradation products were identified using gas chromatography coupled with a mass spectrometry (GC/MS) system. The operating condition of GC/MS is: Instrument GC 2010 (Shimadzu, Japan), injection mode – splitless, carrier gas Helium (99.9999%), injector temperature 250°C , sample volume $1 \mu\text{l}$, column HP-5MS, 30 m (length) \times 0.25 mm (I.D.) with 0.25 μm film thickness, temperature program 40°C (5 min), 300°C ($20^\circ\text{C}/\text{min}$), 300°C for 7 min holding. Instrument MS QP 2010plus (Shimadzu, Japan), mode SCAN, m/z 10-900. The intermediate compounds formed were identified by comparison with the standard mass spectrum of NIST 147 and NIST 27 and WILEY 229 library.

3 RESULTS AND DISCUSSION

Before measurement of kinetic dependencies, UV-VIS spectra of aqueous solution AB62 and wavelengths of absorption maxima were determined. For monitoring kinetic dependence of decolourization of model wastewater, the band with the highest wavelength and calibration dependence of absorbance on concentration of pure dye was chosen, see Figure 2.

UV/VIS spectroscopy was used for monitoring kinetics of indirect electrochemical oxidation. Relatively cheap sodium chloride was chosen as a supporting electrolyte for increasing the conductivity of model wastewater. Sodium chloride is added to the bath during dyeing process for higher use of dye. Amount of sodium chloride was in the range of mass concentration $2.5\text{--}10.0 \text{ g} \cdot \text{L}^{-1}$.

During electrochemical oxidation amino-anthraquinone dyes were measured for changes

of velocity of colourization of model solutions at a concentration cca $1-1.5 \cdot 10^{-4}$ mol.L⁻¹ with dependence on the amount of sodium chloride as a supporting electrolyte at concentrations 2.5; 5; 7.5 and 10 g.L⁻¹.

And then velocity with dependence on voltage of electrodes was monitored. Voltage was constant at values 3; 5; 7.5; 10; 12.5 and 15 V (in some cases where the conditions allowed, voltage was increased up to 22.5 V). Results of kinetic measurements are clearly summarized in Table 1. Generally, the oxidation rate decreased with the decrease of voltage and conductivity of the electrolyte, which depends on the amount of sodium chloride in the wastewater.

In the next step, decolourization of model waters which contained dye AB 62 was tested for dependence on pH from 3 to 11, especially for values 3; 5; 7; 9 and 11, because in context of different pH we can expect different decomposition products of oxidation. Applied voltage was held constant during measurement at the value 5 V, current density was 0.16 A/cm². Duration of electrooxidation was 24 h. After that, samples were collected from the discoloured model water and parameters AOX, COD_{Cr}, TOC and TN were measured. Obtained values of measurements are summarized in Table 2.

