

REMOVAL OF COD AND COLOR FROM REACTIVE RED 45 AZO DYE WASTEWATER USING FENTON AND FENTON-LIKE OXIDATION PROCESSES: KINETIC STUDIES

BAYAR, S. * – ERDOGAN, M.

*Ataturk University, Faculty of Engineering, Department of Environmental Engineering
25240 Erzurum, Turkey
(phone: +90 442 2314826; fax: +90 442 2314818)*

**Corresponding author
e-mail: sbayar@atauni.edu.tr; fax: +90 442 2314818*

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Abstract. The present study dealt with the removal of Reactive Red 45 (RR45) azo dye material through Fenton and Fenton-like oxidation processes. The effects of pH, Fe²⁺ and Fe³⁺ dosages, hydrogen peroxide (H₂O₂), concentration of colorant and temperature were evaluated. Removal of the colorant RR45 was monitored by considering color and Chemical Oxygen Demand (COD). Results showed that Fenton process is more efficient than Fenton-like processes in terms of color and COD removal efficiency. A removal efficiency of 91.1% of COD and 99.90% of color was obtained under optimum experimental conditions where initial solution pH was 3, the concentration of RR45 colorant was 200 mg L⁻¹, rates of Fe²⁺ and H₂O₂ were 75 mg L⁻¹ and 400 mg L⁻¹, respectively, reaction temperature was 50°C and experiment time was 30 min. In addition, the first order, second order and Behnajady-Modirshahla-Ghanbery (BMG) models were applied and the best results were obtained by BMG model.

Keywords: *colorant, Fenton reaction, hydroxyl radical, H₂O₂, kinetic modelling*

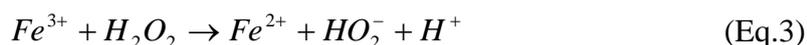
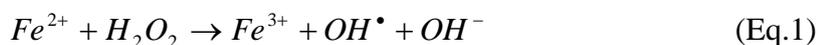
Introduction

Today, industrialization is developing in line with the demand of increasing human population and consumption and several new industries are added to the existing industrial facilities depending on this increasing demand. Pollution parameters may vary depending on the types of industries and wastewater is produced with different characteristics.

The textile industry exhibits higher polluting characteristics in terms of wastewater volume and composition than other industrial sectors (Vandevivere et al., 1998). Water consumption in the textile industry ranges from 25 to 250 m³ per ton of product (Chacón et al., 2006). Numerous different types of dyes are used in different industries for different purposes. Dyes contain different chemical structures. However, they are generally composed of two components, chromophore and function group. Chromophore is an important compound for the color of the dye. The functional group, on the other hand, allows dye to bind to cotton or wool yarn. Different types of functional groups are used for dyeing different types of textile materials (Kayıkooğlu and Debik, 2006). They are characterized in terms of their chemical structures as azo, triaryl methane, anthraquinone, heterocyclic and phthalocyanine dyes. They are also categorized into six groups for their application methods as wattle, reactive, direct, acidic, disperse and cationic dyes (Xu et al., 2004). In recent years, advanced wastewater treatment methods, known to be environmentally friendly in wastewater treatment, have been used since they can oxidize wastewaters which are hard to biodegrade to a more harmless form (e.g. carbon dioxide, water and inorganic salts) (Neyens and Baeyens,

2003; Primo et al., 2008). Fenton process is one of these methods. In Fenton reaction, the hydroxyl radical (OH^\bullet) was shown to form after a series of reactions consisting of iron and iron salts and catalytic cracking of hydrogen peroxide (Harber and Weiss, 1934). This process is based on the formation of (OH^\bullet) under acidic conditions as a homogeneous catalytic oxidation process.

Fenton oxidation involves chemical mechanisms expressed by the following equations (Eqs. 1-5) (Sun et al., 2009a).



As an overview, the Fenton process consists of four steps; pH adjustment, oxidation reaction, neutralization and precipitation reaction through coagulation. In this way, the organic materials are removed in two steps, oxidation and coagulation (Kang and Hwang, 2000). According to the studies conducted in literature, Fenton process is widely used in removing organic materials (Fan et al., 2013), reducing toxicity (Zhang et al., 2014), phenol removal (Mofrad et al., 2015), textile wastewater treatment (Latif et al., 2015), color removal (Bouasla et al., 2010; Ertugay and Acar, 2017) and removal of organic matter from cosmetic waste water (Bayhan and Değermenci, 2017). In this study, Fenton and Fenton-like process studies were evaluated for color and COD removal of wastewaters from synthetic textile products prepared with colorant called commercially Reactive Red 45 and used in textile dyeing. In the experimental studies carried out, the effects of pH, rate of Fe^{2+} or Fe^{3+} salts and H_2O_2 , initial dye concentration and temperature parameters on removal efficiency were investigated. Obtained data of kinetic studies were applied to the kinetic models, first-order, second-order and BMG models.

Materials and Methods

RR45 colorant was obtained from a commercial company, Duraner Boya A.Ş. The molecular weight of azo colorant (RR45) 802.1 g mol^{-1} , whose molecular is $\text{C}_{27}\text{H}_{19}\text{ClN}_7\text{Na}_3\text{O}_{10}\text{S}_3$. RR45 exhibits a complex structure together with azo aromatic groups and is used commonly in textile industry (Swarnkar et al., 2015). As the result of spectrum scanning of colorant, maximum absorbance was found to be 243 nm, 283 nm and 541 nm. Molecular structure of RR45 colorant is given in Fig. 1.

The experimental device was constituted of a perfectly agitated reactor in which a volume (600 ml) of solution was studied. In experiments, pH adjustment of the dye prepared in the desired concentration was performed first by adding diluted H_2SO_4 and NaOH . Following this stage, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ or $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and H_2O_2 were added and stirred fast for 3 min at 150 rpm and then slowly for 27 min at 50 rpm and the resultant

mixture was filtered through 0.45 μm membrane filter. Color and COD measurements were then performed. Both experiments and analysis were repeated twice at the same conditions to ensure the accuracy of data and the averages values were given. Color measurements were conducted and values were registered at 541 nm wave-length spectrophotometrically. COD analyses were also conducted spectrophotometrically at 600 nm, 148°C and Merck Spectroquant TR320 according to Standard Methods (APHA 1998). *Table 1* gives the average COD values for the initial colorant concentration. In Fenton and Fenton-like processes; the investigated parameters and ranges are given in *Table 2*.

