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Treatment of evaporative water from brewer's yeast concentration by Fenton and Fenton-like processes

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Abstract: Evaporative water from yeast slurry concentration is acidic, low mineralized and contains large amounts of dissolved organic contaminants. The treatment of evaporative water from yeast slurry concentration by Fenton $(Fe(II)/H_2O_2)$ and Fenton-like $(Fe(III)/H_2O_2)$ reactions has been studied. The processes in terms of system variables have been compared: catalyst and oxidant doses, initial pH, temperature of reaction, and the reaction kinetic. For determination of mineralization efficiency the total organic carbon (TOC) in water before and after reactions was measured. The Fenton reaction was more efficient for mineralization of organic compounds: the highest efficiency of TOC removal was 45–50%, while for the Fenton-like it was 20–30%. The pH adjustment of evaporative water in the range of 2–5 did not change the efficiency of treatment. Temperature of 30°C was the most favorable for both reactions. The Lumped Kinetic Model fitted very well the experimental results. The reaction rate analysis indicated that the rate of direct mineralization of organic compounds is similar to the rate of its oxidation to organic intermediates, its selectivity factor was more favorable to the Fenton reaction. The strong correlation between chemical oxygen demand (COD) and TOC in evaporative water after the Fenton and Fenton-like reactions has been determined, providing a simple tool for calculating COD on the basis of values of TOC measurement.

Introduction

The Fenton mechanism implies the decomposition of hydrogen peroxide (H_2O_2) by ferrous iron Fe(II), which involves a sequence of reactions leading to the formation of hydroxyl radicals (Nevens and Baeyens 2003). The hydroxyl radicals are strong oxidants which destroy the organic pollutants and mineralise to water and carbon dioxide (Parsons 2004). During the chain reactions ferric ions Fe(III) are formed, which can again be reduced by reaction with excess H₂O₂ and in consequence hydroperoxyl radicals are produced. The hydroperoxyl radicals are less sensitive and react slower than hydroxyl radicals (Babuponnusami and Muthukumar 2014). The reaction of H₂O₂ with Fe(III) is referred to as a Fenton-like reaction (Babuponnusami and Muthukumar 2014, Neyens and Baeyens 2003). The Fenton and Fenton--like reactions, as well as the sono-, electro- and photo-Fenton variants, are popular methods for organic contaminants removal from water, wastewater and landfill leachates (Wang 2008, Wang et al. 2008, Mitsika et al. 2013, Pieczykolan et al. 2013, Babuponnusami and Muthukumar 2014, Bautista et al. 2014,). These are the advanced oxidation processes which are able to degrade biorefractory organic contaminants (Babuponnusami and Muthukumar 2014) and treatment wastewater impervious to biodegradation (Bautista et al. 2007, Perdigon-Melon et al. 2010).

Some type of industrial waste is water which comes from brewer's yeast slurry concentration. This water is low mineralized and it has acidic pH, it contains large amounts of organic contaminants which appear mainly in the form of dissolved organic carbon (Michel et al. 2014). In a dry yeast manufacturing plant, a daily amount of evaporative water is 60–70 m³, that is why a water treatment technological line was built. The evaporative water is treated by coagulation together with flotation and separation in a two stage system of reverse osmosis membranes. The problem is that organic contaminants removal in the system of treatment is not sufficient, which makes it difficult to use the treated water as technological water for the needs of the manufacturing plant. This water contains organic contaminations that are by-products of the fermentation process. Part of them are volatile compounds, which migrate through the two-stage RO system.

The aim of this work was to estimate the Fenton and Fenton-like reactions suitability to decrease the concentration of the organic compounds in the evaporative water from yeast slurry concentration. There were determined the conditions, which have a significant influence on the achievement of the highest mineralization of the organic compounds.

