Discoloration of direct light resistant blue and acid antrachinone blue dyes using metallic iron

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Two representatives of dyes widely used in textile industry – azodye, direct light resistant blue, and acid antrachinone blue were decontaminated using metallic iron. When the excess of iron powder is used, the destruction of dyes obeys the second order reaction equation with the rate constants of 0.0024 $l \cdot mg^{-1} \cdot min^{-1}$ and 0.0002 $l \cdot mg^{-1} \cdot min^{-1}$ for direct light resistance blue and acid antrachinone blue respectively in neutral solutions and 0.0035 $l \cdot mg^{-1} \cdot min^{-1}$ and 0.0014 $l \cdot mg^{-1} \cdot min^{-1}$ respectively in acidic solutions. UV/Vis and FT-IR investigations showed that a part of the dye degradation products remains in the solutions and a part is adsorbed on the precipitate formed during the treatment. The increased values of COD and BOD with the increase in time of destruction indicate that both dyes are decomposed to easily degradable products.

Key words: direct light resistance blue, acid antrachinone blue, metallic iron, discoloration

INTRODUCTION

Colorants are widely used in different branches of industry, i.e. textile, painting, leather, printing, photography etc. In addition to natural organic and inorganic dyes, synthetic organic dyes comprise the main part (~80%) of all the colorants used in practice. Synthetic dyes used in textile industry are not utilized for fabrics completely. The remaining part gets into the wastewater, which requires careful decontamination. These dyes are toxic to aquatic organisms and resistant to natural biological degradation. Due to their high chemical stability and xenobiotic nature, they cannot be destroyed during classical wastewater treatment procedures.

In order to achieve the decomposition of these persistent organic compounds, lots of solutions have been proposed. Acid dyes form insoluble precipitate with Ba(II) salts in the presence of alkaline substances. However, the precipitation of acid dyes containing the amino groups is complicated and not complete. Besides, such treatment has no practical value due to the use of poisonous soluble Ba(II) salts and the difficulties in the disposal of the formed sludge. Promising results in dye treatment were obtained using various sorbents [1, 2].

For the treatment of the dyes containing effluents oxidative destruction is mainly used in practice. Ozone, hydrogen peroxides, Fenton's reagent are used as oxidizing agents [3–7]. In the resent years the reductive destruction of azodyes using metallic iron has been investigated very intensively [4, 8]. The authors of the work [9] established a strong relationship between the composition of the iron oxidized surface layer and kinetics and reaction pathways of azodyes decomposition. The proposed mechanism for azodyes decomposition by zerovalent iron involves the formation of free amino groups

$$R-N=N-R' + 2Fe^0 + 4H^+ \rightarrow R-NH_2 + 2Fe^{2+} + H_2N-R'.$$
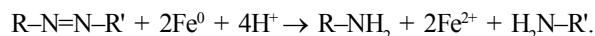
This reaction is catalyzed by iron surface.

Actually, the dissolution of iron is more complicated. The hydrogen evolved during the iron dissolution can act as a reducing agent as well:

$$Fe^0 + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^-.$$
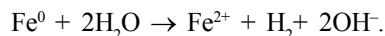
The iron dissolving reaction depending on pH and the presence of an oxidizing agent, for instance oxygen, proceeds with the formation of Fe^{2+} or $Fe3^+$. The latter forms amorphous precipitate.

$$2Fe^{2+} + 1/2\ O_2 + 3H_2O \rightarrow 2FeOOH + 4H^+,$$

$$2Fe^{2+} + 1/2\ O_2 + 2H_2O \rightarrow 2Fe_2O_3 + 4H^+.$$
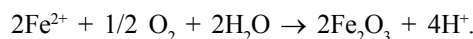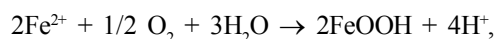
It is well known [10, 11] that this precipitate act as a good sorbent for organic and inorganic substances. Fe^{3+} ions form insoluble precipitate with some organic compounds as well [12]. Synthetic organic dyes having many unsaturated linkages and different functional groups may act as powerful complexing agents for iron ions.
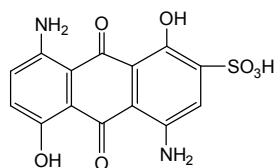
Thus, the mechanism of discoloration of the organic dyes using the treatment with metallic iron could be rather complicated.