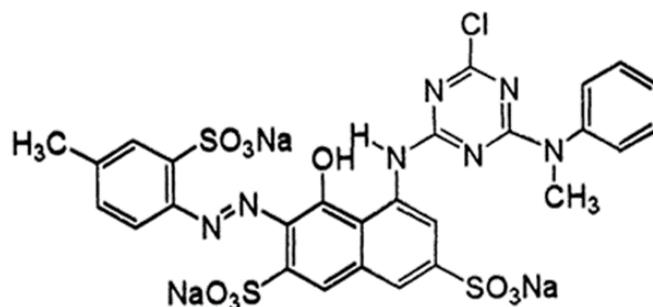


Figure 1. Structure of RR45 dye

Table 1. Title of the table Average COD values for the initial colorant concentration

Initial colorant concentration (mg L ⁻¹)	150	200	250	300	350	500
Average COD value (mg L ⁻¹)	115.08	135.10	186.99	219.44	264.87	326.52

Table 2. Experimental parameters

Process	Parameters	Investigated parameters range	Fixed variables
Fenton Process	Fe ²⁺ concentration (mg L ⁻¹)	25; 50; 75; 100; 125;150; 200	C ₀ =200 mg L ⁻¹ , H ₂ O ₂ =500 mg L ⁻¹ , pH=3, T=20°C, t=30 min
	H ₂ O ₂ concentration (mg L ⁻¹)	100; 200; 300; 400; 500; 600	C ₀ =200 mg L ⁻¹ , Fe ²⁺ =75mg L ⁻¹ , pH=3, T=20°C, t=30 min
	pH	2.5; 3.0; 4.0; 5.0	C ₀ =200 mg L ⁻¹ , Fe ²⁺ =75 mg L ⁻¹ , H ₂ O ₂ is 400 mg L ⁻¹ T=20°C, t=30 min
	Colorant concentration (mg L ⁻¹)	150; 200; 250; 300; 350; 500	Fe ²⁺ = 75 mg L ⁻¹ ; H ₂ O ₂ = 400 mg L ⁻¹ ; pH= 3; T= 20°C; t= 30 min
	Temperature (°C)	20; 30; 40; 50; 60	C ₀ =200 mg L ⁻¹ ; Fe ²⁺ =75 mg L ⁻¹ ; H ₂ O ₂ is 400 mg L ⁻¹ ; t=30 min
Fenton-like process	Fe ³⁺ concentration (mg L ⁻¹)	25; 50; 75; 100; 125;150	C ₀ =200 mg L ⁻¹ , H ₂ O ₂ =500 mg L ⁻¹ , pH=3, T=20°C, t=30 min
	H ₂ O ₂ concentration (mg L ⁻¹)	100; 200; 300; 400; 500; 600	C ₀ =200 mg L ⁻¹ , Fe ³⁺ =75mg L ⁻¹ , pH=3, T=20°C, t=30 min
	pH	2.5; 3.0 ; 4.0; 5.0	C ₀ =200 mg L ⁻¹ , Fe ³⁺ =75 mg L ⁻¹ , H ₂ O ₂ is 500 mg L ⁻¹ T=20°C, t=30 min
	Colorant concentration (mg L ⁻¹)	150; 200; 250; 300; 350; 500	Fe ³⁺ = 75 mg L ⁻¹ ; H ₂ O ₂ = 500 mg L ⁻¹ ; pH= 3; T= 20°C; t= 30 min
	Temperature (°C)	20; 30; 40; 50; 60	C ₀ =200 mg L ⁻¹ ; Fe ³⁺ =75 mg L ⁻¹ ; H ₂ O ₂ is 500 mg L ⁻¹ ; t=30 min

Results and discussion

Effect of iron dosage

The dosage of the Fenton reactive in the Fenton and Fenton-like oxidation process plays a very important role in the degradation of organic substances and the determination of the total cost of the process. In general, as the dosage of Fe^{2+} and Fe^{3+} increases, degradation rate of organic materials increases. However, a very large increase in the Fe^{2+} and Fe^{3+} ions leads to an increase in the amount of total dissolved iron ions. Therefore, it is necessary to avoid the formation of excessive amount of sludge (Saini et al., 2017). Fe^{2+} and Fe^{3+} experiments were first carried out in the determination of color and COD removals in the Fenton and Fenton-like oxidation of RR45. For this aim, experiments were conducted by fixing samples prepared at a dye concentration of 200 mg L^{-1} to 500 mg L^{-1} H_2O_2 and adding Fe^{2+} and Fe^{3+} at the concentrations of 25, 50, 75, 100, 125, 150, 200 mg L^{-1} .

As the result of the experiments (Fig. 2), the largest removal yields were obtained at 100 mg L^{-1} Fe^{2+} concentration for Fenton oxidation and at 75 mg L^{-1} Fe^{3+} concentration for Fenton-like oxidation. In the Fenton process, when Fe^{2+} concentration increased from 25 mg L^{-1} to 100 mg L^{-1} color removal yield continued at 98% level while COD removal yield increased from 55.2% to 80.31%. When Fe^{2+} concentration increases from 100 mg L^{-1} to 200 mg L^{-1} , COD removal yield decreases from 80.31% to 76.72% while color removal decreases from 98.69% to 82.13%. In the case of the Fenton-like oxidation, in all Fe^{3+} dosage experiments, color removal yield was obtained to be nearly 99% while in the same Fe^{3+} dosage range (25 mg L^{-1} to 75 mg L^{-1}) COD removal yield was between 63.80% and 74.10% and at 200 mg L^{-1} it decreased to 52.12%. Since no main factor is present to produce hydroxyl radicals in the absence of iron ion, an effective oxidation based on Fenton reaction cannot be achieved. As the Fe^{2+} and Fe^{3+} concentration increases, theoretically higher rate of OH^\bullet radicals will be produced.

