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Efficiency of Multistep Process of Fenton Oxidation and Bentonite in the Treatment of Ammonia Phenolic Wastewater

Hana Alihodzic[*1], Abdel Dozic[2], Indira Sestan[3], Halid Junuzovic[4]

[*1] PhD. Candidate, Department of Environmental Engineering, Faculty of Technology, University of Tuzla, Tuzla, Bosnia and Herzegovina

[2]Department of Environmental Engineering, Faculty of Technology, University of Tuzla, Tuzla, Bosnia and Herzegovina

[3]Department of Physical chemistry and Electrochemistry, Faculty of Technology, University of Tuzla, Tuzla, Bosnia and Herzegovina

[4]Department of Analytical Chemistry, Faculty of Technology, University of Tuzla, Tuzla, Bosnia and Herzegovina

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ABSTRACT

Industrial production generates enormous amounts of wastewaters with a high content of organic and inorganic substances, which must be treated before discharging into a natural recipient to such a quality that it will not have a negative impact on the aquatic environment. This paper shows the possibility of applying a multi-stage process with Fenton reagents in combination with bentonite as an adsorbent in the treatment of ammonia-phenolic wastewater. The role of bentonite clay in this study was dye removal. The investigation was carried out under laboratory conditions, and the efficiency of the process was determined on the following parameters of COD, ammonia, phenol and thiocyanate. Also, the influence of the pH value, the concentration of oxidant hydrogen peroxide and catalyst iron sulphate heptahydrate was examined. The optimal values obtained for the pH, concentration of hydrogen peroxide and the catalyst iron sulphate heptahydrate was: 3; 30% and 23 g/l, where the efficiency of removal of the COD, ammonia, phenol and thiocyanate was: 96.42 %; 85.17 %; 100 % i 99.13 %.

Keywords: Fenton Process, Adsorption, Treatment, Wastewater, Bentonite

I. INTRODUCTION

The most significant amounts of wastewater originate from the chemical industrial production sector, where the concentration and composition of the effluent depends on the technological process. The waste water produced from the coke production process contains high concentrations of organic and inorganic compounds such as phenols, polyaromatic hydrocarbons, cyanides, ammonia, thiocyanates, etc., most of which have a pronounced negative impact on the aquatic environment.

In general, for the treatment of such polluted wastewaters, primary (mechanical), secondary (biological) and tertiary (chemical) treatment are being used. Within the industrial complex for the production of coke in Lukavac, Bosnia and Herzegovina, they have a plant installed for the biological treatment of ammonia phenolic wastewater. When high concentrations of phenol, ammonia and thiocyanate are present in waste water that is subject to biological treatment, the removal of pollutants in this process is hindered. The concentration of phenol above 200 mg/l significantly affects the nitrification process in biological treatment [1], [2] the presence of phenol suppresses the bacterial degradation of thiocyanate [1], [3]. Similar to the phenol, thiocyanates also show harmful behavior under certain conditions [1], [4].

In order to minimize the toxicity of this wastewater type, conventional treatment techniques such as air stripping, solvent extraction and activated sludge treatment are used, however the presence of a wide range of toxic compounds makes these methods insufficiently efficient [1], [5], [6]. In order to treat such loaded wastewaters, the researchers considered various advanced oxidation processes such as: photocatalysis [7], [8], [9], osonisation [7], [10], [11], [12], wet oxidation [7], [13], [14], electrocoagulation [7], [15], ultrasounds [7], [16], [17], [18], electrochemical [7], [19], [20], [21], Fered-Fenton [7], [22] and classic Fenton process [7], [23]. Among the advanced oxidation processes, Fenton-based processes are considered environmentally friendly technologies and have attracted much attention due to their simplicity and efficiency [24]. High efficiency of this technique is achieved by the reaction of divalent iron ions with hydrogen peroxide (Fenton's reagents), which results in the formation of highly reactive hydroxyl radicals and the oxidation of Fe^{2+} u Fe^{3+}. For additional removal of organic and inorganic compounds, a conventional adsorption method using a bentonite clay as an ecofriendly adsorbent was used. The combination of the Fenton process and adsorption enables a high degree of treatment of wastewater from the coke production process, which by its composition belongs to the group of the most polluted wastewaters. In this work, a two-stage Fenton process was performed, followed by adsorption on bentonite under laboratory conditions. The study also included analysis of a raw wastewater, the determination of the efficiency of the applied process on the following parameters: COD, ammonia, thiocyanate and phenol. Moreover, under laboratory conditions the influence of the: pH value, concentration of hydrogen peroxide and catalyst iron sulphate heptahydrate was examined on the effectiveness of applied Fenton process.