Our investigations were carried out with the purpose to investigate the possibilities to use metallic iron as a decontaminant for the dyes of two different types, i.e azodye, direct light resistance blue,
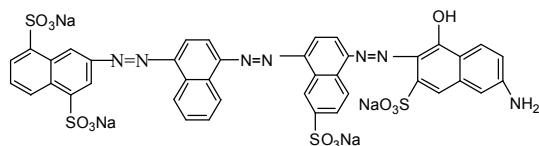
and acid antrachinone blue,

which are widely used in textile industry. The attempts were also made to evaluate the possible mechanisms of their decomposition.

EXPERIMENTAL

Batch experiments of dye decomposition were performed in an open vessel by adding 1 g of iron powder to 100 ml of dye containing solutions and steadily mixing with the magnetic stirrer. In long term experiments iron powder was removed from solutions by a magnet. The efficiency of the discoloration process of azo and atrachinone dyes was evaluated by measuring the absorbance in 2 cm cells at wavelengths of 540 nm and 590 nm respectively. Before measuring the absorbance, the solutions were carefully filtrated through a glass filter.

UV-visible spectra were recorded with a Perkin Elmar Lambda 35 UV/VIS spectrometer at 20 °C in 1 cm length quartz cells.

FT–IR spectra of the precipitate were recorded using a BOMEM MB (Hartman&Braun, Canada) spectrometer in a wave range from 4000 to 450 cm^{-1}. Background corrections were made using KBr as a reference blank.

The chemical oxygen demand (COD) values were established by the dichromate method [13]. Oxidation by potassium dichromate was carried out at 148 °C for 2h with subsequent titration against Mohr salt.

The biochemical oxygen demand (BOD) was determined according to [14] by measuring the decrease of oxygen concentration after 5 days.

RESULTS AND DISCUSSION

It is known that the pH of solutions changes the color of some dyes. The use of metallic iron for the decontamination of wastewaters is also related to the changes in pH. Therefore, first of all, the experiments were carried out with the purpose to determine the in-

fluence of pH on the color of dyes investigated. Both dyes, direct light resistant blue and acid antrachinone blue, have very intensive colours at visible light with absorbance maximums at λ = 540 nm and λ = 540 nm respectively. The results depicted in Fig. 1 show that the pH influence on the absorbance of azodye is negligible in pH range 2 to 11, only in strongly acidic or alkaline solutions the absorbance slightly decreases. The color of antrachinone dye is unchanging in the whole investigated range of pH, i.e. 1 to 13. The persistence of colors depending on pH enabled to use the absorbance for the determination of the concentration of dyes during the kinetic experiments.
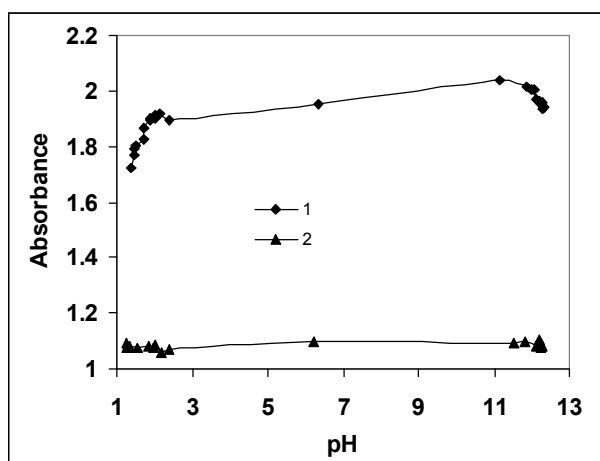

Fig. 1. Influence of pH on light absorption: 1 – azodye at λ = 540 nm and 2 – antrachinone dye at λ = 590 nm. Dye concentration 50 mg/l

A series of experiments were carried out in order to investigate the influence of iron powder on the efficiency of the decontamination process. It was found that the amount of iron higher than 0.5 g per 100 ml of a solution containing 100 mg of dye affects neither the discoloration rate nor the changes in pH in acidic and neutral solutions. Therefore, the further experiments were carried out using the iron powder load of 1 g per 100 ml of the solution.

