Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.909328

54 (2015) 3470–3476
June

Taylor & Francis
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Kinetics studies of catalytic ozonation of distillery effluent

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Received 8 August 2013; Accepted 12 March 2014

ABSTRACT

The decolorization and degradation of pollutant in the distillery effluent using catalytic ozonation process were studied. The effect of various experimental parameters such as ferrous ion concentration (2–10 mM), initial chemical oxygen demand (COD) concentration (250–1000 ppm), effluent initial pH (2–10), and H_2O_2 concentration (25–200 mM) has been studied on the percentage color removal. The color removal increases with increase in ferrous ion concentrations, initial pH, and H_2O_2 concentration. However the percentage color removal decreases with increasing initial COD concentration. Three different systems of O_3; O_3/Fe^{2+}, $O_3/Fe^{2+}/H_2O_2$ were compared for the percentage color removal. It has been observed from investigation that ozonation alone is not effective to decolorize and in removal of COD in the effluent. The results show that catalytic ozonation gives 81.61% color removal for the effluent. Further, the kinetic study has been carried out for the percentage color removal of the distillery effluent.

Keywords: Ozonation; Distillery effluent; Color removal; COD removal; Kinetic study

1. Introduction

The effluents from various industries are discharged from among which highly colored ones increase environmental pollution and soil contamination. Highly colored wastewater can be treated by different combinations of physical, chemical, and biological methods [1–3]. They are very difficult to break down biologically and cannot be treated individually by biological, chemical, and physical methods alone. Each process has its own advantages and disadvantages, and also the main drawback of these processes is the generation of a large amount of sludge or solid waste resulting in high operational costs for sludge treatment and disposal [4]. Many processes are under investigation stage and also researchers are studying the effective treatment method for industrial effluent. To overcome these difficulties, in recent years there has been increasing attention towards advanced oxidation process (AOP) [5]. In AOP, various oxidants have been successfully applied for many wastewater treatment applications [6]. The oxidants are H_2O_2, O_3, O_2, and iron salts-generating ($^\bullet OH$) radicals in the process, which are highly reactive and have a potential of 2.8 V. The hydroxyl radicals are effectively generated by ozonation process.

Ozonation has been very effective in the decolorization and degradation of organic compounds in the water and wastewater. Ozone is one of the strong oxidants having the potential ($E^\circ = 2.08$ V) and reacts with several classes of organic compounds through direct

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or indirect reactions [7,8]. The only disadvantage of ozonation process for water treatment is the high-energy cost required for its generation. In the indirect oxidation, $^\bullet$OH radicals are important for the oxidation of saturated organic compounds. The combination of ozone with other technologies such as electrocoagulation, UV radiation, and ultrasound techniques improves the pollutant removal efficiency of the effluent with lesser treatment cost. Catalytic ozonation utilizes catalysts in order to achieve controlled decomposition of ozone and hydroxyl radicals' formation. Catalytic ozonation should provide fast degradation of organic pollutants and also provide more effective mineralization of both micro pollutants and natural organic matter. Many researchers reported ozonation with other AOPs to be successful in treatment of specific compounds such as dyes, pesticides, phenolic compounds, and other organochlorides [9–14]. Wu and Ng studied the degradation of dye using various AOPs such as O_3, O_3/H_2O_2, O_3/Fe^{3+}, $O_3/H_2O_2/Fe^{3+}$, UV/O_3, $UV/O_3/Fe^{3+}$, $UV/O_3/H_2O_2$, and $UV/O_3/H_2O_2/Fe^{3+}$ processes [15]. They also studied kinetic of the dye removal and power consumption for various systems with UV and without UV. Brillas et al. investigated the mineralization rate herbicide 2-propionic acid solutions using O_3 system was enhanced by the Fe^{2+} catalyst due to the production of oxidizing $^\bullet$OH [16].