II. METHODS AND MATERIAL

For the experimental research samples of ammonia-phenol wastewater from a coke production plant were used.

All chemicals worn in this research (sulfuric acid, hydrogen peroxide, iron sulphate heptahydrate, sodium hydroxide, etc.) are of high analytical purity manufactured by Sigma Aldrich. As an adsorbent, bentonite was used from the Šipovo deposit, Bosnia and Herzegovina.

Determination of COD, ammonia, phenol and thiocyanate concentrations was performed using standard methods shown in Table 1.

Table 1. Presentation of test parameters and methods

Parameter	Method
COD	BAS ISO 15705:2005
ammonia	BAS ISO 7150-1:2002
phenol	Standard methods 5530 (D), izd. APHA-AWWA-WEF, 2017
thiocyanate	Standard methods 4500 (M), izd. APHA-AWWA-WEF, 2017

III.RESULTS AND DISCUSSION

Firstly, samples of raw ammonia phenolic wastewater were collected, and the initial concentrations were determined for the following parameters: COD, ammonia, phenol and thiocyanate: 3991.5; 68.13; 1079.0 and 297.4 mg/l. Experimental studies of the application of the Fenton process in combination with the adsorption with bentonite were carried out under laboratory conditions at ambient pressure and temperature in two steps. The plant for the treatment of ammonia phenolic wastewater was simulated in a laboratory version using a glass beaker as a reactor connected to a mixer, where 300 ml of the sample was treated. The wastewater treatment was preceded by the adjustment of the pH value and the injection of iron sulphate and hydrogen peroxide. After mixing, flocculation was performed, followed by adsorption with bentonite. Furthermore, the samples were subjected to precipitation and filtration. The resulting filtrate or treated wastewater was analysed with the used of parameters defined above, and the obtained concentrations were used to calculate the removal efficiency, the results of which are discussed below. The primary operating conditions that affect the performance of the Fenton processes are: pH value, oxidant and catalyst concentration, and temperature [25], [26], [27], [28].

Influence of the initial pH value

The Fenton process is based on the reaction of hydrogen peroxide as an oxidase and iron sulphate heptahydrate as a catalyst, forming highly reactive hydroxyl radicals characterized with a high oxidation potential. In this process, the pH value plays a major role, which affects the generation of hydroxyl radicals, which, under conditions of atmospheric pressure and temperature, are capable of breaking down most polluting substances in wastewater, such as, for example, alcohols, aldehydes, aromatics, ketones, ethers, etc. At low pH values, the influence of hydroxyl radicals •OH by means of H^+ becomes stronger, which results in a decrease in the oxidation capacity of the Fenton process [29], [30]. At high pH values, the hydrolysis and precipitation of iron (Fe^{3+}) in the solution become stronger, which results in a decrease in the catalytic capacity of iron (Fe^{3+}) [31], [32]. At a pH value of 3 to 5, iron ions are deposited as colloidal particles and at a pH above 5 in the form of iron (III)oxyhydroxide [33], [34], [35]. Accordingly, in this work, the Fenton process combined with adsorption was performed in two phases, where parameters such as temperature, reaction time, mixing speed, dose of hydrogen peroxide and iron sulphate heptahydrate were constant, while the initial pH value during the experiment was variable. The tested range was from 1 to 3, which is shown in Fig 1.; Fig 2.; Fig 3.; Fig 4., on the basis of which it is evident that the optimal pH value for the degradation of the pollutants was 3, where the highest removal efficiency for COD, ammonia, phenols and thiocyanates was achieved in the amount as follows: 96.97%; 84.29%; 100% and 99.37%. By reviewing the available literature, the highest efficiency of pollutant removal was recorded at a pH of 3 to 4, i.e., with hazardous industrial wastewater [36] or landfill wastewater leachate [37], which are similar in composition to the tested waters.