Methods

Evaporative water, drained from the evaporator concentrating the yeast slurry in the dry yeast manufacturing plant, was the research material. The samples of water were taken from the technological production line twice, and the respective research

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series were marked as S1 and S2. The Fenton reaction was carried out in glass vessels containing the samples whose volume was 0.5 L. Then a solution of catalyst and next a solution of hydrogen peroxide were added. All this was mixed with the help of a magnetic stirrer. As catalysts of the Fenton reaction iron(II) sulphate and iron(III) sulphate were used, they were marked respectively as Fe(II) and Fe(III). The solutions of catalysts were acidified with sulfuric acid. In order to determine the progress of oxidation, after a certain time the reaction was interrupted by adding sodium hydroxide until the pH of the reaction mixture reached the range of 8.0-8.5. The obtained precipitate was subject to sedimentation and then the supernatant liquor was decanted and filtered through mediumsized filter paper produced by Alchem. All chemicals were of analytical grade and were produced by Chempur, with the exception of iron(III)sulphate, which was a technical reagent (PIX 113) produced by Kemipol. The solutions were made by dissolving chemicals and reagents into double distilled water. In the filtrates the content of organic contaminants was analyzed by measuring the chemical oxygen demand (COD), total organic carbon (TOC) and ferrous ions concentration. The experiments were carried out in duplicate. The scope of the research included the analysis of the influence of the dose of the catalysts, pH, time of the reaction and its temperature on the efficiency of organic contaminants mineralization in the evaporative water. In further experiments one of the parameters was changed and the others obtained the established values. The ranges of changes of these parameters are shown in Table 1.

Analytical methods

The TOC concentration was measured with the help of a total carbon analyzer with an infrared detector using the non-purgeable organic carbon method. The pH measurements were carried out with a potentiometric method and measurements of conductivity were carried out with a conductometric method. The COD measurements were carried out with the help of photometric LCK 514 Hach Lange cuvette tests. Iron concentration was measured using photometric Hach Lange method No. 8008. All measurements were performed in duplicate. The arithmetic means are presented and analysis error was less than 5 percent.

Data analysis

Percent efficiency (E) of organic contaminants mineralization was calculated with the dependence:

$$E = \left(1 - \frac{TOC_f}{TOC_i}\right) \cdot 100 \tag{1}$$

where TOC_{i} and TOC_{f} are initial and final concentration of total organic carbon in water before and after the Fenton and Fenton-like reactions.

Kinetics of organic contaminants mineralization in the evaporative water was analyzed on the basis of the Lumped Kinetic Model. It was based on works (Ayodele et al. 2012, He and Lei 2004, Iurascu et al. 2009) in which the model was used to describe degradation of phenol in the photo-Fenton reaction.

Variable parameter		Constant parameters		
Туре	Value range	Туре	Value range	
Fe dose		H ₂ O ₂ dose	2.12 g/1g COD*	
	0.225–2.7 g/L (0.1–0.62 g Fe/1g H_2O_2)	рН	3.4 (not corrected)	
		time	3 h	
		temperature	20°C	
H_2O_2 dose		Fe dose	1 g/L	
	2–7 g/L (0.9–3.3 g H ₂ O ₂ /1g COD)	рН	3.4 (not corrected)	
		time	3 h	
		temperature	20°C	
рН	2–5	Fe dose	1 g/L	
		H_2O_2 dose	2.12 g/1g COD	
		time	3 h	
		temperature	20°C	
time		Fe dose	1 g/L	
	30–360 min	H_2O_2 dose	2.12 g/1g COD	
		рН	3.4 (not corrected)	
		temperature	20°C	
temperature	10–40°C	Fe dose	1 g/L	
		H ₂ O ₂ dose	2.12 g/1g COD	
		рН	3.4 (not corrected)	
		time	3 h	

Table 1. Values of the parameters of the Fenton and Fenton-like reactions of the evaporative water in all experiments

* oxidant dose was determined using the stoichiometric dependence presented in work of Bautista et al. (2007)

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There are significant differences between the works regarding the use of symbols, that is why the equation (2) and symbols of the constants were adopted as in work (Ayodele et al. 2012):

$$\frac{TOC_t}{TOC_i} = \left[\frac{k_2 e^{-(k_3)t}}{(k_1 + k_2 - k_3)} + \frac{(k_1 - k_3)e^{-(k_1 + k_2)t}}{(k_1 + k_2 - k_3)}\right]$$
(2)