The treatment of wastewater generated from sugar and distillery industries is a big challenge to the environmentalists. The dark-brown liquid, which comes out as effluent from these industries has a very high organic content both in suspended and dissolved materials. It is mandatory to treat the effluent before letting it out into the environment to meet the specification of pollution control norms. Various treatment techniques have been attempted to treat the distillery effluents [17–20]. Few literatures have been studied the catalytic ozonation of distillery effluent. Sreethawong and Chavadej studied decolorization of distillery wastewater using catalytic ozonation process [21]. From the experimental results, the ozonation system with the iron oxide catalyst gave the highest efficiency in both chemical oxygen demand (COD) and color removals because the hydroxyl-free radical generated from the catalyst is more reactive than the ozone molecule itself. Gehringer et al. studied the color removal of a biologically pretreated wastewater from molasses processing by ozonation and two AOPs studied [22]. Color removal occurred with all three processes with almost the same efficiency, but the BOD increase by ozonation was much higher than that by AOPs. Increasing BOD value increases the biodegradability index (BI = BOD/COD). According to Chamarro et al. for complete biodegradation, the effluent must show a BI of at least 0.4. It is acceptable that a waste with BI ratio > 0.4 can be treated by a biological system [23]. Mohana et al. have discussed various emerging technologies such as electrochemical method, photocatalysis, and sorption as promising techniques for the treatment of distillery effluent [24]. Among these methods electrochemical treatment of industrial effluent is a well-known technique. But electro oxidation method needs high energy cost and the electrocoagulation method produces considerable amounts of sludge that by itself need further treatment [25]. Hence, an alternate treatment technique has been tried to treat the distillery effluent.

The objective of the present investigation is to treat the distillery effluent by homogeneous and heterogeneous catalytic ozonation process. Influences of operating parameters such as ferrous sulfate (Fe_2SO_4), H_2O_2, effluent initial pH, and initial COD concentration were studied on percentage color removal. Kinetics of the process has been studied and the rate constant values calculated, further the ozonation process is compared with catalytic ozonation process.

2. Material and methods

The effluents were collected from nearby distillery industries. The main characteristics of the effluent: pH 4.1–4.3, COD: 80,000–90,000 mg L^{-1}, BOD: 7,000–8,000 mg L^{-1}, TSS: 15.44 g L^{-1}, total dissolved solids: 5,550–5,750 mg L^{-1}, color—dark brown, odor—burn sugar. The effluent characteristics were measured using standard methods for the examination of wastewater [26]. All the chemicals were of analytical reagent grade obtained from Merck and used without further purification. The pH of the effluent was measured using a pH-meter (Elico; Model LI120) and adjusted by the addition of appropriate amounts of 0.1 M NaOH or H_2SO_4 solutions.

3. Experimental

The experimental setup consists of an ozone generator and reactor for the investigation as shown in Fig. 1. Ozone was generated using an ozone generator (Ozonetek Limited, Chennai). The air has been passed at the flow rate of 15 LPM and produces 2 g h^{-1} of O_3 from the ozone generator. The generated ozone is passed to the reactor with a 500 mL volume effluent for the color removal study. The ozone was purged through diffuser located at the reactor base. Ozone concentrations were determined using an iodometric method. A magnetic stirrer is used for complete

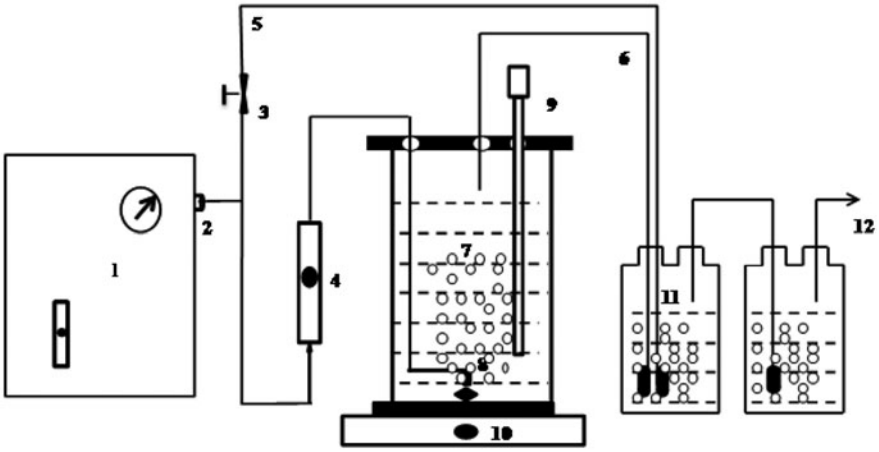

Fig. 1. Experimental setup for the ozonation process for the treatment of distillery effluent. (1) Ozone generator, (2) ozone outlet, (3) control valve, (4) air flow rotameter, (5 and 6) unused ozone, (7) effluent solution, (8) ozone diffuser, (9) sampling port, (10) magnetic stirrer, (11) 2–5% KI solution, and (12) to vent.