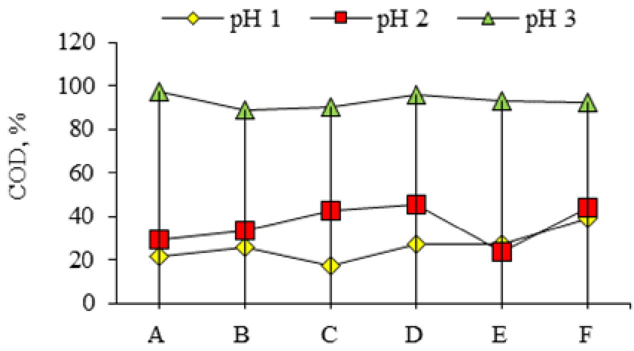

Figure 1: The influence of the initial pH value on the efficiency of COD removal

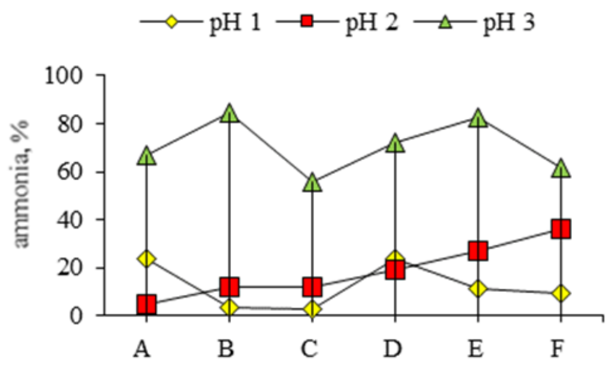

Figure 2: The influence of the initial pH value on the efficiency of ammonia removal

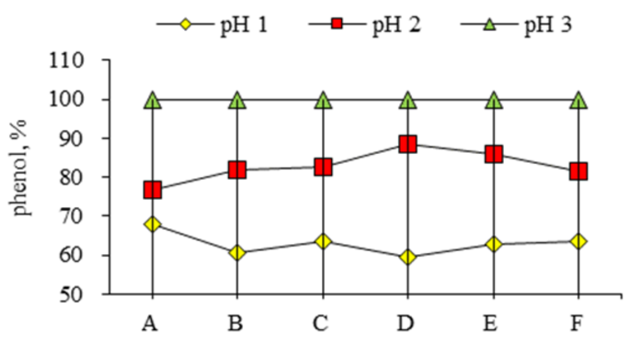

Figure 3: The influence of the initial pH value on the efficiency of phenol removal

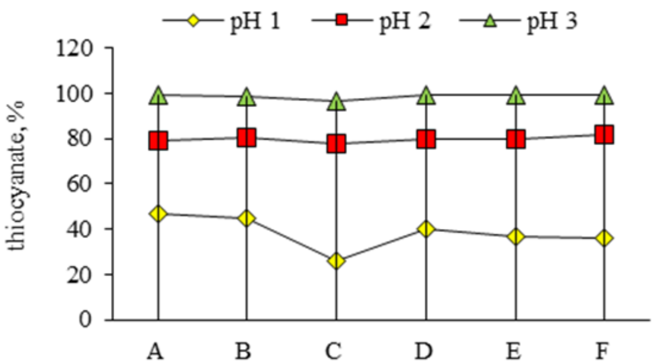

Figure 4: The influence of the initial pH value on the efficiency of thiocyanate removal

Influence of the initial concentration of the catalyst: iron sulphate heptahydrate

