



ORIGINAL ARTICLE

Utilization of Moving Bed Biofilm Reactor for Industrial Wastewater Treatment Containing Ethylene Glycol: Kinetic and Performance Study

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ABSTRACT

Ethylene Glycol (EG) is one of toxic and hazardous materials that was used in many industries such as; synthetic fibers, films, antifreeze, resins, explosives, fibers, paper, leather, protective coatings, printing inks and textile. Many environmental problems such as: negative effects on aquatic life, destruction of aquatic ecosystems, soil pollution, reducing the oxygen level in the water absorption through skin contact, brain damages, damage to the Central Nervous System (CNS) and joints, eye damage, toxicity, etc., have been reported related with EG. In this study, ozone as an advanced oxidation method was used for the treatment of EG containing wastewaters. For this purpose, the impact of contact time and pH variations on EG removal by ozonation at two level including low and high concentration (low= 5, 10, 20, 50, 100 and high=500, 750, 1000, 1500 mg/L) were examined. An EG removal kinetic analysis was determined based on removal rates via several ozonation times. At concentrations of 10, 20 and 50 mg/L after 180 minutes, removal of EG were achieved 93.31, 89.96, and 85.01 % respectively. Increasing pH has a direct impact on system efficiency and maximum efficiency corresponds to a concentration of 1500 mg/L 20.26 % was observed. Very good correlation coefficients at this kinetic study at all concentrations, investigated that EG removal will follow the first-order kinetics. Increasing and decreasing pH has a dramatic effect on the efficiency of the system, so that the efficiency increases significantly at alkaline pH. According to the results ozone system can be an excellent option for EG containing wastewater treatment.

Keywords: Biofilm, ozonation, wastewater treatment

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INTRODUCTION

In order to prevent water resources and environmental pollution, Industrial wastewater treatment is one of the requirements of today's world. For this purpose the removal of hazardous compounds present in these wastewaters is one of the main problems so that many biological methods have been used extensively. Ethylene Glycol (EG) is one of this hazardous materials that was used in many industries such as; synthetic fibers, films, antifreeze, resins, explosives, fibers, paper, leather, protective coatings, printing inks and textile. The first use of EG was happened as an engine coolant in 1925. This use was initially low but gradually increased because of the benefits of EG, and now the largest consume of EG is to produce the engine coolant. absorption through skin contact, brain damages, damage to the Central Nervous System (CNS) and joints, eye damage, toxicity, etc. are the main problems that EG containing wastewaters are responsible for them [1-3].

Several methods were used for treatment of EG containing wastewaters. Zevra et al. [4] were used wet oxidation for treatment of oily wastewater containing alcoholic and phenolic compound with high concentration of organic matter (COD \approx 11000 mg/L). They studied in a high-pressure agitated autoclave reactor in the temperature range of 180–260 °C and oxygen pressure 1 MPa and Increasing COD removal rate with increasing temperature were reported. They observed that, ethylene glycol showed great resistance to this process, among another compounds contained in the wastewater and Temperatures above 240 °C were required for its effective degradation. At 240 °C, WO process could decrease the concentration of ethylene glycol from 0.04 to 0.003 mol/L, while at lower temperatures decreased to 0.025–0.03 mol/L. Advanced oxidation processes (AOPs) were defined as a process in which that in normal temperature and pressure is carried out for the production of free radicals (especially OH \cdot) by

Glaz et al. Reactions have been identified during this process cannot produce highly toxic compounds. Decomposition of whole organic materials also can be done by AOPs. Kinetics of these reactions will occur in order to produce high concentrations of OH and substrate oxidation by free radicals. Among the advanced oxidation methods, ozonation have been introduced as the best possible options [5].

Ozone was discovered by Schonbein during his experiments with electrolysis of sulfuric acid in 1840. However, the ability of ozone to disinfection of contaminated water was first recognized in 1866 by Martinenec and was used in a larger scale for Nice (France) and Oudshoorn (Netherlands) drinking water disinfection. Ozone is a blue gas with pungent odor and strong oxidizing ability [6, 7]. Ozone can react directly with a chemical composition or produce the hydroxyl radical, which then reacts with it. Now a day ozonation, because of ozone oxidation potential and become rigid degradability and biodegradability of compounds to carbon dioxide, was used in water and wastewater treatment widely. In addition of organic and inorganic contaminants removal, ozone has high ability to removing color and odor, and unlike other methods, leaving no waste and sludge [8]. For all the positive features listed for ozonation, this study was conducted for removal of EG containing wastewater by ozone.

MATERIALS AND METHODS

Chemicals and laboratory supplies

All chemicals used in this study such as EG, Sulfuric acid and NaOH was purchased from Merck. Ozone was produced by an ozone generator (ARDA - France (COG-1A) with a production capacity of 5 liters per minute, 2g/h gas output. In addition a closed reactor (in order to ozone and wastewater contact) was used that Figure 1 illustrated it schematically.