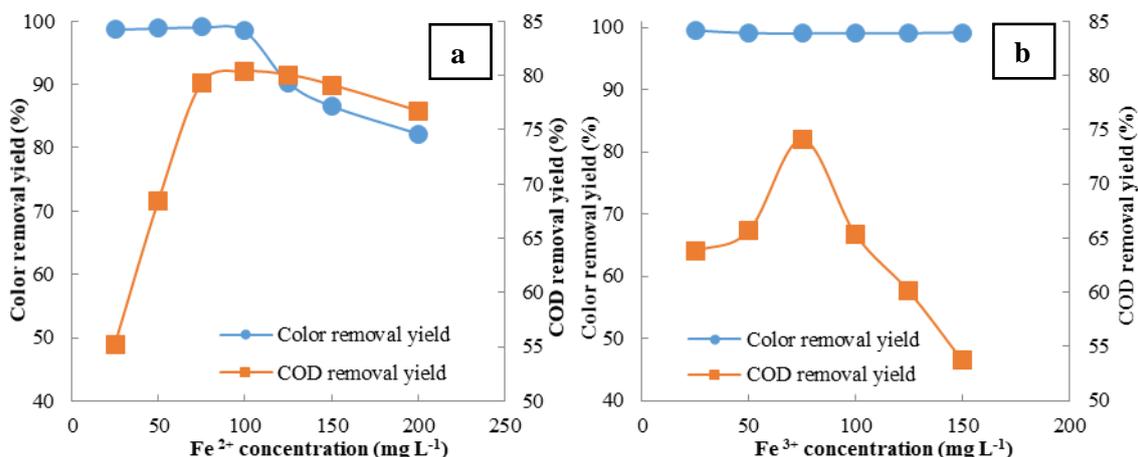
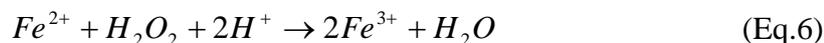


Figure 2. Effect of iron doses on color and COD removal (a) Fenton and (b) Fenton-like processes ($C_0=200 \text{ mg L}^{-1}$, $\text{H}_2\text{O}_2=500 \text{ mg L}^{-1}$, $\text{pH}=3$, $T=20^\circ\text{C}$, $t=30 \text{ min}$)

Such a situation is thought to affect unfavorably oxidation capacity of excessive Fe^{2+} concentration. It is known that in accordance with Eq. 2, higher concentrations of Fe^{2+} , can cause the consumption of OH^\bullet radicals (radical scavenger effect) and thus

decreasing removal yield (Tang and Chen, 1996; Lunar et al., 2000; Ntampegliotis et al., 2006; Pérez-Moya et al., 2007).

In addition, when solution media is acidic, higher Fe^{2+} concentrations can cause based on Eq. 6, and additional reaction resulting in the transformation of H_2O_2 into water (Tarr, 2003).



In Fenton process, as the result of experiments, at the concentrations of 75 mg L^{-1} and 100 mg L^{-1} , color and COD removal yields are nearly the same and therefore, optimum Fe^{2+} dosage was determined to be 75 mg L^{-1} for cost effectiveness. In a condition of fenton-like process, optimum Fe^{3+} dosage was determined to be 75 mg L^{-1} for the highest removal yields.

Effect of H_2O_2 concentration

H_2O_2 concentration is an important parameter in Fenton processes. Determination of the optimum H_2O_2 concentration value in Fenton processes is important for removal yield of the process and for its applicability based on the cost of H_2O_2 . In Fenton reactions, hydrogen peroxide plays very important roles as the production source of hydroxyl radicals (Sun et al., 2009a).

In order to determine the most suitable H_2O_2 rate in fenton and Fenton-like process, doses were adjusted to 100 mg L^{-1} to 600 mg L^{-1} of H_2O_2 concentrations by fixing $C_0=200 \text{ mg L}^{-1}$, Fe^{2+} and $Fe^{3+}=75 \text{ mg L}^{-1}$, $pH=3$ and $T=20^\circ\text{C}$. Experimental results are given in Fig. 3.

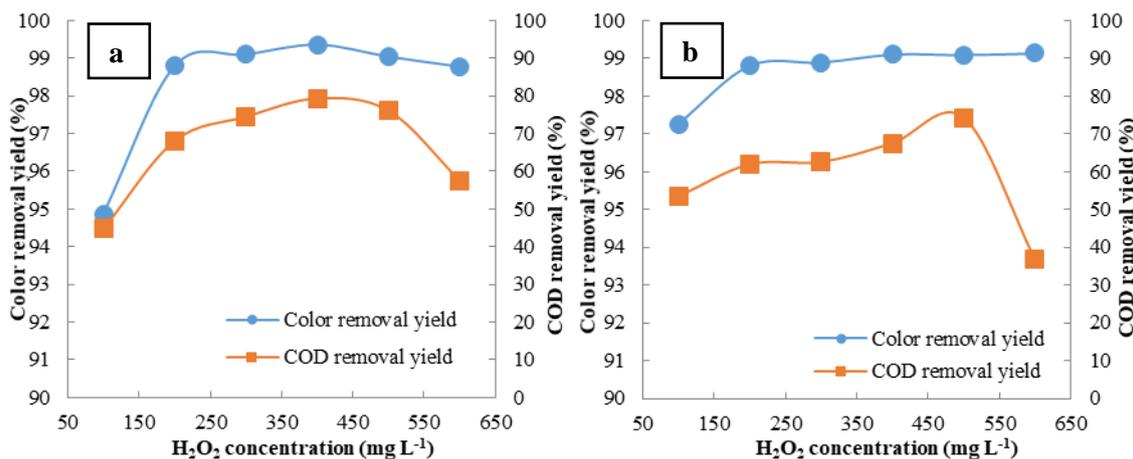


Figure 3. Effect of H_2O_2 doses on color and COD removal (a) Fenton and (b) Fenton-like processes ($C_0=200 \text{ mg L}^{-1}$, Fe^{2+} and $Fe^{3+}=75 \text{ mg L}^{-1}$, $pH=3$, $T=20^\circ\text{C}$, $t=30 \text{ min}$)

When considered (Fig. 3), it is seen that at the end of a 30 – min reaction time, increase of H_2O_2 concentration from 100 mg L^{-1} to 400 mg L^{-1} causes increases in both color and COD removal yields. When H_2O_2 concentration increases from 100 mg L^{-1} to 400 mg L^{-1} , color removal yield rises from 94.87% to 99.35% while COD removal yield rises up from 44.66% to 79.25%. At the concentrations above 400 mg L^{-1} , H_2O_2 dosing

causes decreases in color and COD removal yields. In case H_2O_2 concentration rises from 400 mg L^{-1} to 600 mg L^{-1} , color and COD removals were 98.77% and 57.38%. In the case of the Fenton-like oxidation, in all H_2O_2 concentration experiments, color removal yield was obtained to be nearly 98% while in the same H_2O_2 concentration range (100 mg L^{-1} to 500 mg L^{-1}) COD removal yield was between 53.40% and 74.10% and at 600 mg L^{-1} it decreased to 36.67%.

