

Discoloration of methylene blue and wastewater from a plant by a Fe/Cu bimetallic system

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Abstract

Using a Fe/Cu bimetallic system (Fe/Cu system), the discoloration of both methylene blue in aqueous solution and the colored wastewater from a plant was investigated under the anaerobic condition in batch or continuous reactors. Results show that the Fe/Cu system effectively removed the color with over 88% of color removal efficiency for both methylene blue solution and the wastewater from the plant in batch test. Color removal efficiencies increased rapidly with Fe/Cu dosage and reaction time, respectively, at initial time and slowly to stable values. Optimum pH was neutral range. In addition, in continuous test it also removed the color of the wastewater from the plant with 63% of discoloring efficiency under the condition of 2 h of hydraulic retention time and neutral range of pH (7.0–8.3). High discoloring efficiencies with low chemical oxygen demand removal efficiencies were found in all experiments. The reduction of chromophores in pollutants was the main mechanism of the discoloration in the Fe/Cu system.

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1. Introduction

Wastewater from many industries, such as textile (Rosario et al., 2002), dye (Fu and Viraraghavan, 2001), molasses (Bernardo et al., 1997), olive oil mill (Flouri et al., 1996), yeast (Mutlu et al., 2002), etc., possesses color required to decolorization before discharge. The methods of decolorizing wastewater are mainly zero-valent iron (Fe⁰) (Cao et al., 1999; Deng et al., 2000; Nam and Tratnyek, 2000), coagulation (Kang et al., 2002), activated carbon (Pendyal et al., 1999), membrane (Mutlu et al., 2002), Fenton (Kang et al., 2002), ozone (Chen, 2000), TiO₂/UV (Alaton et al., 2002),

sulfide (Yoo, 2002), bacteria (Banat et al., 1996), Fungus (Fu and Viraraghavan, 2001), enzymes (Young and Yu, 1997), etc.

Of all these methods, only the Fe⁰ is reduction reaction (Larson and Weber, 1994; Weber, 1996; Nam and Tratnyek, 2000). It has been widely investigated and used in discoloration (Larson and Weber, 1994; Weber, 1996; Cao et al., 1999; Deng et al., 2000; Nam and Tratnyek, 2000; Tratnyek et al., 2001). However, some problems have been found in the application of the Fe⁰. Many researchers found that color removal efficiency was very low at neutral range of pH, such as only 9.4% at 6.0 for C.I. reactive red 2 by the Fe⁰ (Deng et al., 2000). High color removal efficiency was only obtained at low pH, such as 58.8% at 3.0. To ensure high color removal efficiency in engineering application of the Fe⁰, therefore, the pH values were generally in acid range. After a period of use, the Fe⁰ bed would become hard,

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resulting in the decrease of color removal efficiency. Fe^0 was largely consumed under the condition of acid pH. In addition, neutral pH range was required for following biological wastewater treatment or final discharge. A lot of precipitant were produced during the neutralization by adding alkaline chemical, increasing the operation cost as well as the load of sludge dewatering and disposal. It was also trouble to adjust the pH value of reaction solution to acid range before the discoloring reaction and then to neutralize it.

Fe^0 was oxidized to ferrous ion, Fe^{2+} , in aqueous environments due to metal corrosion. The standard potential formed by Fe^0 and Fe^{2+} was -0.44 V , making Fe^0 become a reducing agent for many chromophores in pollutants. However, the potential was not enough high to reduce some chromophores, resulting in the low color removal efficiency. A new method, called as an iron and copper bimetallic system (Fe/Cu system) was developed by authors to improve the reduction capacity of Fe^0 with the increase of reaction potential by adding the zero-valent copper (Cu^0). The standard potential formed by Cu^0 and Cu^{2+} was 0.337 V . Fe^0 mixed with Cu^0 , resulting in the formation of infinite galvanic cells with a reaction potential of 0.777 V . High reaction potential made Fe^0 , as anode, more readily lose its electrons, improving its reduction capacity. The discoloring reactions with high efficiency occurred even in neutral range of pH.

This study thus was conducted to investigate the discoloration for both methylene blue in aqueous solution and the colored wastewater from a plant using a Fe/Cu system. Effect factors of this Fe/Cu system for the discoloration were discussed, and optimum conditions were proposed, and its long run in wastewater plant was also investigated.