The following symbols were adopted: TOC_i is initial concentration of total organic carbon in water, TOC_i is concentration of total organic carbon in water in time and k_i , k_2 , k_3 , are the apparent rate constants: k_i – representing direct mineralization of the organic contaminants to CO₂ and H₂O, k_2 – representing transformation of the organic substrates to organic intermediate products, k_3 – representing mineralization of the model to the experimental data was carried out with the method of nonlinear regression by minimizing of quadratic sum of absolute errors using the Solver supplement in Excel spreadsheets. Conformity between the experimental data and the model was determined on the basis of the coefficient of determination (R^2) value and residual distribution analysis of independent variable.

Results and discussion

Evaporative water, which occurs during yeast slurry concentration, was characterized in work by Michel et al. (2014) as slightly acidic and acidic water with small alkalinity and conductivity, as well as with high content of dissolved organic contaminants, pH 4.6–6.3, alkalinity 0.46–1.2 mval/L, conductivity 78.5-205 µS/cm, TOC 100-298 mg/L, COD 356-754 mg/L. The samples of the evaporative water taken for the needs of the presented research were characterized with slightly different properties. They were more acidic, pH of both of the samples was 3.4 (S1) and 3.3 (S2), that is why they did not have any alkalinity. They were also characterized with a higher content of organic contaminants which cumulated during yeast slurry concentration in the phase of distillate. The organic contaminants content in the two analyzed samples of the evaporative water was distinctively different - TOC 375 mg/L, COD 1143 mg/L (S1) and TOC 874 mg/L, COD 2128 mg/L (S2). Its salinity was on the same low level as in work (Michel et al. 2014), its conductivity was 93 µS/cm (S1) and 208 µS/cm (S2).

TOC and COD relation

An organic contaminants content in water and wastewater is usually determined by the COD parameter because it is commonly limited in the environmental norms. On the other hand, TOC is the parameter which allows to determine more accurately the efficiency of mineralization of organic carbon to nonorganic carbon dioxide and water in the Fenton reaction (Bautista et al. 2007) with a direct measurement of its content. That is why in the samples of the evaporative water after the Fenton and Fenton-like reaction the content of organic contaminants was determined by measuring TOC and COD. The average value of the COD/TOC relation in the samples was 2.16 with a standard variation of 0.12. The median (2.15) was close to the average. Minimal and maximal values of the relation were in the range of 1.94–2.45, and the skewness had a very small value of 0.26. It could be assumed that the variability of parameters in the research series did not significantly translate into variability of the COD/TOC relation in the samples after the Fenton and Fenton-like reaction. This may indicate that the content of residual Fe in the samples (< 0.1 mg/L) did not have a significant impact on the COD measurement and the extent of hydrogen peroxide was eliminated. The dependence of COD from TOC was described with the trend line in the linear form whose equation is presented in Figure 1. High value of the coefficient of determination (R^2 0.973) characterizes accurate fit of the trend line to the experimental data. This, as well as a small variability of the COD/TOC factor enables to determine precisely the COD on the basis of the TOC measurement in the evaporative water sample after the Fenton and Fenton--like reaction. In connection with the above, the results of the experiment were presented on the basis of TOC parameter, and the described dependences had the same course in the case of the measuring results of COD.



Fig. 1. Dependence between COD and TOC in the evaporative water samples after the Fenton and Fenton-like reaction for all the experimental series

Doses of reagents

The influence of a dose of the catalyst and oxidant on the efficiency of organic contaminants mineralization in the evaporative water was analyzed in the experiment. Usability of the iron on the second and third degree of oxidation for catalyzing the reaction of mineralization was compared. The results were presented in Figure 2a. In the research series with S1 index the use of the dose of iron 0.75 g/L $(0.3 \text{ g Fe/1 g H}_2\text{O}_2)$ and higher caused maximal removal of the organic contaminants from the water. It was related to both of the catalysts and was connected with the determination of efficiency of the TOC removal on the level of 38% (Fe(II)) and 16% (Fe(III)). In the research series in which the water with a higher organic contaminants content was used (S2) the optimal dose of the iron was similar and it was 0.9 g/L $(0.2 \text{ g Fe/1 g H}_{2}O_{2})$; in the series with Fe(II) catalyst and with the same dose the efficiency of TOC removal was on