The discoloration of both dyes in aqueous solutions without pH adjusting proceeds rather rapidly, whereas the decomposition of azodye is more rapid than that of antrachinone dye (Fig. 2a). The main part of the dyes is decomposed during the first 30–60 minutes, then the process becomes slower and complete discoloration takes several hours. The changes of pH in this case are inconsiderable, they vary in pH range of 5.5–7.5.

The acidification of the solutions remarkably increased the rate of the decomposition of dyes, especially that of antrachinone dye (Fig. 3a). Complete discoloration of solutions was achieved during ~2.5 h for azodye and ~3 h for antrachinone dye. In this case the pH values increased steadily, probably due to an enhanced dissolving of metallic iron in acidic solutions.
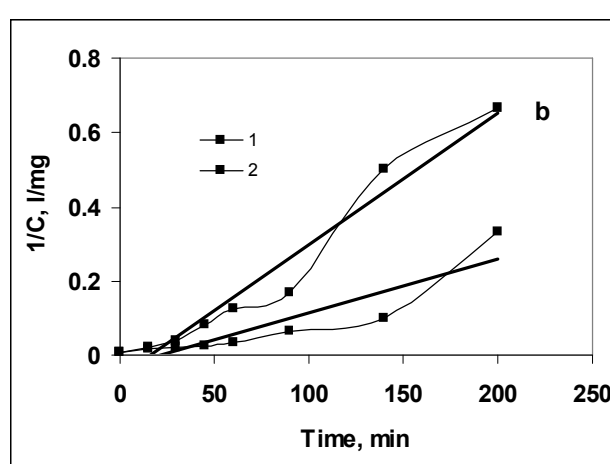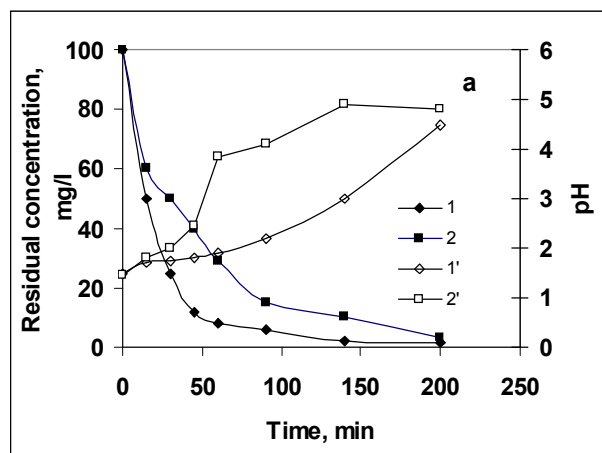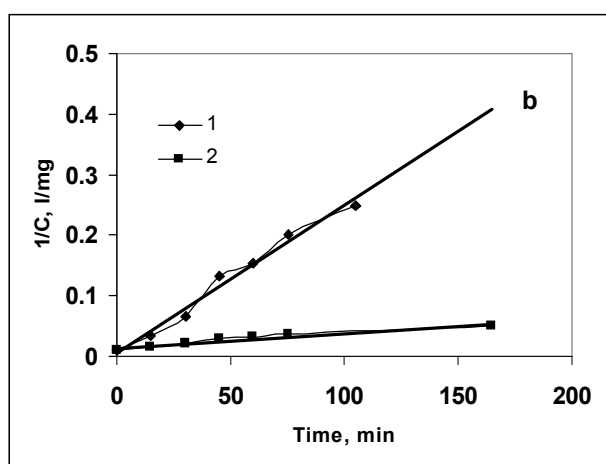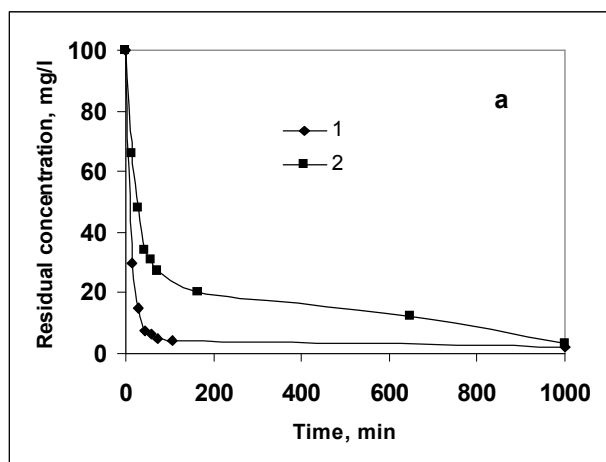
Fig. 2. Decomposition kinetics of azodye (1) and antrachinone dye (2) in neutral solutions (**a**) and the fits to the second order reaction (**b**). Initial pH for azodye – 7.5 and 7.1 – for antrachinone dye