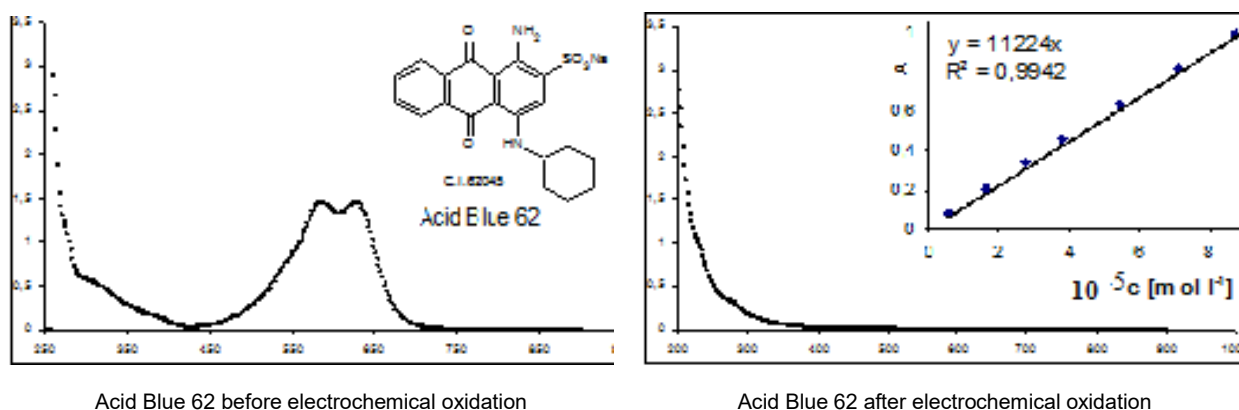


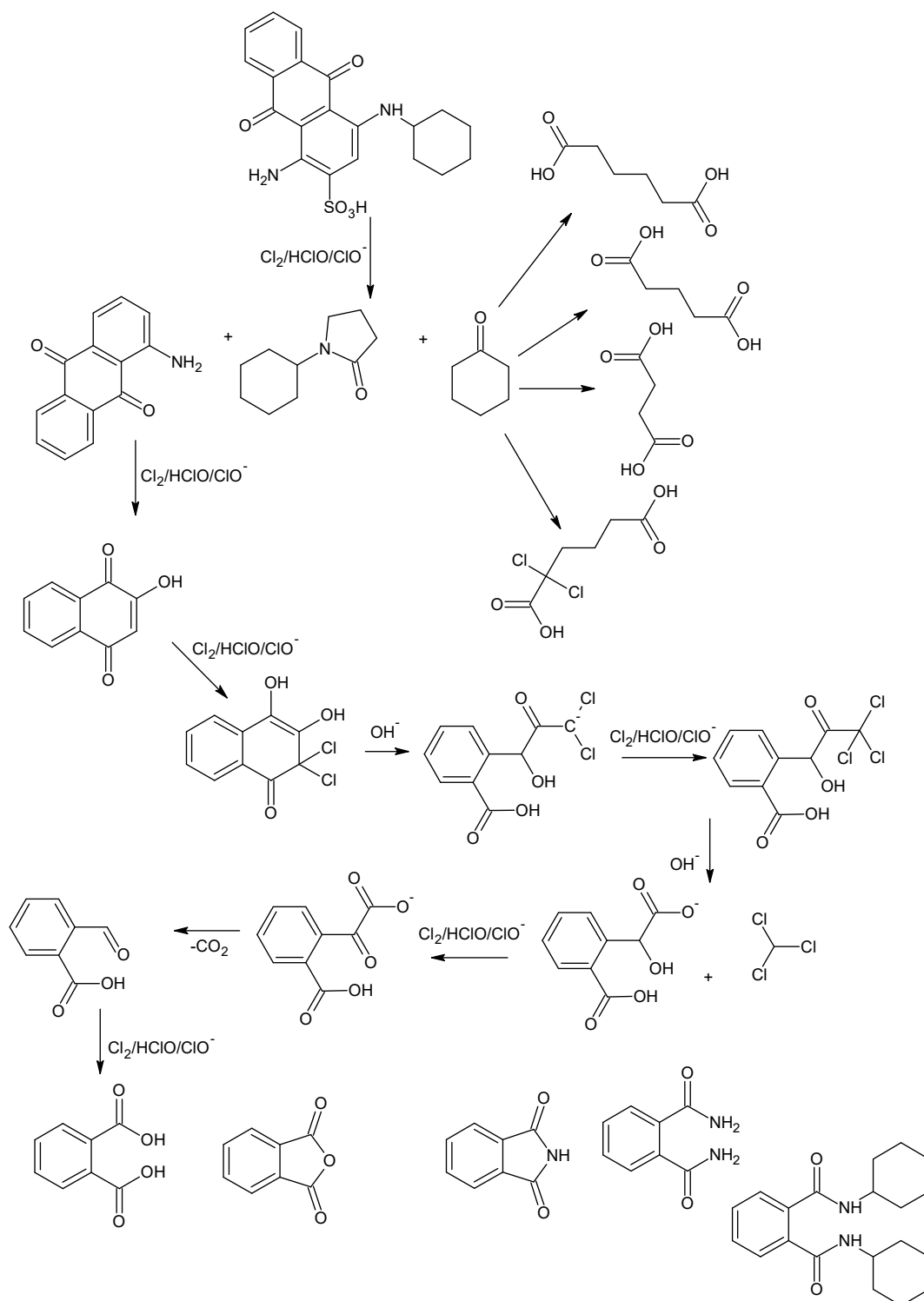
Figure 2 Absorption spectra dependence of absorbance on the wavelength of amino-anthraquinone dyes before and after electrochemical oxidation, measured in distilled water, $t=25^{\circ}\text{C}$, $\lambda=190-900$ nm