In general, increase in H_2O_2 dosage increases the degradation rates of pollutants (Lin and Lo, 1997; Lin et al., 1999; Kang and Hwang, 2000; Babuponnusami and Muthukumar, 2014). However, great care should be taken when deciding on H_2O_2 dosage in the studies. Unused part of H_2O_2 may cause COD in Fenton processes to increase and so at excessive concentration, H_2O_2 is not advisable (Lin and Lo, 1997). In the same way, H_2O_2 is harmful for several living organisms. Another unfavorable effect of H_2O_2 is the radical scavenger effect of (OH^\bullet) radicals (Eq. 5). Such a condition is seen at excessive concentrations and H_2O_2 (Tang and Chen, 1996; Kitis et al., 1999; Ntampeglitis et al., 2006; Sun et al., 2007). At the end of the experiments, optimum H_2O_2 concentration was found to be 400 mg L^{-1} for Fenton process and 500 mg L^{-1} for the Fenton-like process by considering both removal yield and the cost of H_2O_2 .

Effect of pH

pH is a highly important parameter for producing OH^\bullet radicals in Fenton and Fenton-like process (Singh and Tang, 2013; Mofrad et al., 2015). In the experiments in order to determine optimum pH in the treatment of RR45 colorant through Fenton and Fenton-like process, beakers were filled first with RR45 with the concentration of $C_0 = 200 \text{ mg L}^{-1}$ taken from stocked solution and then, 75 mg L^{-1} of Fe^{2+} or Fe^{3+} , H_2O_2 is 400 mg L^{-1} (for Fenton process) or 500 mg L^{-1} (for Fenton-like process) found to be optimum were added and experiments were conducted between pH 2.5 and 5.0. Results obtained are showed graphically in Fig. 4. In the experiments, at the end of 30 – min experiment time, the highest color and COD removal yield for both fenton and Fenton-like processes were achieved at pH 3. In the experiments conducted with pH above and below 3, color and COD removal yields decreased.

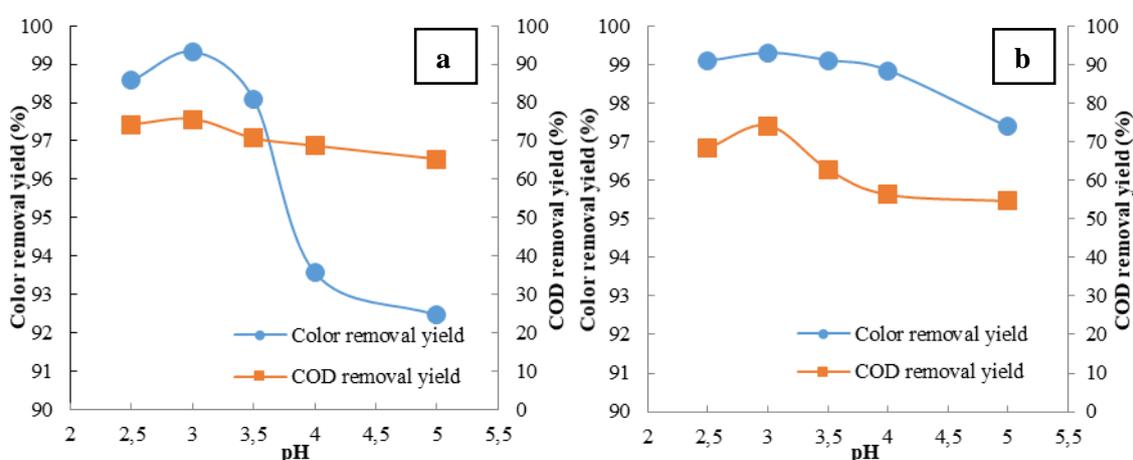


Figure 4. Effect of pH on color and COD removal (a) Fenton and (b) Fenton-like processes ($C_0 = 200 \text{ mg L}^{-1}$, Fe^{2+} and $\text{Fe}^{3+} = 75 \text{ mg L}^{-1}$, H_2O_2 is 400 mg L^{-1} (for Fenton process) or 500 mg L^{-1} (for Fenton-like process), $T = 20^\circ\text{C}$, $t = 30 \text{ min}$)

When pH is below 3, since complex iron types $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Fe}(\text{H}_2\text{O})_5\text{OH}]^{2+}$ reacting with H_2O_2 slower are formed, *reactions 2* and *7* also slow down and in that case oxidation removals also decrease.



In addition, under low pH conditions ($\text{pH} < 3$), formation of oxonium ion $[\text{H}_3\text{O}_2]^+$ which increases the stability of H_2O_2 and limits the production of OH^\bullet radical may cause the *reactions 3* and *8* to slow down (Bouasla et al., 2010; Singh and Tang, 2013).



At pHs lower than 3, reason for the decrease in color and COD removal yields is that excessive amount of H^+ ions reacts with H_2O_2 and forms stable oxonium ion (H_3O_2^+) (Eq. 9).



Production of OH^\bullet radical decreases since precipitating $\text{Fe}(\text{OH})_3$ is formed when pH is above 3 (Eq. 10).



Following this precipitation, production of Fe^{2+} from Fe^{3+} stops and then the production of OH^\bullet radical decreases (Chen and Pignatello, 1997; Bouasla et al., 2010). In addition, as pH increases, rate of self – degradation of H_2O_2 increases (Eq. 11).