mixing of the catalyst with the effluent. The temperature of reactor was maintained at constant with varied 30 ± 2°C. The samples were collected for the regular interval of time and centrifuged using REMI Model: R-24 (10,000 rpm, 15 min). The samples were analyzed for the color removal using UV/vis spectrophotometer (Jasco, V-570). To study the percentage color removal of the effluent three different sets of experiments have been carried out: ozonation, ozone with H_2O_2 catalyst, and ozone with Fenton reagent.

The percentage color removal was calculated by:

$$\text{Percentage color removal} = \frac{\text{Abs}_i - \text{Abs}_t}{\text{Abs}_i} \times 100 \quad (1)$$

where Abs_i and Abs_t are absorbance at initial and at any time t for corresponding wavelength λ_{max}.

4. Results and discussion

4.1. Effect of Fe^{2+}

The effect of Fe^{2+} catalyst concentration on the color removal of the distillery effluent is shown in Fig. 2, for the system of ozone with Fe^{2+} catalyst. It is observed from the figure that the rate of color removal is increased with increasing concentration of Fe^{2+} from 2 to 10 mM. The percentage color removal increased from 41.03 to 71.65% with increasing concentration of Fe^{2+}. This is due to the fact that increasing Fe^{2+} produces more quantity of hydroxyl radical with ozone. This hydroxyl radical enhances the oxidation of pollutant and color removal. This can be explained as the following chemical reaction [27].

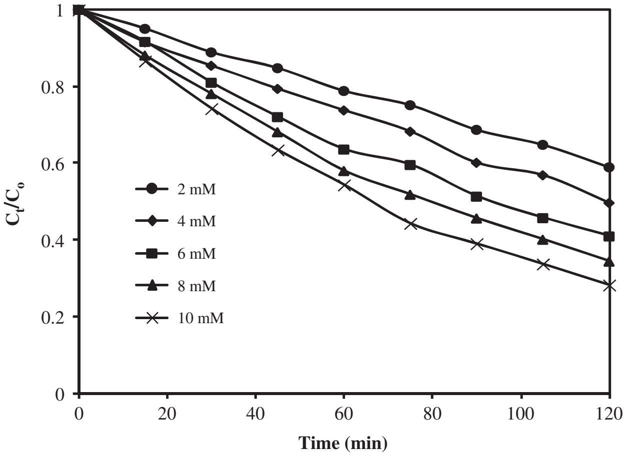

Fig. 2. Effect of Fe^{2+} on color removal (condition: effluent initial COD: 500 ppm, effluent initial pH 6, ozone flow rate: 15 LPM, and time: 120 min).

$$Fe^{2+} + O_3 \rightarrow FeO^{2+} + O_2 \quad (2)$$

$$FeO^{2+} + H_2O \rightarrow Fe^{3+} + OH^{\bullet} + OH^{-} \quad (3)$$

Further increase of Fe^{2+} concentration, the potential oxidants of $^{\bullet}OH$ radical or FeO^{2+} were removed by Fe^{2+}, results reducing the $^{\bullet}OH$ radicals. Hence, further increase of Fe^{2+} in the effluent will not improve the rate of color removal.

4.2. Effect of initial pH

The solubility of ozone is readily affected by solution pH [28]. The effect of initial pH on percentage color removal of distillery effluent for COD concentration of 500 ppm with Fe^{2+} concentration of 10 mM is shown in the Fig. 3, for the heterogeneous ozonation. The results show that the percentage color removal increases from 34.24 to 74.17% with increase pH from 2 to 10. The influence of pH on color removal is result of the relation between oxidation potential and decomposition behavior of ozone. In acidic pH, the ozone is available as molecular ozone and has the oxidation potential of 2.08 V. In the case of alkaline pH, it decomposes into secondary oxidants such as $^{\bullet}$OH, HO_2, HO_3, and HO_4. Among these, $^{\bullet}$OH is one of the oxidants important for oxidation of organic pollutants in the effluent. Hence in the acidic pH, the color removal is less compared to the alkaline pH of the solution [29].