A review of the literature found that various Fenton optimization processes follow a similar oxidation mechanism: iron in the form of Fe^{2+} catalyzes the decomposition of hydrogen peroxide to produce a highly oxidizing hydroxyl radical that can degrade most organic pollutants [6]. Usually, the efficiency of decomposition of organic pollutants increases with increasing the iron concentration (Fe^{2+}) [6], [38], [39]. The influence of the initial concentration iron sulphate heptahydrate was investigated: 18; 20; 23 g/l to remove COD, ammonia, phenol and thiocyanate. Parameters such as reaction time, temperature, dose of hydrogen peroxide, pH value were constant. The experiment carried out determined the optimal concentration of 23 g/l, during which the removal efficiency of: 93.58 % COD; 68.59 % ammonia; 100 % phenol and 99.76 % thiocyanate was achieved, shown in Fig 5.; Fig. 6.; Fig. 7.; Fig. 8. Furthermore, at a concentration of 18 g/l, the lowest removal efficiency of 1.92 %; 11.79 %; 33.42 % and 21.79 % for the removal of COD, ammonia, phenol and thiocyanate was achieved. Based on the obtained results, we can conclude that the increase in concentration increased the degree of removal efficiency of the examined parameters.

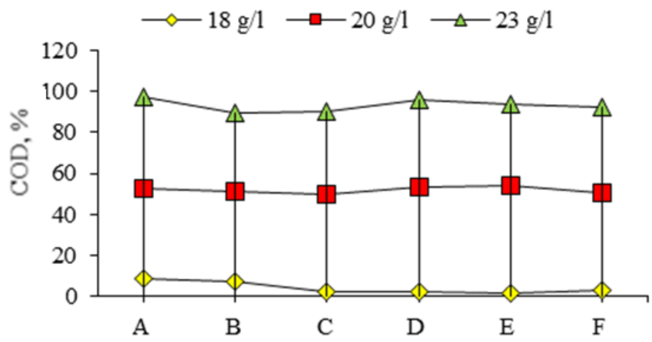

Figure 5: The influence of the initial concentration of iron sulphate heptahydrate on the COD efficiency removal

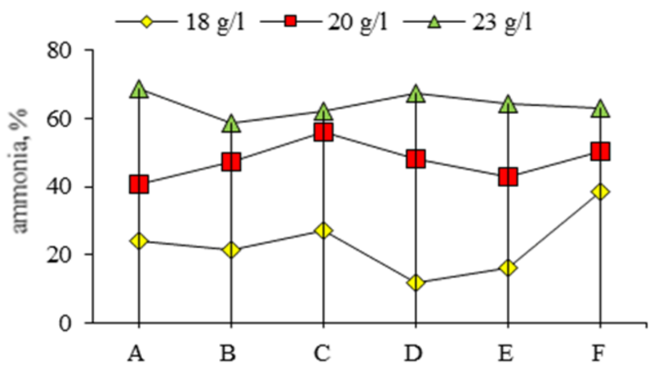

Figure 6: The influence of the initial concentration of iron sulphate heptahydrate on the ammonia efficiency removal

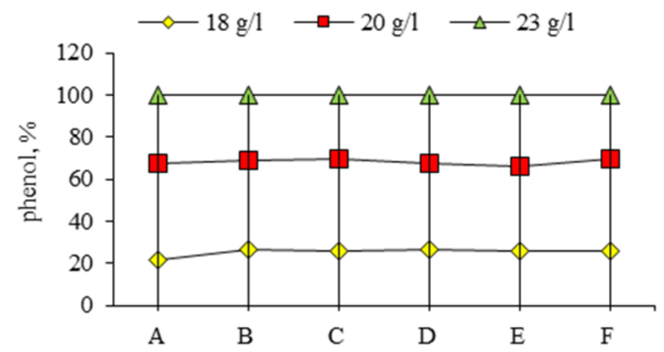

Figure 7: The influence of the initial concentration of iron sulphate heptahydrate on the phenol efficiency removal