The effect of initial colorant concentration

The effect of initial RR45 concentration on the removal yield in the Fenton and Fenton-like oxidation process was studied with dye concentrations of 150, 200, 250, 300, 350 and 500 mg L^{-1} . Experiments were conducted under the conditions, where pH is 3, H_2O_2 is 400 mg L^{-1} (for Fenton process) or 500 mg L^{-1} (for Fenton-like process), T is 30 min and Fe^{2+} is 75 mg L^{-1} or Fe^{3+} is 75 mg L^{-1} . Experimental results are shown graphically in *Fig. 5* and *Fig. 6*. As can be seen from *Fig. 5* and *Fig. 6*, as the initial colorant concentration increases both color and COD removal yields decreased. With the increase in initial colorant concentration from 150 mg L^{-1} to 500 mg L^{-1} , color removal yield decreased from 99.91% to 98.83% while COD removal yield from 77.93% to 55.13% in the Fenton oxidation and 73.80% to 46.70% in the Fenton-like oxidation process, respectively. Reason for this is that as the initial colorant concentration increases the number of dye molecules also increases. In this case, there was no change in the number of OH^\bullet radicals since the concentrations of Fe^{2+} and H_2O_2 did not change in the medium. Reduced removal yields were observed since there would be less OH^\bullet radicals matching with increasing number of dye molecules. Similar

trend is seen in several studies in literature (Malik and Saha, 2003; Lucas and Peres, 2006; Sun et al., 2007; Bouasla et al., 2010; Harichandran and Prasad, 2016).

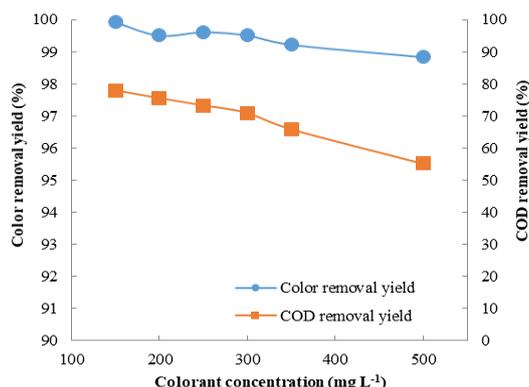


Figure 5. Effect of initial colorant concentration in Fenton oxidation on color and COD removal ($Fe^{2+} = 75 \text{ mg L}^{-1}$; $H_2O_2 = 400 \text{ mg L}^{-1}$; $pH = 3$; $T = 20^\circ\text{C}$; $t = 30 \text{ min}$)

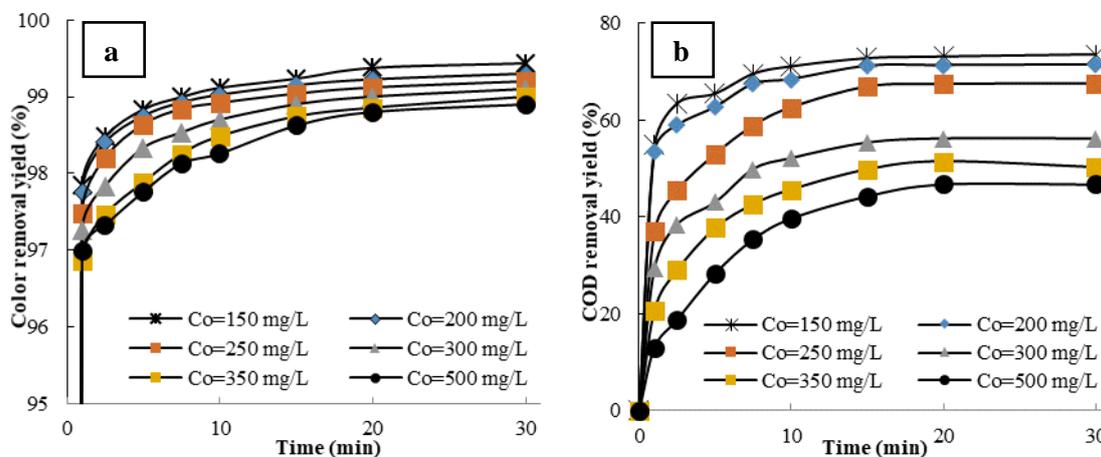


Figure 6. Effect of initial colorant concentration in Fenton-like oxidation on (a) color and (b) COD removal ($Fe^{3+} = 75 \text{ mg L}^{-1}$; $H_2O_2 = 500 \text{ mg L}^{-1}$; $pH = 3$; $T = 20^\circ\text{C}$; $t = 30 \text{ min}$)

The Effect of Temperature

Temperature may have effects on the reactions between H_2O_2 , Fe^{2+} and Fe^{3+} . Experiments were conducted at initial RR45 concentration of 200 mg L^{-1} , H_2O_2 concentration of 400 mg L^{-1} for fenton or 500 mg L^{-1} for fenton-like process, Fe^{2+} and Fe^{3+} concentration of 75 mg L^{-1} , $pH=3$, $t=30 \text{ min}$ and temperature between 20°C and 60°C in order to investigate the effect of RR45 on the temperature in the Fenton reactions.

Experiments were conducted in order to investigate the effect of temperature in the Fenton reactions of RR45. Results obtained are given graphically in Fig. 7. As can be seen from Fig. 7, in all temperature experiments, color removal yield was obtained to be nearly 100% while in the same temperature range (20°C to 50°C) COD removal yield was between 75.50% and 91.11% and at 60°C it decreased to 84.17% for Fenton process and COD removal yield was between 71.42% and 87.80% and at 60°C it decreased to

75.09% for Fenton-like oxidation process. The reason for the increasing removal yield with increasing temperatures may be that the high temperatures can cause both higher Fenton, Fenton-like reaction rates and the formation of larger amount of OH^\bullet radicals (Sun et al., 2009b). The reason for the decrease at 60°C may be the degradation of H_2O_2 at higher temperatures (Bouasla et al., 2010) and evaporation (Bayhan and Değermenci, 2017).