2. Materials and methods

The powder of Fe^0 (Cao et al., 1999; Deng et al., 2000) or granular (Nam and Tratnyek, 2000) was often used by many researchers, resulting in a high cost and a need separating the Fe^0 from solution in following step. In this experiment, both Fe^0 and Cu^0 shavings (Fe/Cu

shavings), the wastes from mechanical process, were used, reaching a purpose of waste recycle and utilization. They were mixedly put to form a bed (Fe/Cu bed) based on weight ratio of 4:1 (Fe:Cu). The Fe/Cu bed was fixed in a reactor, no need separating the Fe/Cu shavings from solution in following step. Methylene blue was dissolved in water to 40 mg l^{-1} . The colored wastewater came from the influent of a local Shanghai Taopu Municipal Wastewater Treatment Plant processing $6 \times 10^4\text{ m}^3\text{ d}^{-1}$ of wastewater, of which 20% from the domestic effluent of inhabitants and 80% from many factories including producing staining agents, dyes, paints, rubbers, pharmaceutical, etc.

Experiments were conducted in both batch and continuous reactors. In the batch test, both methylene blue solution and the colored wastewater from the plant were investigated. Only the colored wastewater was tested in the continuous experiment. Temperature ranged from 12 to $25\text{ }^\circ\text{C}$ in the continuous experiment, and was controlled at $20\text{ }^\circ\text{C}$ for the batch test.

The batch test was conducted in a 2 l of sealed reactor with a fixed Fe/Cu bed, as shown in Fig. 1a. Individual 1 l of methylene blue solution or the colored wastewater was added into the batch reactor and stirred with an agitator to keep efficient contact between reaction solution and the Fe/Cu bed. Both H_2SO_4 and NaOH were used to adjust initial pH value of solution. Color, chemical oxygen demand (COD), and pH in solution were analysed.

The continuous experiment was conducted in a reactor with a fixed Fe/Cu bed as well as a total volume of 12 l and a working volume of 10 l, as illustrated in Fig. 1b. The reactor was covered with a lid to ensure anaerobic condition and the water level was lower than the top of the Fe/Cu bed to avoid short circuit. The continuous reactor was operated for 140 days with 2 h of hydraulic retention time (HRT) and 5 h^{-1} of flow. Effluent recycle with ratio of 5:1 was used to keep an efficient contact and mix between the wastewater and the Fe/Cu bed. Color, COD, total Fe, and pH in both influent and effluent were monitored. The weight of Fe^0 shavings was also measured before and after the experiment.

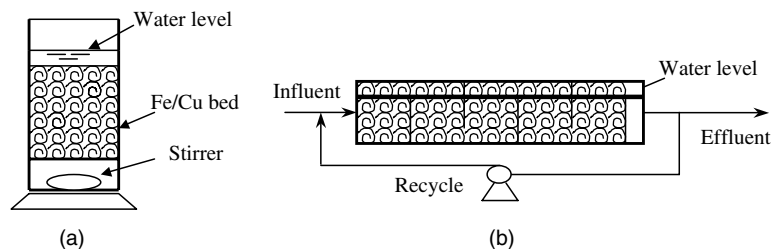


Fig. 1. Experimental set-up: (a) batch and (b) continuous.

Color, COD, and total Fe were measured according to methods in *Standard Methods* (APHA, 1999) and pH was measured using a pH/ISE with a Ross sure-flow pH electrode.

3. Results and discussion

3.1. Batch test

Both methylene blue with 7500 of color and the wastewater with 256 of color from the plant were tested in batch test. Three major factors including Fe/Cu dosage, reaction time, and initial pH were investigated for discoloration. One of three factors varied while keeping other two factors constant levels, 100 g l⁻¹ of Fe/Cu dosage, 120 min of reaction time, and 7.0 of initial pH. During investigating the effect of Fe/Cu dosage, 25, 50, 75, 100, 125, and 150 g l⁻¹ of Fe/Cu shavings were put into the batch reactor, respectively, while keeping 7.0 of initial pH and 120 min of reaction time. Corresponding values were 15, 30, 45, 60, 90, and 120 min for the effect of reaction time, as well as 1, 2, 3, 4, 5, 6, 7, 8, 9 of initial pH values for the effect of initial pH.