Fig.3. Decomposition kinetics (1, 2) and pH changes during the reaction (1', 2') of azodye (1, 1') and antrachinone dye (2, 2') in acidic solutions (**a**) and the fits to the second order reaction (**b**)

The order of the degradation reaction of dyes was determined using the first order and the second order reaction equations.

$$\ln c_t = \ln c_0 - k_1 t,$$
$$\frac{1}{c_t} = k_2 t + \frac{1}{c_o},$$

where c_o is the initial concentration of dye, c_t is the dye concentration at time t, and k_1 and k_2 are the rate constants of the first and second order reactions respectively. Attempts to fit the first order kinetics equation, i.e. plotting $\log c_t$ versus t, has indicated that the correlation coefficients in solutions without pH adjustment and on addition of acid were very small. The application of the second order model, i.e. plotting $1/c_t$ versus t, gave the lines with rather high correlation coefficients (Fig. 2b and 3b, Table 1). The slope of the line gives the value k_2. The calculated values of k_2 (Table 1) show that in both cases the degradation rate of direct light resistant blue dye is remarkably higher than that of acid antrachinone blue.

Table 1. **Rate constants and correlation coefficients in the kinetic experiments**

Experiment conditions	Second order reaction parameters	
	k_2, l·mg^{-1}·min^{-1}	R^2
Fig. 2, curve 1	0.0024	0.9822
curve 2	0.0002	0.9154
Fig. 3, curve 1	0.0035	0.954
curve 2	0.0014	0.9209

The fitness of the discoloration rate to the second order equation shows that the degradation of dyes does not proceed by a direct interaction of dyes with metallic iron, as the latter is used in large excess when the influence of the amount of iron is not observed. The reductive destruction of dyes could take place because of hydrogen evolved during iron dissolution. This confirms also the increase in the rate by the acidification of the solution. During the treatment process there are formed insoluble iron hydroxides which could act as sorbents for dyes and their degradation products.

In alkaline solutions (Fig. 4), the degradation rate is very low and similar for both dyes. Even after several days the discoloration of solutions is not achieved. The reproduction of results is low. It is difficult to obtain reliable results for the estimation of the reaction order. The data depicted in Fig. 4 show only the possibility to destroy the dyes in alkaline solutions. The dissolution of iron is conducted by a decrease in pH due to formation of insoluble iron hydroxides. Apparently, air oxygen acts as an oxidizing agent for metallic iron.
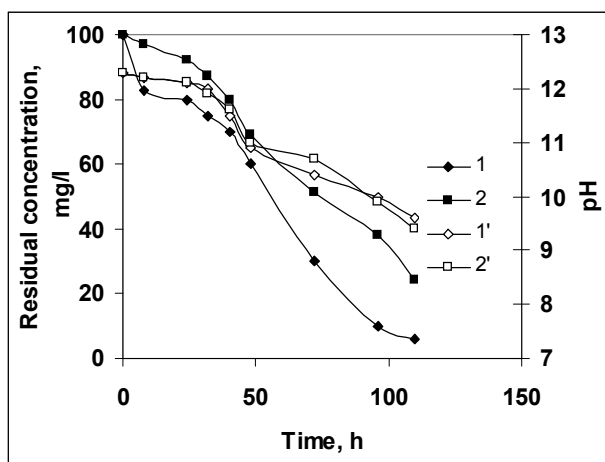

Fig, 4. Decomposition kinetics (1, 2) and pH changes during the reaction (1', 2') of azodye (1, 1') and antrachinone dye (2, 2') in alkaline solutions