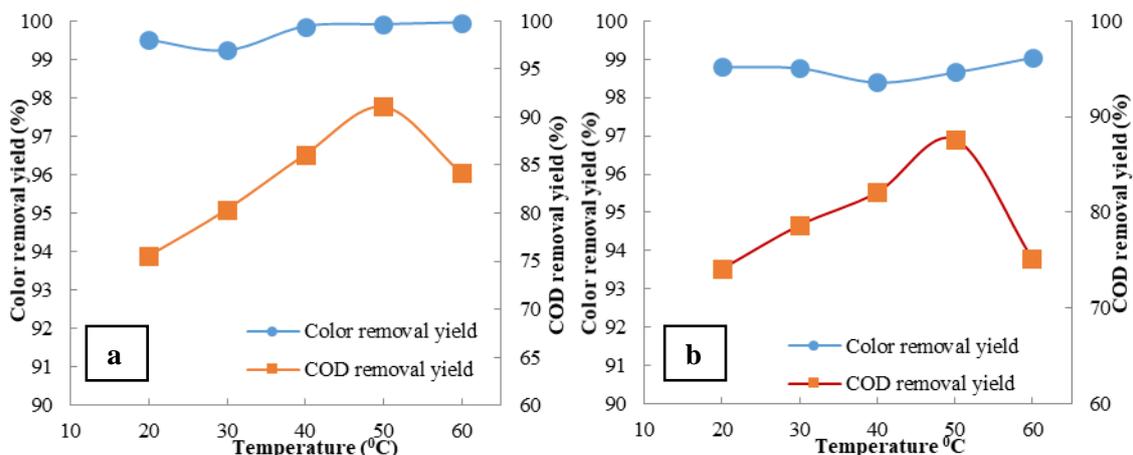


Figure 7. Effect of temperature on color and COD removal (a) Fenton and (b) Fenton-like processes ($C_0=200 \text{ mg L}^{-1}$; Fe^{2+} and $\text{Fe}^{3+} = 75 \text{ mg L}^{-1}$; H_2O_2 is 400 mg L^{-1} (for Fenton process) or 500 mg L^{-1} (for Fenton-like process); $t=30 \text{ min}$)

Kinetic experiments

In the present study, first-order, second-order and BMG reaction kinetics were used to study the removal COD kinetics of RR45 by the Fenton-like oxidation process. Kinetic studies were not performed in the Fenton process because color and COD removal yield have been obtained very fast. The kinetic parameters calculated for each reaction kinetics using the data obtained from experiments at different initial dye concentrations are given in Table 3. The results of kinetic analysis were shown in Table 4. The fitness of kinetic data to the first-order, second-order and BMG reaction kinetics model were given in Figs. 8-9 and 10.

Table 3. The equations of kinetic models

Kinetic model	Mathematical equations	Pilots	Equations	References
Pseudo-first-order	$\ln C_t = \ln C_0 - k_1 t$	$\ln\left(\frac{C_0}{C_t}\right)$ versus t	(Eq.12)	Sun et al., 2009a; Ertugay and Acar 2017
Pseudo-second-order	$\frac{1}{C_t} = \frac{1}{C_0} + k_2 t$	$\frac{1}{C_t}$ versus t	(Eq.13)	Sun et al., 2009a; Ertugay and Acar 2017
Behnajady–Modirshahla–Ghanbery (BMG)	$\frac{C_t}{C_0} = 1 - \frac{t}{m+b}$ $\frac{t}{1 - \left(\frac{C_t}{C_0}\right)} = m + bt$	$\frac{t}{1 - \left(\frac{C_t}{C_0}\right)}$ versus t	(Eq.14) (Eq.15)	Behnajady et al., 2007; Ertugay and Acar 2017

where C_0 (mg L^{-1}) and C_t (mg L^{-1}) are the concentration of COD the concentration at initial and at any time, respectively; k_1 and k_2 are first-order and second-order reaction rate constant; t is the reaction time; b and m are two characteristic constants relating to the reaction kinetics and oxidation capacities

Table 4. The parameters of kinetic models and correlation coefficients (R^2) for the COD removal of RR45

RR45 (mg L ⁻¹)	First-order kinetic model		Second-order kinetic model		BMG kinetic model		
	k ₁ (min ⁻¹)	R ₂	k ₂ (L mg ⁻¹ min ⁻¹)	R ₂	1/m	1/b	R ²
150	0.0280	0.4350	0.0060	0.5825	0.997	0.835	0.9980
200	0.0271	0.4554	0.0050	0.5987	1.678	0.724	0.9995
250	0.0299	0.6276	0.0003	0.7400	0.718	0.697	0.9977
300	0.0213	0.5918	0.0002	0.6788	0.590	0.581	0.9976
350	0.0198	0.6456	0.0001	0.7093	0.381	0.531	0.9951
500	0.0200	0.7555	0.00009	0.8047	0.185	0.512	0.9840

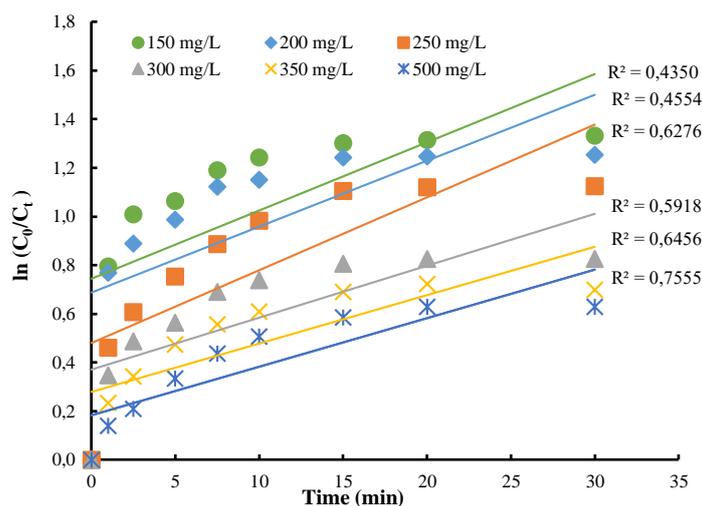


Figure 8. First-order reaction kinetic for the COD removal of RR45 by Fenton-like oxidation ($Fe^{3+} = 75 \text{ mg L}^{-1}$; $H_2O_2 = 500 \text{ mg L}^{-1}$; $pH = 3$; $T = 20^\circ C$; $t = 30 \text{ min}$)

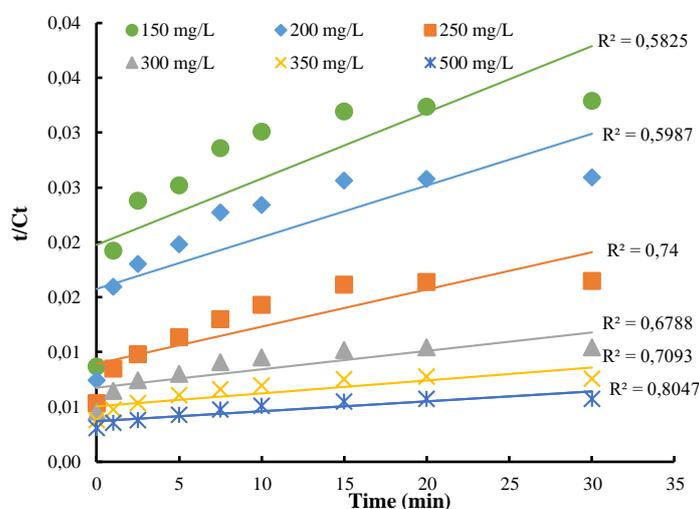


Figure 9. Second-order reaction kinetic for the COD removal of RR45 by Fenton-like oxidation ($Fe^{3+} = 75 \text{ mg L}^{-1}$; $H_2O_2 = 500 \text{ mg L}^{-1}$; $pH = 3$; $T = 20^\circ C$; $t = 30 \text{ min}$)