3.1.1. Effect of Fe/Cu dosage

Fig. 2 shows the effect of Fe/Cu dosage on removal efficiencies of both color and COD for the wastewater from the plant as well as color for methylene blue. Removal efficiency of color for wastewater from the plant increased rapidly from 50% to 88% with the amount of added Fe/Cu shavings from 25 to 75 g l⁻¹, and was consistently 88% as the dosage of Fe/Cu shavings was further increased to 150 g l⁻¹, as illustrated in Fig. 2. The increase of Fe/Cu dosage presumably enlarged the number (or reactive site) of galvanic cell on the surface area of iron and copper, supplying more opportunities to conduct reducing reaction when the amount of Fe/Cu being below 75 g l⁻¹. Similar results were reported by

previous researchers during the investigation of the discoloration (Cao et al., 1999; Deng et al., 2000) or reductive degradation of carbaryl (Ghauch et al., 2001) by the Fe⁰ system. When the amount of Fe/Cu was over 75 g l⁻¹, mass transfer would become the control factor. Some researchers (Nam and Tratnyek, 2000) also reported that the reduction rate of dye varied with the square-root of mixing rate in the Fe⁰ system, proving that mass transfer was a key control factor.

Fig. 2 also illustrates that COD removal efficiency had same trend as the removal efficiency of color with the added Fe/Cu dosage for wastewater from the plant, increasing stably from 16% to 32% below 100 g l⁻¹ and keeping stable over it. However, color removal efficiencies were almost three times higher than corresponding COD removal efficiencies at same Fe/Cu dosage. The maximum COD removal efficiency was only 34%. The high color removal efficiency but low COD removal efficiency illustrates that only chromophores were destroyed and reduced instead of completely oxidizing the organic pollutants to CO₂ and H₂O in the Fe/Cu system. Some researchers (Larson and Weber, 1994; Weber, 1996; Nam and Tratnyek, 2000) also reported that aromatic azo compounds were only reduced to aromatic amines by the Fe⁰. In addition, aromatic amines with much higher biodegradability than aromatic azo compounds were more easily removed by bacteria in following biological wastewater treatment process (Elsine and Appleton, 1996). The production of Fe²⁺ due to the loss of electron of Fe⁰ during electrochemical reaction would result in an increase of COD level in solution. These low COD removal efficiencies illustrate that some organic pollutants were also removed from solution. The removal of organic pollutants might be attributed by the coagulation of formed Fe(OH)₂. The coagulation of Fe(OH)₂ also may supply part removal of color.

Similar results were found during the research in effect of Fe/Cu dosage on the removal efficiency of color for methylene blue solution as for the colored wastewater from the plant, as shown as in Fig. 2. However, the color removal efficiencies for methylene blue were higher than those for wastewater from the plant at the same Fe/Cu dosage, although the initial color of the former was 29 times of the latter. In addition, color removal efficiency was 94% at 50 g l⁻¹ of Fe/Cu dosage for the former instead of 88% at 75 g l⁻¹ for the latter. One of the main reasons resulting the difference was that the composition of the latter, containing many chemicals, was more complex than the former. Some other pollutants without chromophores probably consumed the electrons supplied by galvanic cell, resulting in the decrease of the color removal efficiency under same conditions. Johnson et al. (1998) also reported that other chemicals in wastewater affected the reducing reaction in the Fe⁰ system.

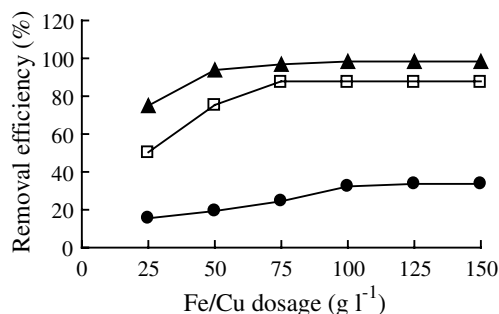


Fig. 2. Effect of Fe/Cu dosage on removal efficiencies of \square : color for wastewater from the plant, \bullet : COD for wastewater from plant, \blacktriangle : color for methylene blue.

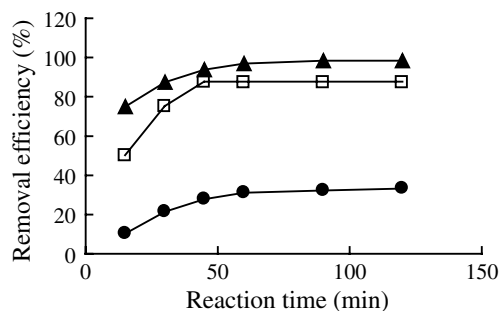


Fig. 3. Effect of reaction time on removal efficiency of \square : color for wastewater from the plant, \bullet : COD for wastewater from plant, \blacktriangle : color for methylene blue.