UV/Vis spectra (Figs. 5 and 6) showed that the decrease in the absorbance using iron as a degradation agent proceeds gradually as in the visible part of wavelengths as well as in the near UV region. High values of the maximum of both dyes are observed only at λ ~200 nm indicating that a part of the degradation products remains in the solution. They should be sulfogroups (probably sulphite) and other degradation products of dyes containing unsaturated bonds. The differences in
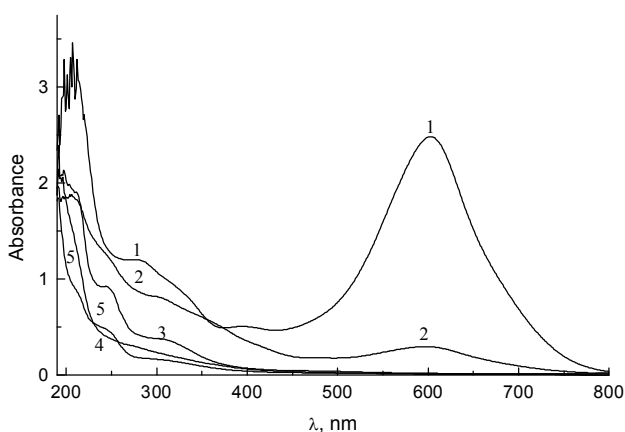

Fig. 5. The effect of iron treatment on UV/Vis spectra of the solutions containing 100 mg/l acid antrochinone blue dye: 1 – before treatment, 2 – after 30 min in neutral solutions, 3 – after 10 h in neutral solutions, 4 – after 5 h in acidic solutions, 5 – after 10 days (diluted 1:3) in alkaline solutions (diluted 1:3)
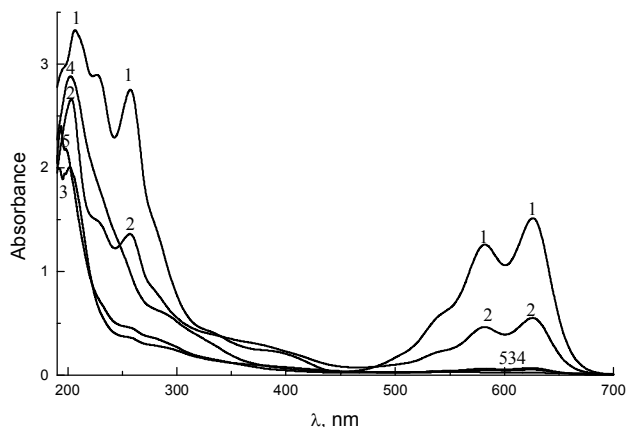

Fig. 6. The effect of iron treatment on UV/VIS spectra of the solutions containing 100 mg/l direct light resistance blue dye: 1 – before treatment, 2 – after 1 h in neutral solutions (diluted 1:1), 3 – after 10 h in neutral solutions, 4 – after 10 days in alkaline solutions (diluted 1:3), 5 – after 5 h in acidic solutions (diluted 1:3)

UV/Vis spectra between the solutions obtained after the treatment under different values of pH i.e. in acidic, neutral and alkaline solutions, are inconsiderable.

In order to verify the assumption that freshly precipitated iron hydroxides and oxides act as good sorbents for organic compounds, the FT–IR investigations of the formed precipitate were carried out. FT–IR spectra of these precipitates were studied in the interval of wavelength between 3600 and 450 cm⁻¹. Comparisons were made with the spectra of free acid antrachinone blue dye (Fig. 7, curve 1) and free direct light resistance blue dye (Fig. 7, curve 4). The absorption bands characteristic of these dyes were between 3500–3300 cm⁻¹ (stretching vibration of –OH and –NH), at 1590 cm⁻¹ (bending vibration of –NH) and in the region 1260–1110 cm⁻¹ (bending vibration of sulfogroup). The spectra of the precipitate obtained after the treatment of both dyes with metallic iron in the acidic and alkaline solutions (Fig. 7, curves 2, 3, 5, 6) do not show any IR absorption in the region 1260–1110 cm⁻¹, indicating the absence of sulfogroups. In the precipitate formed during the treatment, the intensity of bands in the region 1600–1410 cm⁻¹, the vibration characteristic of aromatic and amino compounds, decreases in comparison with that of the free dyes and can be attributed to the degradation process of dye. Very strong IR absorption bands of the precipitate around 3450 cm⁻¹ and in the region 600–450 cm⁻¹ were related to the stretching vibration of OH (apparently, Fe(OH)₃) and the stretching vibration of Fe-O. Thus, the FT–IR investigations showed that the precipitate formed during the degradation of both direct light resistance blue and acid antrachinone blue dyes using metallic iron sorbed mainly the degradation products. The formation of insoluble compounds of the degradation products of dyes with iron ions is also possible.