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the level of 46%. However, with the Fe(III) catalyst it was 24%. Further increase of the iron dose did not influence the decrease of the organic contaminants content (the changes of the efficiency were on the level of 2-3%), especially that the increase of Fe(II) in relation to H₂O₂ leads to the increase of coagulation share regarding chemical oxidation (Nevens and Baeyens 2003). The organic contaminants in the evaporative water were mainly in the dissolved forms which are not prone to coagulation. A similar effect was achieved in the experiments on mineralization of the organic contaminants in cork cooking wastewater: the weight ratio of Fe/H₂O₂ which was 0.2 was found to be optimal for the Fenton reaction which was carried out (Guedes et al. 2003). The influence of the dose of the oxidant on the Fenton reaction's efficiency in the evaporative water was presented in Figure 2b. The increase of the oxidant dose had more influence on the TOC decrease in the Fenton reaction rather than in the Fenton-like reaction, especially for the doses less than 2.12 g $H_2O_2/1g$ COD (4.5 g H_2O_2/L). Higher doses of the oxidant did not cause much significant decrease of the TOC in water, and the efficiency of the mineralization increased by 2-3%. The experiment series presented in Figure 2a and b show distinctly that Fe(II) was a more efficient catalyst in the Fenton reaction used for mineralization of the organic contaminants in the evaporative water which occur at yeast slurry concentration. By applying Fe(II) catalyst a larger decrease of organic contaminants concentration in the evaporative water was achieved than when using Fe(III) as a catalyst. The efficiency of mineralization was 21-26% higher in the series with Fe(II) in comparison to the series with Fe(III). Higher efficiency of the Fenton reaction regarding the Fenton-like reaction is not a rule. Works of other authors point out similar efficiency of the both processes (Wang 2008) or a reverse tendency (Bautista et al. 2014). It is obvious, regarding totally different organic contaminants which occur in wastewater and subject to mineralization in the works mentioned above, that it is difficult to build direct analogies. Comparing the research results with other scientific works it should be noted that the doses of the catalysts and the oxidant used for mineralization of the organic contaminants in the evaporative water were relatively high in

comparison to the doses of reagents used for mineralization of the model solutions of the organic compounds (Zúñiga--Benítez and Peñuela 2016). They can be rather compared to the doses of the reagents used for mineralization of the organic contaminants present in wastewater from cosmetic industry (Bautista et al. 2007, Perdigon-Melon et al. 2010), or cork manufacturing (Guedes et al. 2003). The application of the Fenton reaction for treatment of the evaporative water occurring at yeast slurry concentration enables mineralization of the organic contaminants with efficiency of about 45-50%. This value can be considered to be moderate in comparison to the applications of the Fenton process to the treatment of water and wastewater described by other authors. Guedes et al. (2003) reported 66.4% efficiency of TOC removal from cork boiling wastewater, Wang et al. (2017) reported 61.1% COD removal from oilfield wastewater and Xu et al. (2017) informed about 61.9% efficiency of COD removal from petrochemical secondary effluent. Very high efficiency (80–90%) of COD removal in wastewater from dye production factory was described by Zou et al. (2015). In the work by Wang et al. (2017) the authors indicate the possibility of increasing the effectiveness of oilfield wastewater treatment by introducing an additional activation of UV radiation to the Fenton reaction. This seems to be a reasonable direction for research on evaporative water treatment occurring at yeast slurry concentration.

pH of the reaction

The evaporative water was subject to pH correction and the influence of pH on efficiency of mineralization of organic contaminants in the Fenton reaction was analyzed. The research results presented in Figure 3a confirmed a lack of influence of the pH correction of the evaporative water in the range of 2–5 on the decrease of the TOC content. No dependence was observed in the experimental series for both of the catalysts. The reason is seen in specific properties of the evaporative water, i.e. a lack of buffer capacity following from the acidic pH (pH 3.4), a lack of alkalinity and very low conductivity. The pH of the mixture of the evaporative water subject to pH correction and with added reagents was measured. It turned