4.3. Effect of initial COD concentration

The effect of initial COD concentration on the color removal of the O_3/Fe^{2+} system has been studied and shown in Fig. 4 with various COD concentrations from 250 to 1,000 ppm for the Fe^{2+} concentration of 10 mM and fixed-ozone mixture flow rate of 15 LPM. The COD of the effluent has been adjusted by diluting the real effluent using water. It can be observed from the figure, that the color removal is decreased from 70.84 to 47.94% with increasing initial COD concentration. The reason can be that under the constant dosage conditions of ozone and Fe^{2+} concentrations, the amount of $^{\bullet}$OH formed is constant, consequently the same amount of $^{\bullet}$OH could be produced at different COD concentrations. Hence, the percentage of color removal is decreased.

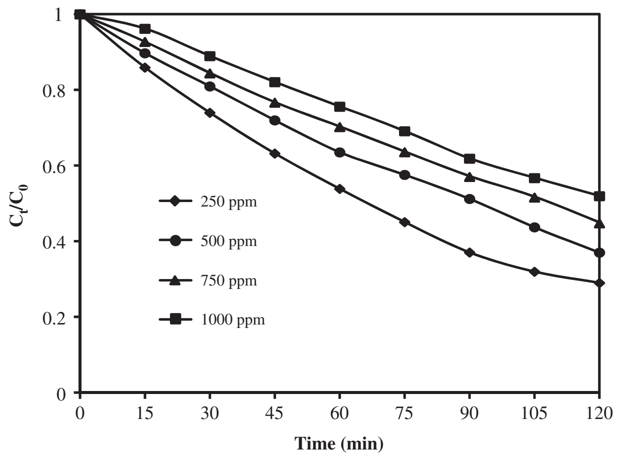

Fig. 4. Effect of initial COD concentration of the effluent on color removal (condition: concentration of Fe^{2+}: 10 mM, effluent initial pH 6, ozone flow rate: 15 LPM, and time: 120 min).

4.4. Effect of hydrogen peroxide

The effect of H_2O_2 concentration on percentage color removal has been studied for an initial COD concentration of 500 ppm; Fe^{2+} concentration of 10 mM with fixed ozone mixture flow rate of 15 LPM. It has been observed from Fig. 5 that the percentage color removal increases from 71.65 to 88.32% with increasing

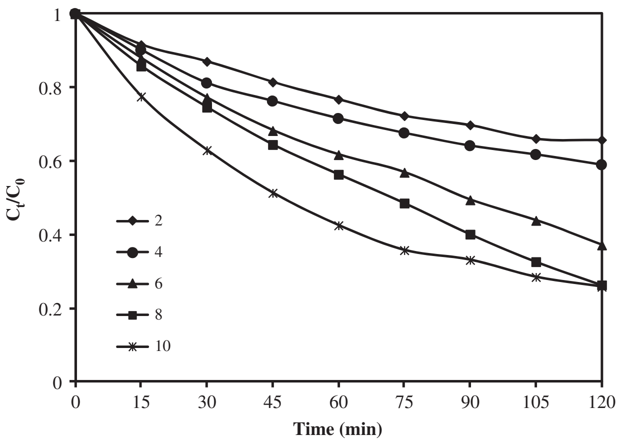

Fig. 3. Effect of initial effluent solution pH on color removal (condition: effluent initial COD: 500 ppm, concentration of Fe^{2+}: 10 mM, ozone flow rate: 15 LPM, and time: 120 min).

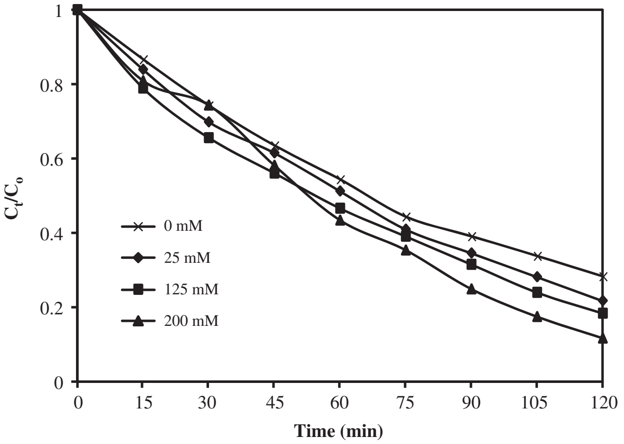

Fig. 5. Effect of H_2O_2 concentration on color removal (condition: effluent initial COD: 500 ppm, concentration of Fe^{2+}: 10 mM, effluent initial pH 6, ozone flow rate: 15 LPM, and time: 120 min).