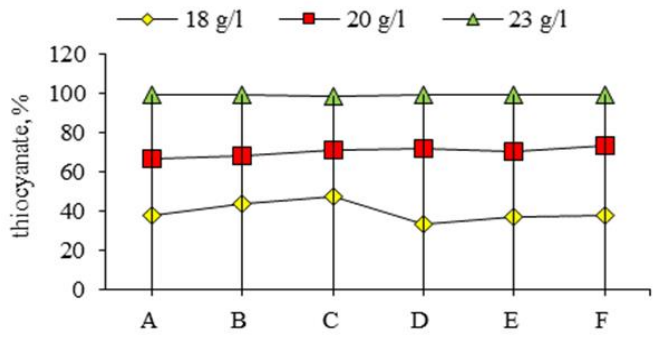

Figure 8: The influence of the initial concentration of iron sulphate heptahydrate on the thiocyanate efficiency removal

Influence of initial concentration of oxidant: hydrogen peroxide

On the degradation of organic and inorganic pollutants, and according to the reaction of hydrogen peroxide and iron ions (Fe^{2+}), which precedes the formation of hydroxyl radicals, the oxidant concentration plays a significant role, and determining its optimal value is crucial for the entire process. An excess of hydrogen peroxide in the Fenton reaction not only increases the operational costs of the treatment, but also contributes to an increase in the concentration of chemical oxygen consumption. To determine the optimal concentration of hydrogen peroxide, the experiment was carried out by dosing the initial concentrations of oxidants, namely: 15; 20 and 30%, and by keeping other parameters constant such as reaction time, temperature, dose of iron sulphate heptahydrate and pH value. The obtained results shown in Fig. 9.; Fig. 10.; Fig. 11.; Fig. 12 indicate that the degree of purification of ammonia phenolic wastewater increased with the increase of the concentration of oxidants after treatment. The lowest efficiency of COD, ammonia, phenol and thiocyanate removal was achieved at a concentration of hydrogen peroxide of 15%, namely: 3.77 %; 16.34 %; 11.88 % and 32.4 2%, while the highest was recorded using 30% hydrogen peroxide in the amount of: 96.42%; 85.17%; 100% and 99.13%. Based on the conducted investigation, the optimal concentration of hydrogen peroxide for the treatment of such heavily polluted wastewater was determined to be 30%.

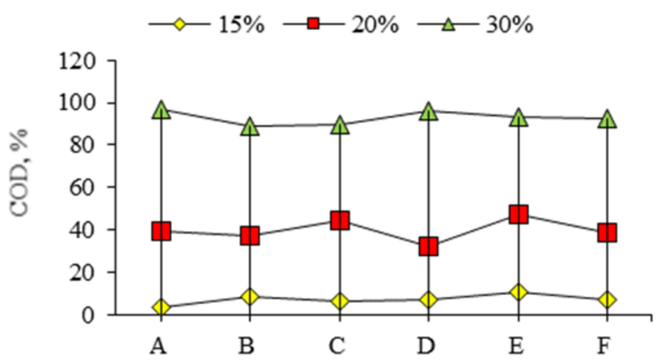

Figure 9: The influence of the initial concentration of hydrogen peroxide on the COD efficiency removal

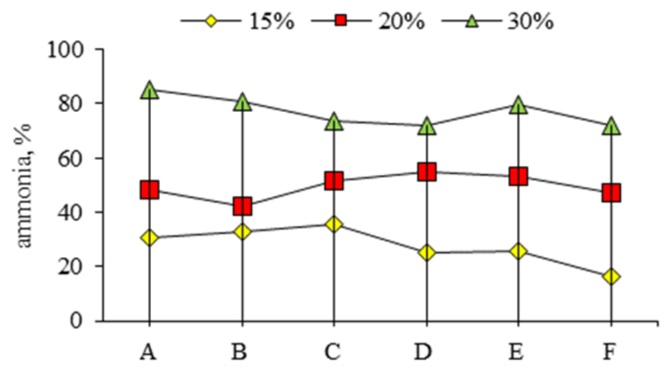

Figure 10: The influence of the initial concentration of hydrogen peroxide on the ammonia efficiency removal