3.1.2. Effect of reaction time

Fig. 3 shows the effect of reaction time on removal efficiencies of both color and COD for the wastewater from the plant as well as color for methylene blue.

Removal efficiency of color increased rapidly from 0% to 50% in initial 15 min and then to 88% in following 30 min, and kept it during following reaction time, from 45 to 120 min, for the wastewater from the plant, as illustrated in Fig. 3. Previous researcher also reported that the discoloring rate (Cao et al., 1999; Deng et al., 2000) and reductive degradation rate of some chemicals (Ghauch et al., 2001) followed first-order reaction in the Fe^0 system.

Fig. 3 also illustrates that the high removal efficiency of color but low COD removal efficiency with same trend was found during the investigation of effect of reaction time for the wastewater from the plant, as well as higher color removal efficiency for methylene blue solution than that for the wastewater from the plant at same time. These results were similar to those found in effect of Fe/Cu dosage. The reasons resulting the difference were similar to as those discussed previously.

3.1.3. Effect of pH

Fig. 4 shows the effect of initial pH on removal efficiencies of both color and COD for the wastewater from the plant as well as color for methylene blue.

Removal efficiency of color was kept 75% in the range of 1–5 of pH and 88% in 6–9 for the wastewater from the plant, as illustrated in Fig. 4, indicating that acid condition had an adverse effect on the discoloration and optimum pH was in neutral and alkaline solution. Fig. 4 also illustrates that in the tested range of 1–9, pH had no obvious effect on the COD removal efficiency, varying from 25% to 33% with the average of 28% for the wastewater from the plant, as well as the color removal efficiency from 94% to 97% with the average of 96%, for methylene blue solution. Low COD removal

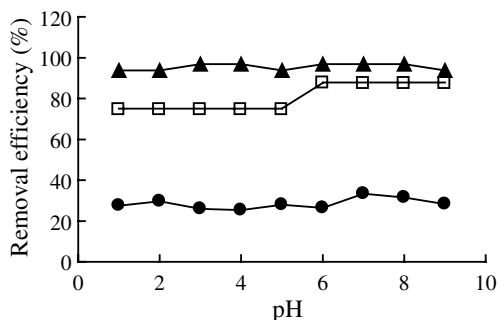


Fig. 4. Effect of initial pH on removal efficiency of \square : color for wastewater from the plant, \bullet : COD for wastewater from plant, \blacktriangle : color for methylene blue.

efficiency indicates that the effluent from the Fe/Cu system must be further purified by biological treatment conducting in neutral range. Neutral pH made the subsequent treatment become easy, no need to adjust the pH.

In formed infinite galvanic cell, Fe^0 was anode, losing electrons to form the Fe^{2+} into the solution. Fe^{2+} in the form of ion had the color itself under the acid condition, increasing the color of the reaction solution. The color of the wastewater from the plant was only 256, not very high. The color of Fe^{2+} ion itself resulted in the decrease of color removal efficiency for the wastewater from the plant in acid condition. However, the color of methylene blue was 7500, very high. Therefore, the color caused by Fe^{2+} ion itself could be neglected during the investigation for the effect of pH on the color removal efficiency of methylene blue. Fe^{2+} will form the precipitation of $Fe(OH)_2$ under neutral and alkaline conditions, resulting in the decrease of effect of the color of Fe^{2+} ion itself and the increase of color removal for the reaction solution by coagulation and adsorption for both the colored wastewater and methylene blue.

Results of this experiment are different from previous reports of other researchers in the Fe^0 system. Deng et al. (2000) found that discoloration efficiency increased greatly from 9.4% to 58.8% with the decrease of pH from 6.0 to 3.0 for the dye of C.I. reactive red 2. Cao et al. (1999) reported that the degradation rate increased with the acidity, rate constants of acid orange II being 0.178, 0.153, and 0.058 $mmol\ l^{-1}\ min^{-1}$, respectively, at pH of 5, 7, 9.