H_2O_2 dosage from 0 to 200 mM. This is due to the effect of increases in hydroxyl radicals' generation with increasing H_2O_2 concentration. But the excess amount of hydrogen peroxide will not improve the color removal. This could be due to recombination of hydroxyl radicals and also hydroxyl radicals reaction with H_2O_2, contributing to the $^\bullet$OH scavenging capacity.

4.5. Comparisons of color removal by O_3, O_3/Fe^{2+}, $O_3/Fe^{2+}/H_2O_2$

The percentage color removal of distillery effluent by the various system of O_3, O_3/Fe^{2+} and $O_3/Fe^{2+}/H_2O_2$ are shown in the Fig. 6. It is noticed from the figure percentage color removal of distillery effluent is 17.95, 71.65 and 81.61% by the system of O_3, O_3/Fe^{2+}, $O_3/Fe^{2+}/H_2O_2$, respectively. It is clearly observed from the figure, the percentage color is not significant in the O_3 system alone. It can be improved by the addition of homogenous and heterogeneous catalyst in the ozone system. This is due to that ozone alone produces hydroxyl radicals but the generation of hydroxyl radicals is less than that of catalytic ozonation process. The hydroxyl radical generation has been improved by addition Fe^{2+} and H_2O_2 in the ozone process [30].

4.6. Kinetics of catalytic ozonation

Kinetic study of distillery effluent color removal has been performed by varying different experimental parameter. Many authors reported that ozonation process follows the pseudo first order kinetics [31–38].

Hence the kinetics of the color removal can be written as:

$$-\frac{dC}{dt} = kC \tag{4}$$

The equation can be written as a pseudo first order reaction with respect to color removal.

$$-\ln\left(\frac{C_t}{C_0}\right) = kt \tag{5}$$

where C_0 is the initial absorbance of the effluent; C_t is the absorbance of the effluent as a function of time, t, k is the rate constant. The term ln (C_0/C_t) was plotted vs. time and the slope gives k value of rate constant. The k value for the percentage color removal in each experimental condition is calculated.

The kinetics study of distillery effluent color removal for various Fe^{2+} concentrations for the O_3/Fe^{2+} system is shown in the Fig. 7. The plot −ln (C_t/C_0) vs. time t follows the straight line. The R^2 is an index of the goodness-of-fit to the first-order kinetics. The R^2 values in O_3/Fe^{2+} systems for all the Fe^{2+} concentration are typically ≥ 0.998. It can be observed that, the color removal follows the first order kinetics. When the concentration of Fe^{2+} increased from 2 to 10 mM, the rate constant also increased from 0.004 to 0.01 min^{-1}. This means that Fe^{2+} addition enhances the rate of color removal for the distillery effluent. Fig. 8.

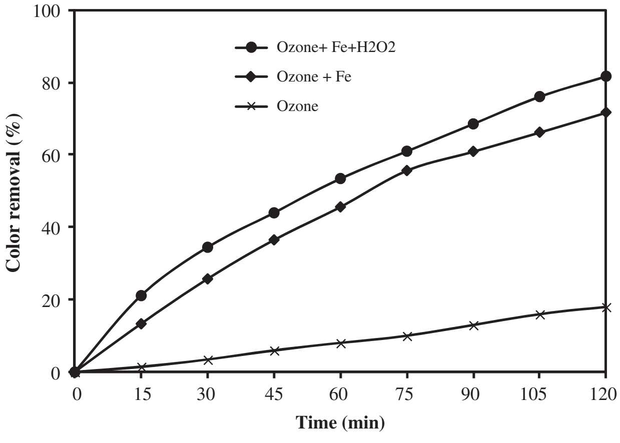

Fig. 6. Comparisons of O_3, O_3/Fe^{2+}, $O_3/Fe^{2+}/H_2O_2$ for the percentage color removal of the distillery effluent (condition: effluent initial COD: 500 ppm, effluent initial pH 6, H_2O_2 concentration: 25 mM, concentration of Fe^{2+}: 10 mM, and ozone flow rate: 15 LPM).