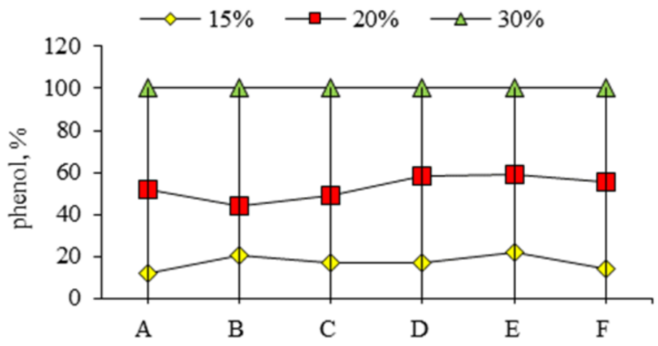

Figure 11: The influence of the initial concentration of hydrogen peroxide on the phenol efficiency removal

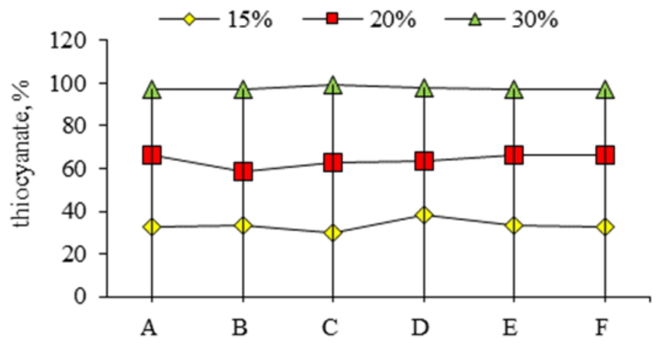

Figure 12: The influence of the initial concentration of hydrogen peroxide on the thiocyanate efficiency removal

IV.CONCLUSION

The treatment of ammonia phenolic wastewater using the multi-stage Fenton process in combination with bentonite as an adsorbent proved to be very effective and efficient in reducing the concentrations of COD; ammonia, phenol and thiocyanate, resulting in a satisfactory degree of treated water quality. Both techniques are reflected in the simplicity of implementation and operation, have low capital costs and as such represent a cheap and feasible option for removing the already mentioned parameters.

V. REFERENCES

[1]. Tamang, M., & Paul, K. K. (2022). Advances in treatment of coking wastewater–a state of art review. Water Science and Technology, 85(1), 449-473.

[2]. Liu, M., Preis, S., Kornev, I., Hu, Y., & Wei, C. H. (2018). Pulsed corona discharge for improving treatability of coking wastewater. Journal of Environmental Sciences, 64, 306-316.

[3]. Liu, J., Ou, H. S., Wei, C. H., Wu, H. Z., He, J. Z., & Lu, D. H. (2016). Novel multistep physical/chemical and biological integrated system for coking wastewater treatment: technical and economic feasibility. Journal of Water Process Engineering, 10, 98-103.

[4]. Kim, Y. M., Park, D., Lee, D. S., & Park, J. M. (2008). Inhibitory effects of toxic compounds on nitrification process for cokes wastewater treatment. Journal of Hazardous Materials, 152(3), 915-921.

[5]. Wang, C., Zhang, M., Cheng, F., & Geng, Q. (2015). Biodegradation characterization and immobilized strains' potential for quinoline degradation by Brevundimonas sp. K4 isolated from activated sludge of coking wastewater. Bioscience, biotechnology, and biochemistry, 79(1), 164-170.

[6]. Zheng, M., Xu, C., Zhong, D., Han, Y., Zhang, Z., Zhu, H., & Han, H. (2019). Synergistic degradation on aromatic cyclic organics of coal pyrolysis wastewater by lignite activated coke-active sludge process. Chemical Engineering Journal, 364, 410-419.