Experimental methods

All experimental methods used in this study were in accordance with the procedures described in the standard method reference handbook. Input ozone concentration was measured by titration iodometric method. Measurement of pH was done with using pH Meter (WTW-Germany). The method was used for measuring EG in samples was gas chromatography (GC).

Kinetics of the reaction

The study of chemical reaction kinetic can be a great help to give better understanding of the process. With assuming that, first order reaction was accruing, EG elimination kinetic by ozone was determined from Equation (1):

$$-dc/dt = k.C \quad (1)$$

Equation 2 will achieved with integration Equation 1.

$$\ln C / \ln C_0 = -kt \quad (2)$$

With plotting $(-\ln C / \ln C_0)$ vs. time, reaction kinetic scan be calculated from scope of diagram.

RESULTS AND DISCUSSION

Effect of concentration

Figure 2 and figure 3 demonstrate the results of the first and second phase of research respectively. As can be seen in Figure 2 clearly, increasing the EG removal efficiency was occurred with increasing ozonation time. In concentration of 100mg/L, the EG removal efficiencies was about 10% in the first 20 minutes of ozonation and it seemed very low. After 180 minutes this number improved to a maximum amount of 70%. It was very different results for the concentration of 5 mg/L so that at the first hour, 64.4% of EG was removed by ozone and after 180 min the removal efficiency increased to 95.85%. At other concentrations of 10, 20 and 50mg/L, the removal of EG after 180 minutes was 93.31, 89.96, and 85.01% respectively. In the last 60 minutes of all the contact times, a very low significant scope was seen in increasing the efficiency of ozonation. With a careful look at the removal efficiency of the EG at 120 min, it can be seen that, with increasing the ozonation time from 120 to 180 min this removal rate increased 6.33% averagely. This confirms that the optimized time for ozonation was 120 min. This trend was not observed at higher concentrations, as can be seen in Figure 2 this EG removal increasing rate at concentrations of 500 to 1500mg/L was 21.25% in average. Maximum and minimum removal efficiencies in this phase, was obtained 55.87% for the concentration of 500 mg/L with ozonation time of 180 min and 2.47% for the concentration of 1500mg/L with ozonation time of 30 min. because of economical aspect of ozonation time, to increasing the time up to 180 min was avoided.

Effect of pH on ozonation

After the time variation and obtaining optimized ozonation contact time, the effect of pH changes on the efficiency of the system was determined. The results of this stage are summarized in tables 1 and 2. As can be seen in the tables, best results was observed near alkaline pH due to OH⁰ radicals

production and Whatever we went to the acidic pH, because of consuming the OH^\bullet radicals, efficiency declining was observed. At this stage, the concentrations of 5, 10, 20, 50 and 100 mg/L at 120 min of ozonation time was selected and pH of 3, 5, 7, 9 and 11 was set for determination the optimized pH. As results shows, With increasing the pH to 11, the system was showed increasing in EG removal efficiency dramatically, at Concentration of 100 mg/L, so that from 65.05% improved to 86.12%. This trend was followed in other concentrations and increasing the efficiency around 33/13 at concentration of 50 mg/L from 18/78 to 51/91% was achieved. This increasing of system efficiency at concentrations of 20, 10, and 5 mg/L was achieved 14.06, 10.79, and 8.8, respectively. But this manner was different at acidic pH so that, decreasing in system efficiency was happened and this decrease was more visible and more evident. As results shows, a decrease in pH from 7 to 3 at concentrations of 100, 50, 20, 10 and 5 mg/L, reduction efficiencies equivalent to 18.45, 27.79, 23.16, 22.66, 22.15% was observed.

Effect of pH on ozone removal efficiency results at higher concentrations was summarized in Table 2. The decrease inefficiency (acidic pH) and an increase in efficiency (alkaline pH) were achieved in the same way. pH decreasing from 7 to 3 at concentrations of 500, 750, 1,000 and 1,500 mg/L lead to the efficiency decreasing equal to 4, 10.08, 9.85, 5.86%. The significant increase in the EG removal rate in alkaline pH is Notable. As is clear from Table 2, with increasing pH from 7 to 11 at 500 mg/L, improving the system performance was equal to 17.72%. This trend for concentrations of 750, 1000 and 1500 mg/L was achieved 16.94, 14.02 and 20.26% respectively.

Kinetics study of ethylene glycol ozonation

Kinetic analyses can help to better understanding of the reactions mechanism, so in this study kinetic of treatment of EG containing wastewater by ozone were also discussed. The reaction kinetics was studied in two stages. Figure 4 shows the kinetic analyses results at concentrations of 5, 10, 20, 50 and 100 mg/L. As is evident from the correlation coefficients for all the concentrations, investigated that EG removal was follow the first-order kinetic order.