Table 1 Kinetic measurement of electrochemical oxidation of Acid Blue 62 in distilled water, observed rate constant, half of reaction and its standard deviation with dependence on concentration of salt NaCl 2.5; 5; 7.5 and 10 g.L⁻¹, $V=0.4$ l, $t=25^{\circ}\text{C}$, $\lambda=626$ nm, $\text{pH}=7$

Acid Blue 62												
U [V]	2.5 g NaCl.L ⁻¹			5 g NaCl.L ⁻¹			7.5 g NaCl.L ⁻¹			10 g NaCl.L ⁻¹		
	k [s ⁻¹]	t _{1/2} [s]	s	k [s ⁻¹]	t _{1/2} [s]	s	k [s ⁻¹]	t _{1/2} [s]	s	k [s ⁻¹]	t _{1/2} [s]	s
3	1.64E-04	4214.80	76.60	1.04E-04	6655	107.3	2.76E-04	2508.6	51.58	7.64E-04	906.78	3.27
5	5.71E-04	1218.36	68.75	6.01E-03	115.33	3.65	1.27E-02	54.44	0.37	7.12E-03	97.37	0.22
7.5	2.17E-03	320.13	8.41	1.14E-03	60.65	1.22	2.15E-02	32.23	0.41	3.93E-02	17.65	0.39
10	5.37E-03	129.24	3.71	1.35E-02	51.34	0.98	2.95E-02	23.44	0.23	5.55E-02	12.48	0.23
12.5	8.13E-03	85.27	1.38	1.55E-02	44.69	0.61	3.54E-02	19.60	0.23	7.75E-02	8.95	0.03
15	9.56E-03	72.47	0.31	1.67E-02	41.41	0.24	3.97E-02	17.47	0.21	8.20E-02	8.45	0.03
17.5	1.08E-02	64.06	0.10	2.33E-02	29.77	0.66	5.17E-02	13.41	0.27			
20	1.16E-02	59.58	0.31	2.93E-02	23.65	0.53	8.29E-02	8.37	0.14			
22.5	1.55E-02	44.62	0.26									

Table 2 Results of analysis COD, TOC, TN and AOX before and after indirect electrochemical oxidation of AB 62 for the pH range 3-11, $t=25^{\circ}\text{C}$ and concentration of NaCl 5 g.L⁻¹, $U=5$ V, $i=0.16$ A.cm⁻²

	Before oxidation	After oxidation at pH				
		3	5	7	9	11
COD [mg.L ⁻¹]	841	62	118	116	141	161
TOC [mg.L ⁻¹]	33.33	20.53	25.27	26.30	27.15	29.11
TN [mg.L ⁻¹]	3.35	1.43	1.73	2.07	2.42	2.72
AOX [mg.L ⁻¹]	-	6.44	10.40	8.68	5.57	5.35



Scheme 1 Expected mechanism of decomposition of dye Acid Blue 62

In analogy with literature, decomposition of this amino-anthraquinone dye was expected. After decomposition of chromophore, it leads to discoloration of the solution and cyclohexane and cyclohexanol occurred among intermediates. Based on the results of the analyses GC-MS and AOX, expected mechanism of decomposition of dye Acid Blue 62 was proposed, see Scheme 1.