Fig. 2. Decrease of TOC content in the evaporative water: (a) in the function of doses of the catalyst Fe(II) and Fe(III) (S1, S2 – series for independent samples of water), (b) in the function of the dose of the oxidant

out that initial pH of water samples (2; 3; 3.4; 4 and 5) has significantly changed through the addition of acidic solutions of iron salts and hydrogen peroxide. pH of all reaction mixtures was 2.2-2.4, regardless of the initial pH value of water. It is probable that in the case of acidic and a little saline evaporative water the pH correction in the range of 2-5 before the Fenton reaction does not have any significant influence on the increase of the process efficiency. In both of the experimental series (Figure 3a) the samples after the Fenton reaction without pH correction (the grey marker) were characterized by the same content of the organic contaminants as the samples subject to pH correction (black marker). That is why in further experiments pH correction of the evaporative water was not applied. Moreover, pH value of the evaporative water was close to 3, which is considered to be more favourable to carry out the Fenton reaction (Babuponnusami and Muthukumar 2014). Similar observations were presented by Wang et al. 2008 - wastewater from a detergent manufacturing plant was subject to the Fenton reaction applying large doses of iron which as a result of acid hydrolysis caused that the pH level of the reaction mixture was on the level of 3-5. Due to the fact that the Fenton reaction took place in the acid conditions, the authors considered that the additional pH correction would be unnecessary. Authors of other research (Kavitha and Palanivelu 2005) also noted the decrease of the pH solution after the Fenton reaction, which they explained by the occurrence of acid reaction products of organic contaminants. In the reaction compound of the evaporative water the pH was measured directly after the addition of the reagents as well as at the reaction end. After 3 hours of the reaction a slight decrease of the sample's pH took place, which was in the range of 0.1-0.3, which did not indicate an occurrence of significant amounts of acid reaction products. In the case of the influence of pH on the efficiency of water or wastewater treatment in the Fenton process the properties of the treated medium might have much more significance (Babuponnusami and Muthukumar 2014). Research results of cosmetic wastewater treatment were published in which a strong influence of pH on the Fenton reaction was indicated. It caused even a 30% difference of the efficiency of the process (Bautista et al. 2007). It is of a particular importance if pH measurement is carried out in the wastewater before the reaction or in the reaction mixture, and what buffer capacities the water or wastewater has.

Temperature of the reaction

At the manufacturing plant hot evaporative water occurring during yeast slurry concentration is collected in a container where it gets partially cooled. Additionally, it is cooled in a heat exchanger to a temperature below 40°C before it goes to the water treatment installation, as it is the maximum temperature for exploitation of the water reuse system (Michel et al. 2014). The influence of the reaction mixture temperature on the efficiency of mineralization of the organic contaminants in the Fenton reaction was studied in the experiment. The results were presented in Figure 3b. The increase of the temperature intensified the process of organic contaminants mineralization. The highest influence of this parameter was observed in the case of Fe(III) catalyst where the greatest difference between the TOC concentration occurred in the samples of water after the reaction was carried out in the temperature of 10, 20 and 30°C. The efficiency of the treatment is 13%, 22% and 30% respectively. In the research series with the Fe(II) catalyst a significant difference of the TOC concentration occurred between the samples of the temperature of 10 and 20°C (E 38% and 46%). It can be assumed from the results that excessive cooling of the evaporative water to the temperature of 10°C decreases efficiency of its treatment. In both of the experimental series, the change of the reaction compound temperature between 30 and 40°C did not significantly influence the increase of organic contaminant mineralization (the changes were on the level of 1-3%). It might follow from the fact that from the temperature of 40°C starts the decomposition of hydrogen peroxide to water and oxygen, which has the lowest oxidation capacity, and which was also described by other authors (Nesheiwat and Swanson 2000, Guedes et al. 2003, Lucas and Peres 2009). The temperature of 30°C was favourable for the treatment of evaporative water in Fenton reaction as with other studies on the treatment of industrial wastewater (Guedes et al. 2003, Wang 2008), although, of course, this is not the rule.