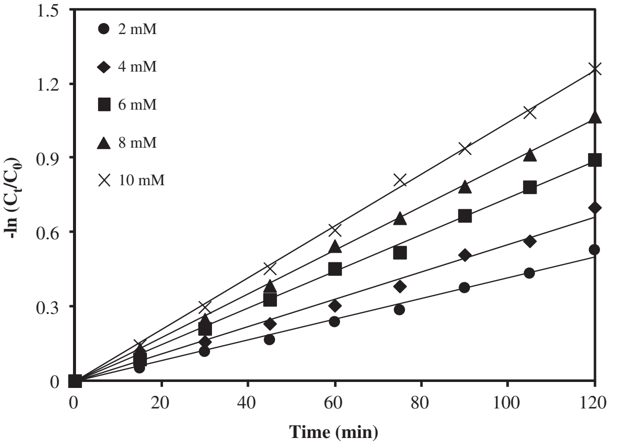

Fig. 7. Effect of Fe^{2+} concentration on rate constant (conditions: effluent initial COD: 500 ppm, effluent initial pH 6, ozone flow rate: 15 LPM, and time: 120 min).

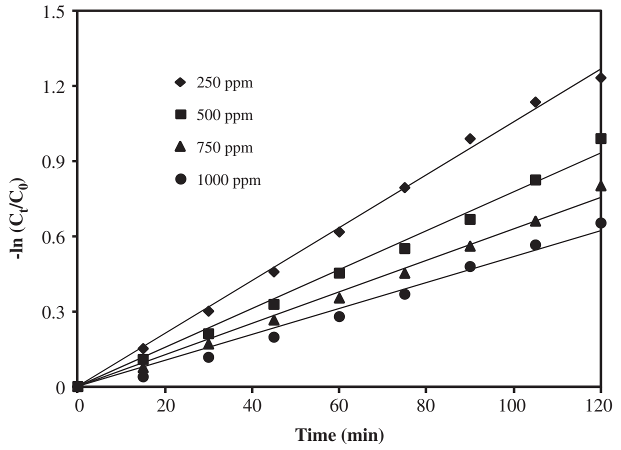

Fig. 8. Effect of initial COD concentration on rate constant (condition: concentration of Fe^{2+}: 10 mM, effluent initial pH 6, ozone flow rate: 15 LPM, and time: 120 min).

shows the kinetic plot of color removal for the O_3/Fe^{2+} system with various initial COD concentration of effluent. The first order rate constant decreases from 0.01 to 0.005 min^{-1} with increasing initial COD concentration from 250 to 1,000 ppm.

The distillery effluent after the treatment process is characterized using UV–vis spectrophotometer. Color removal of the distillery effluent was investigated for the λ_{max} 295 nm during the catalytic ozonation process as the results are shown in the Fig. 9. It can be observed from figure the maximum absorbance peak at 295 nm which a reference a distillery effluent disappear gradually during the catalytic ozonation process.

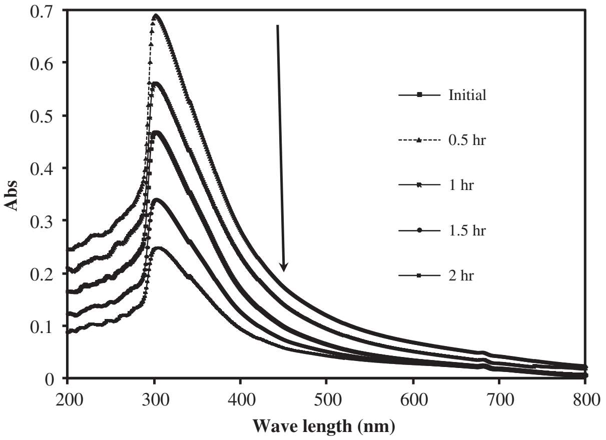

Fig. 9. Absorbance spectra of the distillery effluent solution as a different reaction time in the system of ozone/fenton–reagent system.