The determination of the COD and BOD values is widely used in wastewater treatment shops to evaluate the toxicity of the effluents. Theoretically calculated va-
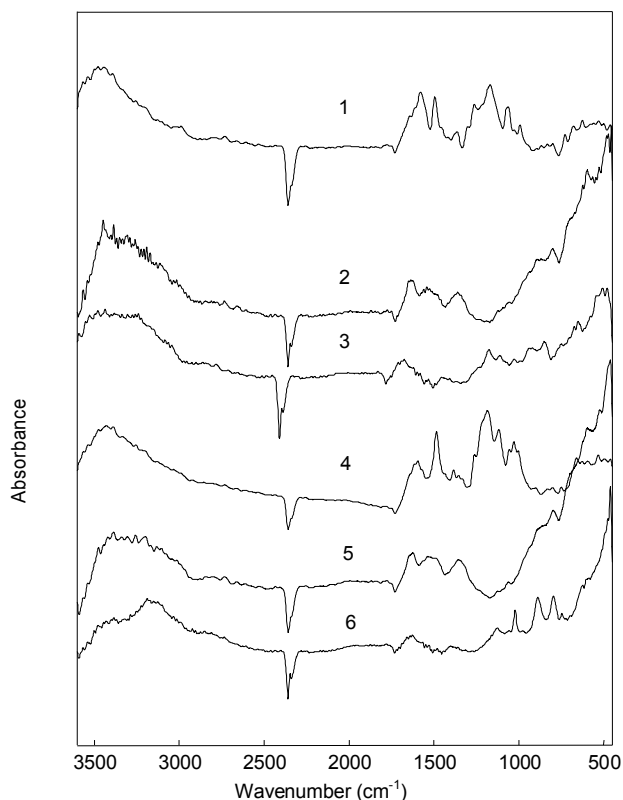
Fig. 7. FT-IR spectra of acid antrachinone blue (1) and its precipitate (2, 3) and direct light resistant blue (4) and its precipitate (5, 6) formed after their treatment with Fe in alkaline (2, 5) and acidic soliutions (3, 6)

lues of oxygen demand for a complete decontamination of solutions containing 100 mg of dyes are 187 mg/l and 152 mg/l for direct light resistance blue and acid antrachinone blue respectively. However, the COD determined in these solutions is several times lower than those calculated theoretically (Table 2) indicating high persistence of these dyes. During the treatment with metallic iron, the COD increases steadily and reaches the values exceeding the theoretical value. This is possible owing to reductive destruction of organic compounds. The further treatment causes decrease in COD. Possible oxidation of Fe(II) ions by the determination of COD values is avoided by adding NaOH to the samples and keeping them in open vessels for several hours.

The values of BOD (Table 3) are also very low in the initial solutions indicating the toxic nature of the dyes investigated. These values increase by the treatment of the solutions containing dyes with metallic iron. The relation between the values of COD and BOD, which indicates the toxicity of the effluents, in this case is not significant as the persistence of the dyes gives very low values of COD. Anyway, in all cases, the BOD values are lower than the COD values. The increase in the COD and BOD values with the treatment time indicates that both, direct light resistance blue and acid antrachinone blue dyes, are decomposed to more easily biodegradable products. Considerably lower values of both COD and BOD in alkaline solutions could be attributed to the increased formation of iron hydroxides that are able to sorb the degradation products of the dyes.

Table 2. **The effect of the treatment conditions using metallic iron on chemical oxygen demand (COD) of direct light resistance blue and acid antrachinone blue dyes**

Treatment conditions	COD, mg/l	
	Direct light resistance blue	Acid antrachinone blue
Before treatment	44	23
After 30 min treatment in neutral solutions	63	59
After 1 h treatment in neutral solution	68	70
After 7 h treatment in neutral solution	350	350
After 7 h treatment in acidic solutions	300	260
After 80 h treatment in alkaline solutions	83	119

Table 3. **The effect of the treatment conditions using metallic iron on biochemical oxygen demand (BOD) of direct light resistance blue and acid antrachinone blue dyes**