Fig. 3. Decrease of the TOC content in the evaporative water depending on: (a) initial pH of water (grey mark shows the sample without pH adjustment); (b) temperature of the reaction; (S1, S2 – series for independent samples of water)

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Kinetics of the reaction

In the experiment the effect of the mineralization of organic contaminants in time was compared for the Fenton and Fenton-like reaction for the evaporative water with different TOC content (S1 and S2). Table 2 presents the results of calculations of the constants of kinetics of the reaction. High values of coefficient of determination provide evidence of very good fit of the Lumped Kinetic Model to the experiment data, which is shown in Figure 4. The correct choice of the model also was confirmed by the random distribution of residues. The Fenton reaction was characterized by higher values of the selectivity coefficient α (k_1/k_2) in both of the series S1 and S2 than in the Fenton-like reaction. However, all the values of α coefficient are relatively low, 0.130–1.22, in comparison to the results obtained in other works: 3.76-12.8 (Ayodele et al. 2012) and 1.28-4.74 (He and Lei 2004). It can be concluded about generally similar or faster reaction in which intermediates are formed than reaction of direct mineralization. The selectivity of the reaction is slightly higher if the Fe(II) catalyst was used. It is very important, that the constant k_3 is several times smaller than the constant k_2 , which is typical for all the experimental series. This provides evidence that the reaction of appearing of the intermediate products from the organic contaminants in the evaporative water goes much

faster than the reaction of mineralization of these products. In fact, such small values of the constant k_{3} (especially for the S2 series) allow us to believe that intermediate products do not degrade to CO₂ and H₂O at all. Thus, the presence of the substances which are not susceptible to mineralization can be an explanation of the obtainment of low efficiency of TOC removal from evaporative water in the Fenton and Fenton-like reactions and somehow discredit industrial application of the process. Values of total apparent reaction constant K (k_1+k_2) presented in Table 2 were significantly higher in the series in which the evaporative water contained lower concentration of TOC (S1) in comparison to the series with a higher content of TOC (S2). Higher concentration of the organic compounds in the evaporative water caused the reaction to slow down. It is similar to observations of other authors (Ayodele et al. 2012, He and Lei 2004), who show that the increase of the initial concentration of the organic compounds in the sample solution subject to the photo-Fenton reaction, decreased the rate of its degradation.

Conclusions

The evaporative water which occurs during brewer's yeast slurry concentration is characterized by a high content

Catalyst	Series	<i>k</i> 1 (10 ⁻³ ·min ⁻¹)	k ₂ (10 ^{-3.} min ⁻¹)	k₃ (10 ⁻³ ·min⁻¹)	α	<i>К</i> (10 ⁻³ ·min ⁻¹)	R^2
Fe(II)	S1	12.2	13.3	0.174	0.917	25.5	0.984
Fe(II)	S2	6.84	5.59	0.060	1.22	12.4	0.979
Fe(III)	S1	3.72	28,6	0.499	0.130	32.3	0.978
Fe(III)	S2	2.96	5.05	0.059	0.586	8.01	0.971

Table 2. Kinetic parameters of TOC removal from the evaporative water calculated from the LKM



Fig. 4. The influence of time of the reaction on the decrease of the TOC content in the evaporative water when the Fe(II) and Fe(III) catalysts are used (S1, S2 – series for independent samples of water)