5. Conclusion

Color removal of distillery effluent has been studied by the catalytic ozonation process. Three different systems of O_3; O_3/Fe^{2+}, $O_3/Fe^{2+}/H_2O_2$ were compared for the percentage color removal. The effect of various operating parameters such as Fe^{2+} concentration, H_2O_2 concentration, effluent initial pH, and initial COD concentration has been analyzed on percentage color removal. The results show that $O_3/Fe^{2+}/H_2O_2$ system has higher color removal of 81.61% under the operating condition of 25 mM of H_2O_2, 10 mM of Fe^{2+}, and pH 6.0 for an initial COD concentration of 500 ppm. The kinetic study had been carried out for the color removal of ozonation process and found that it follows the pseudo-first-order kinetics.

References

[1] C. Sagne, C. Fargues, R. Lewandowski, M. Lameloise, M. Decloux, Screening of reverse osmosis membranes for the treatment and reuse of distillery condensates into alcoholic fermentation, Desalination 219 (2008) 335–347.

[2] S.H. Lin, M.L. Chen, Treatment of textile wastewater by chemical methods for reuse, Water Res. 31 (1997) 868–876.

[3] W. Zhang, R. Xiong, G. Wei, Biological flocculation treatment on distillery wastewater and recirculation of wastewater, J. Hazard. Mater. 172 (2009) 1252–1257.

[4] P. Gogate, A.B. Pandit, A review of imperative technologies for wastewater treatment II: Hybrid methods, Adv. Environ. Res. 8 (2004) 553–597.

[5] I. Oller, S. Malato, J.A. Sánchez-Pérez, Combination of advanced oxidation processes and biological treatments for wastewater decontamination—A review, Sci. Total Environ. 409 (2011) 4141–4166.

[6] J.M. Poyatos, M.M. Muñio, M.C. Almecija, J.C. Torres, E. Hontoria, F. Osorio, Advanced oxidation processes for wastewater treatment: State of the art, Water Air Soil Pollut. 205 (2010) 187–204.

[7] K. Turhan, I. Durukan, S.A. Ozturkcan, Z. Turgut, Decolorization of textile basic dye in aqueous solution by ozone, Dyes Pigm. 92 (2012) 897–901.

[8] C. Tizaoui, N. Grima, Kinetics of the ozone oxidation of reactive orange 16 azo-dye in aqueous solution, Chem. Eng. J. 173 (2011) 463–473.

[9] S. Gul, O. Ozcan-Yıldırım, Degradation of reactive red 194 and reactive yellow 145 azo dyes by O_3 and H_2O_2/UV-C processes, Chem. Eng. J. 155 (2009) 684–690.

[10] P. Ormad, S. Cortes, A. Puig, J.L. Ovelleiro, Degradation of organochloride compounds by O_3 and O_3/H_2O_2, Water Res. 31 (1997) 2387–2391.

[11] S. Chiron, A. Fernandez, A. Rodriguez, E. Garcıa, Pesticide chemical oxidation: State-of-the-art, Water Res. 34 (2000) 366–377.

[12] J. Beltran-Heredia, J. Torregrosa, R. Joaquin, J.R. Dominguez, J.A. Peres, Kinetics of the reaction between ozone and phenolic acids present in agro-industrial wastewaters, Water Res. 35 (2001) 1077–1085.

[13] M. Koch, A. Yediler, D. Lienert, G. Insel, A. Kettrup, Ozonation of hydrolyzed azo dye reactive yellow 84 (CI), Chemosphere 46 (2002) 109–113.

[14] J.J. Wu, S.J. Masten, Oxidation kinetics of phenolic and indolic compounds by ozone: Applications to synthetic and real swine manure slurry, Water Res. 36 (2002) 1513–1526.

[15] C.-H. Wu, H.Y. Ng, Degradation of C.I. Reactive Red 2 (RR2) using ozone-based systems: Comparisons of decolorization efficiency and power consumption, J. Hazard. Mater. 152 (2008) 120–127.

[16] E. Brillas, P.-L. Cabot, R.M. Rodríguez, C. Arias, J.A. Garrido, R. Oliver, Degradation of the herbicide 2,4-DP by catalyzed ozonation using the $O_3/Fe^{2+}/$UVA system, Appl. Catal. B 51 (2004) 117–127.