[7]. Arimi, M. M. (2017). Integration of Fenton with biological and physical–chemical methods in the treatment of complex effluents: a review. Environmental technology reviews, 6 (1), 156-173.

[8]. Alaton IA, Balcioglu IA, Bahnemann DW. Advanced oxidation of reactive dyebath effluent: comparison of O3, H2O2/UV-C and

TiO2/UV-process. Water Res. 2002;36:1143–1154.

[9]. Zimmermann, S. G., Wittenwiler, M., Hollender, J., Krauss, M., Ort, C., Siegrist, H., & von Gunten, U. (2011). Kinetic assessment and modeling of an ozonation step for full-scale municipal wastewater treatment: micropollutant oxidation, by-product formation and disinfection. Water research, 45(2), 605-617.

[10]. Antoniou, M. G., Hey, G., Vega, S. R., Spiliotopoulou, A., Fick, J., Tysklind, M., ... & Andersen, H. R. (2013). Required ozone doses for removing pharmaceuticals from wastewater effluents. Science of the total environment, 456, 42-49.

[11]. Tripathi, S., & Tripathi, B. D. (2011). Efficiency of combined process of ozone and bio-filtration in the treatment of secondary effluent. Bioresource technology, 102(13), 6850-6856.

[12]. Sangave, P. C., Gogate, P. R., & Pandit, A. B. (2007). Ultrasound and ozone assisted biological degradation of thermally pretreated and anaerobically pretreated distillery wastewater. Chemosphere, 68(1), 42-50.

[13]. Tembhekar, P. D., Padoley, K. V., Mudliar, S. L., & Mudliar, S. N. (2015). Kinetics of wet air oxidation pretreatment and biodegradability enhancement of a complex industrial wastewater. Journal of Environmental Chemical Engineering, 3(1), 339-348.

[14]. Malik, S. N., Saratchandra, T., Tembhekar, P. D., Padoley, K. V., Mudliar, S. L., & Mudliar, S. N. (2014). Wet air oxidation induced enhanced biodegradability of distillery effluent. Journal of environmental management, 136, 132-138.

[15]. Asaithambi, P., Susree, M., Saravanathamizhan, R., & Matheswaran, M. (2012). Ozone assisted electrocoagulation for the treatment of distillery effluent. Desalination, 297, 1-7.

[16]. Sangave, P. C., & Pandit, A. B. (2006). Ultrasound and enzyme assisted biodegradation of distillery wastewater. Journal of Environmental Management, 80(1), 36-46.

[17]. Gonze, E., Commenges, N., Gonthier, Y., & Bernis, A. (2003). High frequency ultrasound as a pre-or a post-oxidation for paper mill wastewaters and landfill leachate treatment. Chemical Engineering Journal, 92(1-3), 215-225.

[18]. Entezari, M. H., & Pétrier, C. (2003). A combination of ultrasound and oxidative enzyme: sono-biodegradation of substituted phenols. Ultrasonics sonochemistry, 10(4-5), 241-246.

[19]. Deng, Y., & Englehardt, J. D. (2007). Electrochemical oxidation for landfill leachate treatment. Waste management, 27(3), 380-388.

[20]. Eskelinen, K., Särkkä, H., Kurniawan, T. A., & Sillanpää, M. E. (2010). Removal of recalcitrant contaminants from bleaching effluents in pulp and paper mills using ultrasonic irradiation and Fenton-like oxidation, electrochemical treatment, and/or chemical precipitation: A comparative study. Desalination, 255(1-3), 179-187.

[21]. Raju, G. B., Karuppiah, M. T., Latha, S. S., Priya, D. L., Parvathy, S., & Prabhakar, S. (2009). Electrochemical pretreatment of textile effluents and effect of electrode materials on the removal of organics. Desalination, 249(1), 167-174.