Treatment conditions	BOD, mg/l	
	Direct light resistance blue	Acid antrachinone blue
Before treatment	31	21
After 30 min treatment in neutral solutions	63	29
After 1 h treatment in neutral solution	102	59
After 7 h treatment in neutral solution	208	183
After 7 h treatment in acidic solutions	338	176
After 80 h treatment in alkaline solutions	108	78

CONCLUSIONS

The use of metallic iron powder allows to discolorate the solutions containing azodye direct light resistance blue and acid antrachinone blue completely. When the excess of iron powder is used, the degradation of both dyes takes place according to the second order reaction kinetics. The increase in the COD and BOD values during the treatment process indicates that both dyes are decomposed to easily biodegradable products. A part of these products is sorbed onto iron hydroxides and oxides formed in the treatment process.

References

1. Y. C. Wong, Y. S. Szeto, W. H. Cheung and G. McKay, *Process Biochemistry,* **39**(6), 693 (2004).

2. K. H. Keith Choy, J. F. Porter and G. McKay, *J. Chem. Eng. Data,* **45**(4), 575 (2000).

3. H.-Y. Shu, M.-Ch. Chang and W.-P. Hsieh, *J. Haz. Mat.,* **B128**, 60 (2006).

4. W. S. Pereira and R. S. Freire, *J. Braz. Chem. Soc.,* **17**(5), 832 (2006).

5. P. Verma, P. Baldrian and F. Nerud, *Chemospehre,* **50**(8), 975 (2003).

6. D. Nansheng, W. Feng, L. Fan and X. Mei, *Chemosphere,* **36**(15), 3101 (1998).

7. K. Swaminathan, S. Sandhya, A. Carmalin Sophia, K. Pachhade and Y. V. Subrahmanyam, *Chemosphere,* **50**(5), 619 (2003).

8. J. Cao, L. Wei, Q. Huang, L. Wang and Sh. Han, *Chemosphere,* **38**(3), 565 (1999).

9. A. J. Mielczarski, G. M. Atenas, E. Mielczarski, *Applied Catalysis B: Environmental,* **56**(4), 289 (2005).

10. M. Ptashekas, J. Budilovskij, V. Zaitsev and S. Makarov, *Chemija* **4**(179), 41 (1990).

11. M. Fan, M. Asce, R.C. Brown, Th. D. Wheelock and F.C. Laabs, *Journal of Environmental Engineering,* **128**, 483 (2002).

12. O. Gylienė, M. Šalkauskas and R. Juškėnas *J. Chem. Techn. Biotechn.,* **70**(1), 111 (1997).

13. Water quality – Determination of the chemical oxygen demand. *ISO 6060*:1989.

14. Water quality – Determination of the biochemical oxygen demand. *ISO 5815*:2003.

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TIESIOGINIO ŠVIESAI ATSPARAUS MĖLYNOJO IR RŪGŠTINIO ANTRACHNONINIO MĖLYNOJO DAŽŲ BLUKINIMAS METALINE GELEŽIMI

S a n t r a u k a

Dviejų dažų tipų, plačiai naudojamų tekstilės pramonėje, pavyzdžiai, t. y. azodažas – tiesioginis šviesai atsparus mėlynasis ir rūgštinis antrachinoninis mėlynasis buvo nukenksminami metaline geležimi. Naudojant geležies miltelių perteklių, dažų suardymo greitis atitinka antro laipsnio reakcijos kinetinę lygtį, kurios greičio konstantos neutralioje terpėje tiesioginiam šviesai atspariam mėlynajam ir rūgštiniam antrachinoniniam mėlynajam yra atitinkamai 0,0024 $l \cdot mg^{-1} \cdot min^{-1}$ 0,0002 $l \cdot mg^{-1} \cdot min^{-1}$, o rūgštinėje terpėje atitinkamai 0,0035 $l \cdot mg^{-1} \cdot min^{-1}$ ir 0,0014 $l \cdot mg^{-1} \cdot min^{-1}$. UV/Vis ir FT–IR tyrimai parodė, kad dalis dažų skilimo produktų lieka tirpale, o dalis yra sorbuojama ant geležies hidroksidų nuosėdų, susidariusių tirpstant geležiai. Didesnės nei pradinės ChDS ir BDS reikšmės nukenksminimo metu ir po apdorojimo rodo, kad susidarę dažų skilimo produktai yra lengviau nukenksminami nei patys dažai.