3.2. Continuous test

During the 140 days of continuous test, influent wastewater from the plant with the color ranged from 32 to 256 and 143 of the average value. Corresponding values were 156 to 1342 and 360 $mg\ l^{-1}$ for influent COD, 6.6–7.8 and 7.2 for influent pH, and 7.0–8.3 and

7.6 for effluent pH. Fig. 5 shows removal efficiencies of color and COD for the wastewater from the plant in continuous test. Removal efficiency of color ranged 50–88% with the average of 63%. Removal efficiency of COD varied in wide range of 8–80% with the average of 38%. The average removal efficiency of color in the continuous test was only 63%, lower than the corresponding value, 88%, in batch test. The reason resulted in the difference might be that the mixing strength in the former by effluent recycle was smaller than that in the latter by magnetic stir. Mass transfer was also reported to be a limited factor of discoloration of dye in the Fe^0 system (Nam and Tratnyek, 2000).

Fig. 5 also illustrates that the Fe/Cu system effectively decreased the color of the wastewater from the plant but not for COD. The results are similar to those in the batch test. The reason resulted in the difference was also discussed in previous section.

Total iron consumed in the continuous reactor with the Fe/Cu system was 0.65 kg in 140 days, averaging 39 mg l^{-1} of Fe^{2+} in effluent. This data matched measured $35\text{--}37 \text{ mg l}^{-1}$ of total Fe^{2+} in effluent.

There were conflicting reports on if the discoloration of the dyes came from the adsorption of iron powder in the Fe^0 system. Some researchers (Tang and Chen, 1996) attributed the discoloration of the dyes to adsorption by iron powder and oxidation by photo-Fenton's reagent during a $\text{H}_2\text{O}_2/\text{Fe}^0$ system. However, other researchers (Nam and Tratnyek, 2000) proved that the adsorption of the dyes on iron particles was below 4% of the initial concentration, and over 90% mass balance was achieved by summing aqueous concentrations of dye and product amine. In this research, the reactor with the fixed Fe/Cu bed continuously removed the color of the wastewater from the plant with only the lost of 0.65 kg of iron during 140 days of run, indicating that adsorption was not the main contribution for the discoloration of the wastewater.

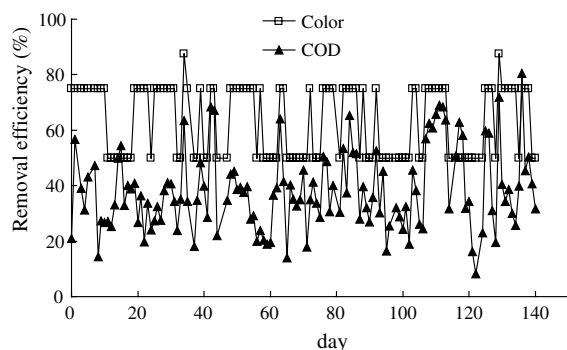


Fig. 5. Removal efficiency of \square : color and \blacktriangle : COD for wastewater from the plant in continuous test.

4. Conclusion

- (1) The Fe/Cu system effectively removed the color of both methylene blue and the colored wastewater from influent of the wastewater treatment plant with maximum color removal efficiencies of 98% and 88%, respectively, in batch test.
- (2) Removal efficiency of color increased rapidly with Fe/Cu dosage and reaction time, respectively, at initial time and slowly to stable values.
- (3) The Fe/Cu system had a wide pH application range. pH, ranging 1–9, had no obvious effect on the color removal efficiency for methylene blue solution. However, low pH reduced the color removal efficiency for the wastewater from the plant. Optimum pH ranged from 6 to 9, neutral range, making subsequent treatment become easy, no need to adjust the pH.
- (4) The results of 140 days operation in the continuous test show that the Fe/Cu system supplied a long and stable removal of color for the wastewater from the plant, with the average of 63% color removal efficiency under the condition of neutral range of pH (7.0–8.3) and 2 h of HRT.
- (5) The results, high color removal efficiency but low COD removal efficiency at same time for the wastewater from the plant, found in both batch and continuous tests show that discoloration mainly resulted from the reduction of chromophores instead of their oxidation. The formed $\text{Fe}(\text{OH})_2$ also attributed some removal of both color and organic pollutants by coagulation and adsorption.
- (6) The materials of the Fe/Cu system were the wastes from mechanical process, reaching the purpose of waste recycle and utilization.