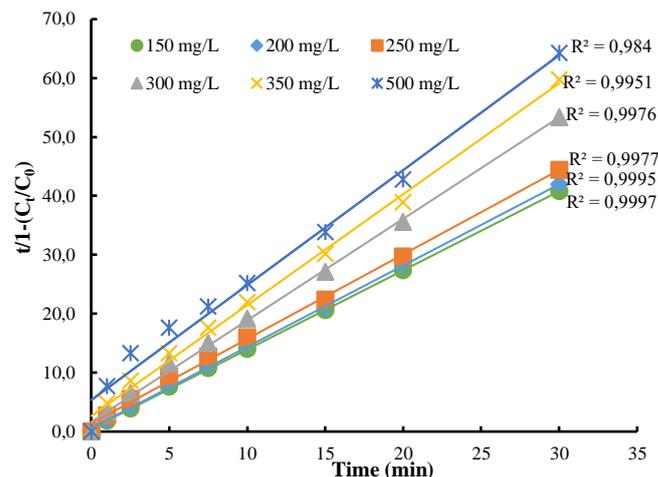


Figure 10. BMG kinetic for the COD removal of RR45 by Fenton-like oxidation ($Fe^{3+} = 75 \text{ mg L}^{-1}$; $H_2O_2 = 500 \text{ mg L}^{-1}$; $pH = 3$; $T = 20^\circ C$; $t = 30 \text{ min}$)

As seen in Table 4, correlation coefficient for BMG model are higher than the first-order and the second-order models. The correlation coefficients for the the first order reaction kinetic equation have changed in the range of 0.435–0.755 for the second order reaction kinetic have changed in the range of 0.549–0.913 and for the BMG kinetic model have changed in the range of 0.9840–0.9995. These results have shown that the experimental data did not fit the first-order and second-order kinetic model.

Conclusion

The degradability of the reactive red 45 dye from azo colorants group through the fenton and fenton-like oxidation processes, was investigated in the present study. Degradability of RR45 was evaluated by considering color and COD parameters. Experiments were carried out for 30 minutes.

Effect of the rates of Fe^{2+} or Fe^{3+} (25, 50, 75, 100, 125, 150 and 200 mg L^{-1}), H_2O_2 (100, 200, 300, 400, 500 and 600 mg L^{-1}), pH (2.5; 3; 3.5; 4 and 5), the concentration of the dye (150, 200, 250, 300, 350 and 500 mg L^{-1}) and the temperature (20, 30, 40, 50 and 60 $^\circ C$) were investigated in the studies conducted on the degradation of RR45 colorant belonging to azo group through fenton and fenton-like oxidation processes. A removal efficiency of 91.1% of COD and 99.90% of color was obtained under optimum experimental conditions where initial solution pH is 3, the concentration of RR45 colorant is 200 mg L^{-1} , rates of Fe^{2+} and H_2O_2 are 75 mg L^{-1} and 400 mg L^{-1} , reaction temperature is 50 $^\circ C$ and experiment time is 30 min. The experimental results obtained indicate clearly that the oxidation of RR45 by the Fenton and Fenton-like process is effective with a low concentration of H_2O_2 , Fe^{2+} or Fe^{3+} and pH. High concentrations of iron and H_2O_2 concentrations cause consumption of hydroxyl radicals (radical scavenger effect). In addition, the increase in temperature from 20 to 50 increased the efficiency of removal in both processes. Kinetic studies were not performed in the fenton process because color and COD removal yield have been obtained very fast. In Fenton-like process, the BMG kinetic model provided the best correlation of the used experimental data compared to the pseudo-first and second-order kinetic models.

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REFERENCES

- [1] APHA. (1985): AWWA and WPCF. Standart Methods for the Examination of Water and Wastwater, Sixteenth ed. – Washington DC: 76-538.
- [2] Babuponnusami, A., Muthukumar, K. (2014): A Review on Fenton and Improvements to the Fenton Process for Wastewater Treatment. – Journal of Environmental Chemical Engineering 2: 557-572.
- [3] Bayhan, Y. K., Değermenci, G. D. (2017): Kozmetik Atık Sularından Fenton Prosesiyle Organik Madde Gideriminin ve Kinetiğinin İncelenmesi. – Journal of the Faculty of Engineering and Architecture of Gazi University 32: 8.
- [4] Behnajady, M. A., Modirshahla, N., Ghanbary, F. (2007): A kinetic model for the decolorization of C.I. Acid Yellow 23 by Fenton process. – Journal of Hazardous Materials 148: 98-102.
- [5] Bouasla, C., Samar, M. E. H., Ismail, F. (2010): Degradation of Methyl Violet 6b Dye by the Fenton Process. – Desalination 254: 35-41.
- [6] Chacón, J. M., Leal, M. T., Sánchez, M., Bandala, E. R. (2006): Solar Photocatalytic Degradation of Azo-Dyes by Photo-Fenton Process. – Dyes and Pigments 69: 144-150.
- [7] Chen, R., Pignatello, J. J. (1997): Role of Quinone Intermediates as Electron Shuttles in Fenton and Photoassisted Fenton Oxidations of Aromatic Compounds. – Environmental Science & Technology 31: 2399-2406.
- [8] Ertugay, N., Acar, F. N. (2017): Removal of Cod and Color from Direct Blue 71 Azo Dye Wastewater by Fenton's Oxidation: Kinetic Study. – Arabian Journal of Chemistry 10: 1158-1163.
- [9] Fan, C., Horng, C. Y., Li, S. J. (2013): Structural Characterization of Natural Organic Matter and Its Impact on Methomyl Removal Efficiency in Fenton Process. – Chemosphere 93: 178-183.
- [10] Harber, F., Weiss, J. (1934): The Catalytic Decomposition of Hydrogen Peroxide by Iron Salts. – Proceedings of the Royal Society of London. Series A - Mathematical and Physical Sciences 147: 332-351.
- [11] Harichandran, G., Prasad, S. (2016): SonoFenton Degradation of an Azo Dye, Direct Red. – Ultrasonics Sonochemistry 29: 178-185.
- [12] Kang, Y. W., Hwang, K. Y. (2000): Effects of Reaction Conditions on the Oxidation Efficiency in the Fenton Process. – Water Research 34: 2786-2790.
- [13] Kaykioğlu, G., Debik, E. (2006): Removal from Textile Wastewater with Anaerobic Treatment Process. – Journal of Engineering and Natural Sciences 4: 10.
- [14] Kitis, M., Adams, C. D., Daigger, G. T. (1999): The Effects of Fenton's Reagent Pretreatment on the Biodegradability of Nonionic Surfactants. – Water Research 33: 2561-2568.
- [15] Latif, M. I., Qazi, M. A., Khan, H., Ahmad, N., Khan, N. I., Mahmood, K. (2015): Physiochemical Treatment of Textile Industry Effluents. – Journal of Chemical Society of Pakistan 37: 7.
- [16] Lin, S. H., Lo, C. C. (1997): Fenton Process for Treatment of Desizing Wastewater. – Water Research 31: 2050-2056.
- [17] Lin, S. H., Lin, M., Leu, H. G. (1999): Operating Characteristics and Kinetic Studies of Surfactant Wastewater Treatment by Fenton Oxidation. – Water Research 33: 1735-1741.
- [18] Lucas, M. S., Peres, J. A. (2006): Decolorization of the Azo Dye Reactive Black 5 by Fenton and Photo-Fenton Oxidation. – Dyes and Pigments 71: 236-244.