of dissolved organic compounds which are moderately susceptible to mineralization in the Fenton reaction. The efficiency of the TOC removal was obtained in the level of 45–50%. Mineralization using the Fenton-like reaction was less effective, and its efficiency was within the range of 20-30%. Higher reaction selectivity (α) which indicated faster reaction of mineralization of the organic contaminants was observed in the series with the Fe(II) catalyst -0.917 and 1.22. In both Fenton and Fenton-like reactions the influence of the doses of the catalyst and the oxidant on the efficiency of mineralization was comparable. The efficient doses of the catalysts and the oxidant were high, namely 0.2 and 0.3 g Fe/ 1 g H₂O₂ (0.75 and 0.90 g Fe/L), 2.12 g H₂O₂/1 g COD (4.5 g H₂O₂/L) and were rather similar to the doses used in wastewater treatment than water treatment. The evaporative water is characterized by a lack of buffer capacity and that is why the correction of its pH in the range of 2-5 before the Fenton reaction did not have a significant influence on the increase of the process effectiveness. It is important that the water has an acidic pH which is beneficial for the Fenton reaction. The temperature of 30°C was favourable for the evaporative water treatment in the Fenton and Fenton-like reactions and in general was similar to the temperature maintained in the manufacturing plant in the technological evaporative water treatment line. Evaporative water is characterized by the variability of the content of organic compounds, therefore the above results indicate the potential of the method for treating this type of water, rather than attempts to generalize. It can be problematic to apply the Fenton reaction in the technological system of treatment of water from yeast slurry concentration because the reaction of appearance of intermediate products from the organic compounds which are present in it goes as fast as the reaction of their direct mineralization and additionally the rate of mineralization of the occurred intermediate products is marginal. There is a strong correlation between the TOC and COD parameters which determine the content of organic contaminants in the evaporative water subject to the Fenton reaction, which allows us to predict effectively the values of COD on the basis of TOC measurements, which are more legitimate for the Fenton reaction.

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References

- Ayodele, O.B., Lim, J.K. & Hameed, B.H. (2012). Degradation of phenol in photo-Fenton process by phosphoric acid modified kaolin supported ferric-oxalate catalyst: Optimization and kinetic modelling, *Chemical Engineering Journal*, 197, pp. 181–192.
- Babuponnusami, A. & Muthukumar, K. (2014). A review on Fenton and improvements to the Fenton process for wastewater treatment, *Journal of Environmental Chemical Engineering*, 2, pp. 557–572.
- Bautista, P., Mohedano, A.F., Gilarranz, M.A., Casas, J.A. & Rodríguez, J.J. (2007). Application of Fenton oxidation to

cosmetic wastewaters treatment, *Journal of Hazardous Materials*, 143, pp. 128–134.