[17] R. Krishna Prasad, S.N. Srivastava, Electrochemical degradation of distillery spent wash using catalytic anode: Factorial design of experiments, Chem. Eng. J. 146 (2009) 22–29.

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

[19] M.N. Vineetha, M. Matheswaran, K.N. Sheeba, Photocatalytic colour and COD removal in the distillery effluent by solar radiation, Sol. Energy 91 (2013) 368–373.

[20] P. Asaithambi, L. Garlanka, N. Anantharaman, M. Matheswaran, Influence of experimental parameters in the treatment of distillery effluent by electrochemical oxidation, Sep. Sci. Technol. 47 (2012) 470–481.

[21] T. Sreethawong, S. Chavadej, Color removal of distillery wastewater by ozonation in the absence and presence of immobilized iron oxide catalyst, J. Hazard. Mater. 155 (2008) 486–493.

[22] P. Gehringer, W. Szinovatz, H. Eschweiler, R. Haberl, Oxidative treatment of a wastewater stream from a molasses processing using ozone and advanced oxidation technologies, Ozone Sci. Eng. 19 (1997) 157–168.

[23] E. Chamarro, A. Marco, S. Esplugas, Use of fenton reagent to improve organic chemical biodegradability, Water Res. 35 (2001) 1047–1051.

[24] S. Mohana, B.K. Acharya, D. Madamwar, Distillery spent wash: Treatment technologies and potential applications, J. Hazard. Mater. 163 (2009) 12–25.

[25] G. Chen, Electrochemical technologies in wastewater treatment, Sep. Sci. Technol. 38 (2004) 11–41.

[26] L.S. Clesceri, A.E. Greenberg, A.D. Eaton, Standard Methods for the Examination of Water and Wastewater, 20th ed., APHA, Washington, DC, 1995.

[27] X. Zhang, W. Dong, W. Yang, Decolorization efficiency and kinetics of typical reactive azo dye RR2 in the homogeneous Fe(II) catalyzed ozonation process, Chem. Eng. J. 233 (2013) 14–23.

[28] K. Sarayu, K. Swaminathan, S. Sandhya, Assessment of degradation of eight commercial reactive azo dyes individually and in mixture in aqueous solution by ozonation, Dyes Pigm. 75 (2007) 362–368.

[29] J. Beltran-Heredia, J. Torregrosa, J.R. Dominguez, J.A. Peres, Comparison of the degradation of p-hydroxybenzoic acid in aqueous solution by several oxidation processes, Chemosphere 42 (2001) 351–359.

[30] F.M. Saunders, J.P. Gould, C.R. Southerland, The effect of solute competition on ozonolysis of industrial dyes, Water Res. 17 (1983) 1407–1419.

[31] B. Langlais, D.A. Reckhow, D.R. Brink, Ozone in water treatment: Application and engineering, Lewis, Boca Raton, 1991, pp. 31–54.

[32] J. Carriere, P. Jones, A.D. Broadbent, Decolorization of textile dye solutions, Ozone Sci. Eng. 15 (1993) 189–200.

[33] W. Chu, C. Ma, Quantitative prediction of direct and indirect dye ozonation kinetics, Water Res. 34 (2000) 3153–3160.

[34] J. Wu, T. Wang, Ozonation of aqueous azo dye in a semibatch reactor, Water Res. 35 (2001) 1093–1099.

[35] K. Turhan, Z. Turgut, Decolorization of direct dye in textile wastewater by ozonization in a semi-batch bubble column reactor, Desalination 242 (2009) 256–263.

[36] K. Turhan, Z. Turgut, Treatment and degradability of direct dyes in textile wastewater by ozonation: A laboratory investigation, Desalin. Water Treat. 11 (2009) 184–191.

[37] K. Turhan, S.A. Ozturkcan, Decolorization and degradation of reactive dye in aqueous solution by ozonation in a semi-batch bubble column reactor, Water Air Soil Pollut. 224 (2013) 1353–1366.

[38] K. Pachhade, S. Sandhya, K. Swaminathan, Ozonation of reactive dye, procion red MX-5B catalyzed by metal ions, J. Hazard. Mater. 167 (2009) 313–318.