- [19] Lunar, L., Sicilia, D., Rubio, S., Pérez-Bendito, D., Nickel, U. (2000): Degradation of Photographic Developers by Fenton's Reagent: Condition Optimization and Kinetics for Metol Oxidation. – *Water Research* 34: 1791-1802.
- [20] Malik, P. K., Saha, S. K. (2003): Oxidation of Direct Dyes with Hydrogen Peroxide Using Ferrous Ion as Catalyst. – *Separation and Purification Technology* 31: 241-250.
- [21] Mofrad, M. R., Nezhad, M. E., Akbari, H., Atharizade, M., Miranzadeh, M. B. (2015): Evaluation of Efficacy of Advanced Oxidation Processes Fenton, Fenton-Like and Photo-Fenton for Removal of Phenol from Aqueous Solutions. – *Journal of Chemical Society of Pakistan* 37: 6.
- [22] Neyens, E., Baeyens, J. (2003): A Review of Classic Fenton's Peroxidation as an Advanced Oxidation Technique. – *Journal of Hazardous Materials* 98: 33-50.
- [23] Ntampeglitis, K., Riga, A., Karayannis, V., Bontozoglou, V., Papapolymerou, G. (2006): Decolorization Kinetics of Procion H-Exl Dyes from Textile Dyeing Using Fenton-Like Reactions. – *Journal of Hazardous Materials* 136: 75-84.
- [24] Pérez-Moya, M., Graells, M., del Valle, L. J., Centelles, E., Mansilla, H. D. (2007): Fenton and Photo-Fenton Degradation of 2-Chlorophenol: Multivariate Analysis and Toxicity Monitoring. – *Catalysis Today* 124: 163-171.
- [25] Primo, O., Rivero, M. J., Ortiz, I. (2008): Photo-Fenton Process as an Efficient Alternative to the Treatment of Landfill Leachates. – *Journal of Hazardous Materials* 153: 834-842.
- [26] Saini, R., Mondal, M. K., Kumar, P. (2017): Fenton Oxidation of Pesticide Methyl Parathion in Aqueous Solution: Kinetic Study of the Degradation. – *Environmental Progress & Sustainable Energy* 36: 420-427.
- [27] Singh, S. K., Tang, W. Z. (2013): Statistical Analysis of Optimum Fenton Oxidation Conditions for Landfill Leachate Treatment. – *Waste Management* 33: 81-88.
- [28] Sun, J. H., Sun, S. P., Wang, G. L., Qiao, L. P. (2007): Degradation of Azo Dye Amido Black 10b in Aqueous Solution by Fenton Oxidation Process. – *Dyes and Pigments* 74: 647-652.
- [29] Sun, S. P., Li, C. J., Sun, J. H., Shi, S. H., Fan, M. H., Zhou, Q. (2009a): Decolorization of an Azo Dye Orange G in Aqueous Solution by Fenton Oxidation Process: Effect of System Parameters and Kinetic Study. – *Journal of Hazardous Materials* 16: 1052-1057.
- [30] Sun, J. H., Shi, S. H., Lee, Y. F., Sun, S. P. (2009b): Fenton Oxidative Decolorization of the Azo Dye Direct Blue 15 in Aqueous Solution. – *Chemical Engineering Journal* 155: 680-683.
- [31] Swarnkar, A. K., Kakodiya, A. K., Sharma, B. K. (2015): Use of Photo-Fenton Reagent for Photocatalytic Degradation of Reactive Red 45. – *International Journal of Advanced Research in Chemical Science* 2: 6.
- [32] Tang, W. Z., Chen, R. Z. (1996): Decolorization Kinetics and Mechanisms of Commercial Dyes by H₂O₂/Iron Powder System. – *Chemosphere* 32: 947-958.
- [33] Tarr, M. A. (2003): *Chemical Degradation Methods for Wastes and Pollutants: Environmental and Industrial Applications*. – University of New Orleans. USA.
- [34] Vandevivere, P. C., Bianchi, R., Verstraete, W. (1998): Review: Treatment and Reuse of Wastewater from the Textile Wet-Processing Industry: Review of Emerging Technologies. – *Journal of Chemical Technology & Biotechnology* 72: 289-302.
- [35] Xu, X. R., Li, H. B., Wang, W. H., Gu, J. D. (2004): Degradation of Dyes in Aqueous Solutions by the Fenton Process. – *Chemosphere* 57: 595-600.
- [36] Zhang, J., Chen, S., Zhang, Y., Quan, X., Zhao, H., Zhang, Y. (2014): Reduction of Acute Toxicity and Genotoxicity of Dye Effluent Using Fenton-Coagulation Process. – *Journal of Hazardous Materials* 274: 198-204.