4 CONCLUSIONS

During decolourization respective decomposition of amino-anthraquinone dye Acid Blue 62 via indirect electrochemical oxidation in an aqueous solution of sodium chloride was detected by GC-MS analysis which was performed in the reaction mixture after total decolourization of the solution

of AB 62, the presence of some of the expected decomposition products, e.g. cyclohexanone. Together with that, GC-MS clearly showed the presence of chloroform, followed by dichloro carboxylic acid and chloro carboxylic acid which are generated by chlorination of cyclohexanol.

The presence of chlorinated hydrocarbons was also confirmed by an independent analysis, where a positive determination of AOX in the same reaction mixture was carried out.

From the obtained results we can already deduce some partial conclusions. Primarily, and that is unchallengeable, it is necessary to correct the classical conception of the reaction mechanism. Final products of the chlorination are chloroform and mono- and dicarboxylic acids. These compounds are generated in all of studied pH range 3-11 and they are influenced by their ratio and total amount, based on the GC-MS analysis and determination of the parameter AOX.

Maximal concentration of AOX is ca 5 to 11 mg.L⁻¹ and this value is achieved within ca 24 h of electrooxidation. Consequently, the volume of AOX decreases, probably due to volatilization of POX compounds (purgeable organic halogens, which can be released from water at 60°C). A representative of POX is chloroform which was detected in the reaction mixture. Maximal amount of AOX, more than 11 mg.L⁻¹, is generated at pH 5, which corresponds to oxidation and chlorination of electrochemically generated acid HClO (pKa = 7.5). Acid HClO is practically unique, but simultaneously also the most powerful oxidizing and chlorinating agent, at this pH value.

In the context of determined values of AOX, it is necessary to note the Government Order of the Czech Republic No. 82 from March 22nd, 1999, where the threshold limit of AOX is 0.025 mg.L⁻¹ for watercourses, and for other surface waters, 0.05 mg.L⁻¹. The comparison of these limits and experimentally determined values of AOX, which are 100-200 times higher in optimal pH range, indicates a detriment of indirect electrochemical oxidation in the sodium chloride medium.

During decolourisation of highly saline process waters and wastewater from paper mills, textile mills, dye houses and in other industrial branches using AB 62 and other amino-anthraquinone dyes with analogous structure, it is necessary to not operate this very effective treating and decolourizing process as the final technological stage. It may be better to use indirect electrochemical oxidation only for pretreatment of wastewater or complete it with a suitable final process, e. g. adsorption on activated carbon.

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5 REFERENCES

1. Alkan M., CelikCapa S., Demirbas Ö., Dogan M.: *Dyes and Pigments* 65(2), 251-259, 2005
2. Dušek L., Horňáková B., Novotný L.: *Chemické listy* 106(11), 1054-1060, 2012
3. Carlos A., Martínez H., Brillas E.: *Applied Catalysis B Environmental* 87, 105-145, 2009
4. Perkowski J., Kos L., Ledakowicz S., Zylla R.: *Fibres & Textiles in Eastern Europe* 11(2), 88-94, 2003
5. Morsi M.S., Al-Sarawy A.A., El-Dein W.A.: *Desalination and Water Treatment* 26(1-3), 301-308, 2011
6. Maljaei A., Arami M., Mahmoodi N.M.: *Desalination* 249(3), 1074-1078, 2009
7. Boxall C.; Kelsall G.H.: *Inst. Chem. Eng. Symp. Ser.* 127, 59, 1992
8. Horáková M. et al.: *Analitics of water* (in Czech: *Analytika vody*), 2nd Ed., VŠCHT, Praha 2007
9. ČSN EN ISO 9562 (75 7531) *Jakost vod – Stanovení adsorbovatelných organicky vázaných halogenu.* ČNI Praha 1995
10. *Standard Methods for the Examination of Water and Wastewater*, 21st Ed., APHA, AWWA and WEF, Washington 2005
11. U.S. EPA 1650 *Adsorbable Organic Halides by Adsorption and Coulometric Titration*