- Bautista, P., Casas, J.A., Zazo, J.A., Rodriguez, J.J. & Mohedano, A.F. (2014). Comparison of Fenton and Fenton-like oxidation for the treatment of cosmetic wastewater, *Water Science and Technology*, 70, 3, pp. 472–478.
- Guedes, A., Madeira, L., Boaventura, R. & Costa, C. (2003). Fenton oxidation of cork cooking wastewater – overall kinetic analysis, *Water Research*, 37, pp. 3061–3069.
- He, F. & Lei, L. (2004). Degradation kinetics and mechanisms of phenol in photo-Fenton process, *Journal of Zhejiang University Science*, 5, pp. 198–205.
- Iurascu, B., Siminiceanu, I., Vione, D., Vicente, M.A. & Gil, A. (2009). Phenol degradation in water through a heterogeneous photo-Fenton process catalyzed by Fe-treated laponite, *Water Research*, 43, pp. 1313–1322.
- Kavitha, V. & Palanivelu, K. (2005). Destruction of cresols by Fenton oxidation process, *Water Research*, 39, pp. 3062–3072.
- Lucas, M.S. & Peres, J.A. (2009). Removal of COD from olive mill wastewater by Fenton's reagent: Kinetic study, *Journal of Hazardous Materials*, 168, pp. 1253–1259.
- Michel, M.M., Reczek, L., Siwiec, T. & Rudnicki, P. (2014). Applying the coagulation and reverse osmosis for water recovery from evaporative water, *Annals of Warsaw University of Life Science* – SGGW Land Reclamation, 46, 4, pp. 29–38.
- Mitsika, E.E., Christophoridis, Ch. & Fytianos, K. (2013). Fenton and Fenton-like oxidation of pesticide acetamiprid in water samples: Kinetic study of the degradation and optimization using response surface methodology, *Chemosphere*, 93, pp. 1818–1825.
- Nesheiwat, F.K. & Swanson, A.G. (2000). Clean contaminated sites using Fenton's reagent, *Chemical Engineering Progress*, 96, pp. 61–66.
- Neyens, E. & Baeyens, J. (2003). A review of classic Fenton's peroxidation as an advanced oxidation technique, *Journal of Hazardous Materials*, B98, pp. 33–50.
- Parsons, S. (2004). Advanced oxidation processes for water and wastewater treatment, IWA Publishing, London 2004.
- Perdigon-Melon, J.A., Carbajo, J.B., Petre, A.L., Rosal, R. & Garcia-Calvo, E. (2010). Coagulation–Fenton coupled treatment for ecotoxicity reduction in highly polluted industrial wastewater, *Journal of Hazardous Materials*, 181, pp. 127–132.
- Pieczykolan, B., Płonka, I., Barbusiński, K. & Amalio-Kosel, M., (2013). Comparison of landfill leachate treatment efficiency using the advanced oxidation processes, *Archives of Environmental Protection*, 39(2), pp. 107–115.
- Wang, S. (2008). A comparative study of Fenton and Fenton-like reaction kinetics in decolourisation of wastewater, *Dyes and Pigments*, 76, pp. 714–720.
- Wang, X-J., Song, Y. & Mai, J-S. (2008). Combined Fenton oxidation and aerobic biological processes for treating a surfactant wastewater containing abundant sulphate, *Journal of Hazardous Materials*, 160, pp. 344–348.
- Wang, S., Li, Z. & Yu, Q. (2017). Kinetic degradation of guar gum in oilfield wastewater by photo-Fenton process, *Water Science and Technology*, 75 (1), pp. 11–19.
- Xu, M., Wu, Ch. & Zhou, Y. (2017). Advanced treatment of petrochemical secondary effluent by Fenton: performance and organics removal characteristics, *Water Science and Technology*, 75, 6, pp. 1431–1439.
- Zou, H., Ma, W. & Wang, Y. (2015). A novel process of dye wastewater treatment by linking advanced chemical oxidation with biological oxidation, *Archives of Environmental Protection*, 41(4), pp. 33–39.
- Zúñiga-Benítez, H. & Peñuela, G.A. (2016). Degradation of ethylparaben under simulated sunlight using photo-Fenton, *Water Science and Technology*, 73, 4, pp. 818–826.



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Oczyszczanie wody wyparnej z zatężania gęstwy drożdżowej w procesie Fentona

Streszczenie: Woda wyparna z zatężania gęstwy drożdżowej jest kwaśna, nisko zmineralizowana i zawiera dużą ilość rozpuszczonych związków organicznych. W pracy badano oczyszczanie wody wyparnej w reakcji Fentona (Fe(II)/H₂O₂) i pokrewnej (Fe(III)/H₂O₂). Porównywano procesy przy następujących zmiennych: dawki katalizatorów i utleniacza, pH początkowe, temperatura i kinetyka reakcji. Efektywność oceniano poprzez pomiar ogólnego węgla organicznego przed i po reakcji. Związki organiczne były bardziej skutecznie mineralizowane w reakcji Fentona: najwyższa efektywność usuwania OWO wynosiła 45–50%, a w reakcji pokrewnej jedynie 20–30%.Korekta odczynu wody wyparnej w zakresie 2–5 pH nie wpłynęła na efektywność oczyszczania. Temperatura 30°C była najbardziej korzystna dla obydwu reakcji. Model kinetyczny o parametrach skupionych bardzo dobrze opisywał wyniki badań eksperymentalnych. Analiza szybkości reakcji wykazała, że jest ona zbliżona w przypadku mineralizacji organicznych składników oraz utleniania do produktów pośrednich, a współczynnik selektywności reakcji był korzystniejszy dla procesu Fentona. Określono silną korelację pomiędzy parametrami ChZT i OWO w wodzie po reakcji Fentona i pokrewnej, co może być przydatnym do obliczania ChZT na podstawie pomiaru OWO.

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