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References

- Alaton, I.A., Balcioglu, I.A., Bahnemann, D.W., 2002. Advanced oxidation of a reactive dyebath effluent: comparison of O_3 , $\text{H}_2\text{O}_2/\text{UV-C}$ and $\text{TiO}_2/\text{UV-A}$ processes. *Water Res.* 36, 1143–1154.
- APHA, 1999. *Standard Methods—for the Examination of Water and Wastewater*, 20th ed. American Public Health Association, American Water Works Association, Water Pollution Control Federation, Washington, DC.
- Banat, I.M., Nigam, P., Singh, D., Marchant, R., 1996. Microbial decolorization of textile-dye-containing effluents: a review. *Bioresour. Technol.* 58, 217–227.

- Bernardo, E.C., Egashira, R., Kawasaki, J., 1997. Decolorization of molasses' wastewater using activated carbon prepared from cane bagasse. *Carbon* 35, 1217–1221.
- Cao, J., Wei, L., Huang, Q., Wang, L., Han, S., 1999. Reducing degradation of azo dye by zero-valent iron in aqueous solution. *Chemosphere* 38, 565–571.
- Chen, L.C., 2000. Effects of factors and interacted factors on the optimal decolorization process of methyl orange by ozone. *Water Res.* 34, 974–982.
- Deng, N., Luo, F., Wu, F., Xiao, M., Wu, X., 2000. Discoloration of aqueous reactive dye solution in the UV/Fe⁰ system. *Water Res.* 34, 2408–2411.
- Elsine, L., Appleton, A., 1996. A nickel-iron wall against contaminated groundwater. *Environ. Sci. Technol.* 30, 536–539.
- Flouri, F., Sotirchos, D., Ioannidou, S., Balis, C., 1996. Decolorization of olive oil mill liquid wastes by chemical and biological means. *Int. Biodeter. Biodegr.* 38, 189–192.
- Fu, Y., Viraraghavan, T., 2001. Fungal decolorization of dye wastewaters: a review. *Bioresour. Technol.* 79, 251–262.
- Ghauch, A., Gallet, C., Charef, A., Rima, J., Martin-Bouyer, M., 2001. Reductive degradation of carbaryl in water by zero-valent iron. *Chemosphere* 42, 419–424.
- Johnson, T.L., Fish, W., Gorby, Y.A., Tratnyek, P.G., 1998. Degradation of carbon tetrachloride by iron metal: complexation effects on the oxide surface. *J. Contam. Hydrol.* 29, 377–396.
- Kang, S.F., Liao, C.H., Chen, M.C., 2002. Pre-oxidation and coagulation of textile wastewater by the Fenton process. *Chemosphere* 46, 923–928.
- Larson, R.A., Weber, E.J., 1994. Reaction Mechanisms in Environmental Organic Chemistry. CRC Press, Boca Raton. pp. 181–185.
- Mutlu, S.H., Yetis, U., Gurkan, T., Yilmaz, L., 2002. Decolorization of wastewater of a baker's yeast plant by membrane processes. *Water Res.* 36, 609–616.
- Nam, S., Tratnyek, P.G., 2000. Reduction of azo dyes with zero-valent iron. *Water Res.* 34, 1837–1845.
- Pendyal, B., Johns, M.M., Marshall, W.E., Ahmedna, M., Rao, R.M., 1999. Removal of sugar colorants by granular activated carbons made from binders and agricultural by-products. *Bioresour. Technol.* 69, 45–51.
- Rosario, L.C., Abel, G.E., Marta, I.L., 2002. Photodegradation of an azo dye of the textile industry. *Chemosphere* 48, 393–399.
- Tang, W.Z., Chen, R.Z., 1996. Discoloration kinetics and mechanisms of commercial dyes by H₂O₂/iron powder system. *Chemosphere* 32, 947–958.
- Tratnyek, P.G., Reilkoff, T.E., Lemon, A., Scherer, M.M., Balko, B.A., Feik, L.M., Henegar, B., 2001. Visualizing redox chemistry: probing environmental oxidation–reduction reactions with indicator dyes. *Chem. Educat.* 16, 172–179.
- Weber, E.J., 1996. Iron-mediated reductive transformations: investigation of reaction mechanism. *Environ. Sci. Technol.* 30, 716–719.
- Yoo, E.S., 2002. Kinetics of chemical decolorization of the azo dye C.I. reactive orange 96 by sulfide. *Chemosphere* 47, 925–931.
- Young, L., Yu, J., 1997. Ligninase-catalyzed decolorization of synthetic dyes. *Water Res.* 31, 1187–1193.