[22]. Chang, P. H., Huang, Y. H., Hsueh, C. L., Lu, M. C., & Huang, G. H. (2004). Treatment of non-biodegradable wastewater by electro-Fenton method. Water Science and Technology, 49(4), 213-218

[23]. Bautista, P., Mohedano, A. F., Gilarranz, M. A., Casas, J. A., & Rodriguez, J. J. (2007). Application of Fenton oxidation to cosmetic wastewaters treatment. Journal of Hazardous Materials, 143(1-2), 128-134.

[24]. Pliego, G., Zazo, J. A., Garcia-Muñoz, P., Munoz, M., Casas, J. A., & Rodriguez, J. J. (2015). Trends in the intensification of the Fenton process for wastewater treatment: an overview. Critical

Reviews in Environmental Science and Technology, 45(24), 2611-2692.
[25]. Ribeiro, J. P., & Nunes, M. I. (2021). Recent trends and developments in Fenton processes for industrial wastewater treatment–A critical review. Environmental Research, 197, 110957.
[26]. Guo, Y., Xue, Q., Zhang, H., Wang, N., Chang, S., Wang, H., & Chen, H. (2018). Treatment of real benzene dye intermediates wastewater by the Fenton method: characteristics and multi-response optimization. RSC advances, 8(1), 80-90.
[27]. Hermosilla, D., Merayo, N., Gascó, A., & Blanco, Á. (2015). The application of advanced oxidation technologies to the treatment of effluents from the pulp and paper industry: a review. Environmental Science and Pollution Research, 22, 168-191.
[28]. Mandal, T., Maity, S., Dasgupta, D., & Datta, S. (2010). Advanced oxidation process and biotreatment: Their roles in combined industrial wastewater treatment. Desalination, 250(1), 87-94.
[29]. Nieto, L. M., Hodaifa, G., Rodríguez, S., Giménez, J. A., & Ochando, J. (2011). Degradation of organic matter in olive-oil mill wastewater through homogeneous Fenton-like reaction. Chemical Engineering Journal, 173(2), 503-510.
[30]. Hodaifa, G., Ochando-Pulido, J. M., Rodriguez-Vives, S., & Martinez-Ferez, A. (2013). Optimization of continuous reactor at pilot scale for olive-oil mill wastewater treatment by Fenton-like process. Chemical engineering journal, 220, 117-124.
[31]. Ifelebuegu, A. O., & Ezenwa, C. P. (2011). Removal of endocrine disrupting chemicals in wastewater treatment by Fenton-like oxidation. Water, Air, & Soil Pollution, 217, 213-220.
[32]. Fan, X., Hao, H., Wang, Y., Chen, F., & Zhang, J. (2013). Fenton-like degradation of nalidixic acid with Fe 3+/H 2 O 2. Environmental Science and Pollution Research, 20, 3649-3656.
[33]. Neyens, E., & Baeyens, J. (2003). A review of classic Fenton's peroxidation as an advanced oxidation technique. Journal of Hazardous materials, 98(1-3), 33-50.
[34]. Al-Momani, F. (2003). Combination of photo-oxidation processes with biological treatment. Universitat de Barcelona.
[35]. Sedlak, D. L., & Andren, A. W. (1991). Oxidation of chlorobenzene with Fenton's reagent. Environmental Science & Technology, 25(4), 777-782.
[36]. Deng, Y., & Englehardt, J. D. (2006). Treatment of landfill leachate by the Fenton process. Water research, 40(20), 3683-3694.
[37]. Bianco, B., De Michelis, I., & Vegliò, F. (2011). Fenton treatment of complex industrial wastewater: Optimization of process conditions by surface response method. Journal of hazardous materials, 186(2-3), 1733-1738.
[38]. Li, X.H., Chen, S., Angelidaki, I., Zhang, Y.F., 2018. Bio-electro-Fenton processes for wastewater treatment: advances and prospects. Chem. Eng. J. 354, 492–5
[39]. Wang, Q., Tian, S., & Ning, P. (2014). Degradation mechanism of methylene blue in a heterogeneous Fenton-like reaction catalyzed by ferrocene. Industrial & Engineering Chemistry Research, 53(2), 643-649.

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