The results of the reaction kinetics analysis at concentrations of 500, 750, 1000 and 1500 mg/L were shown in Figure 5. The results of the correlation coefficient were achieved equivalent 96.13, 95.92, 96.94 and 92.11 for concentrations of 500, 750, 1000 and 1500 mg/L. K values and correlation coefficients obtained are summarized in Table 3.

CONCLUSIONS

In this study, waste water containing ethylene glycol as an environmental problem was purified good by ozone. Increasing and decreasing pH had a dramatic effect on the removal efficiency of the system, so that the alkaline pH improved it significantly. The effect of increasing the initial concentration of EG in the removal efficiency was negative and decreased with increasing the inlet substrate concentration. Elimination kinetics study, confirm first-order kinetic rate and for the design of the systems must be carefully examined and considered.

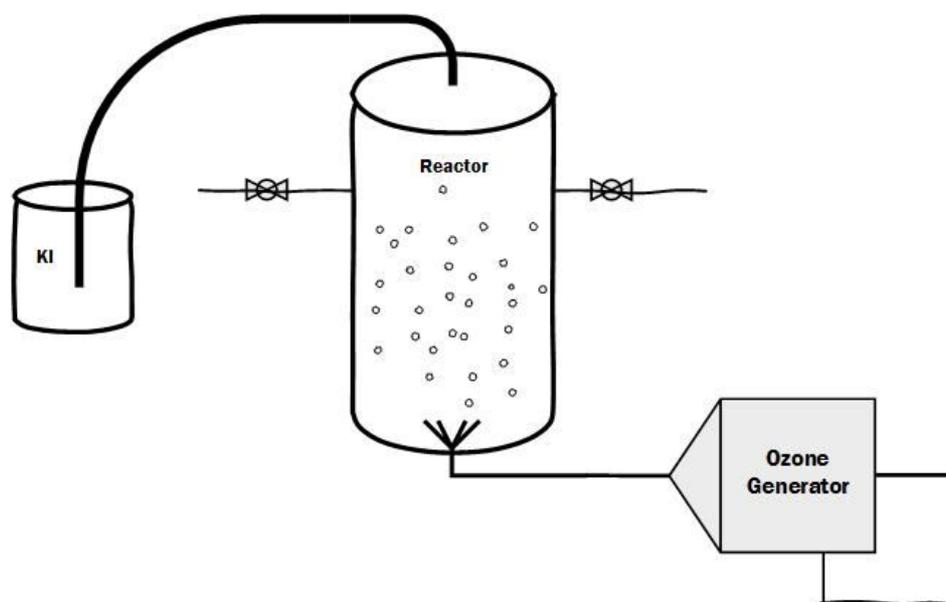


Figure :1: Schematic of ozonation reactor

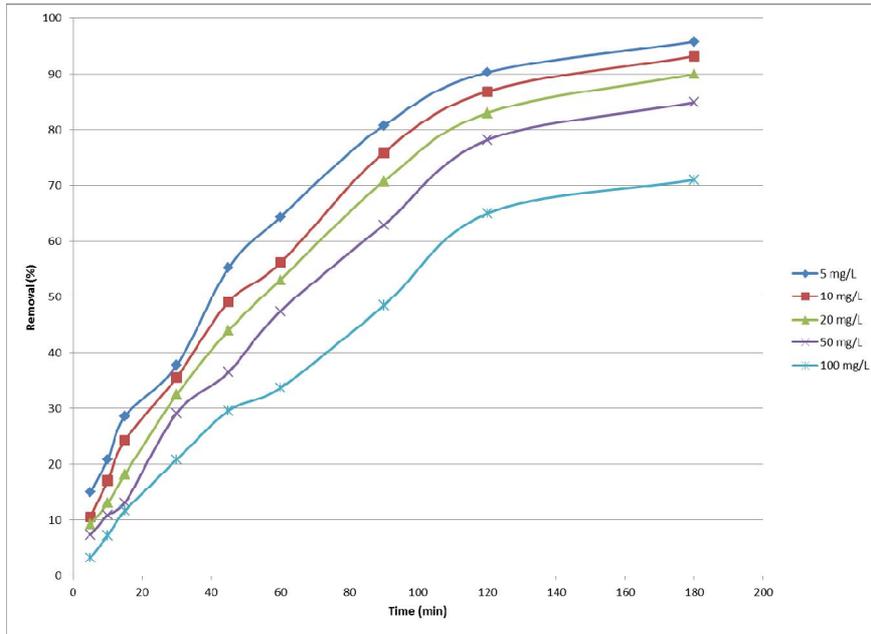


Figure 2 effect of ozonation time on EG removal efficiency (low concentration)

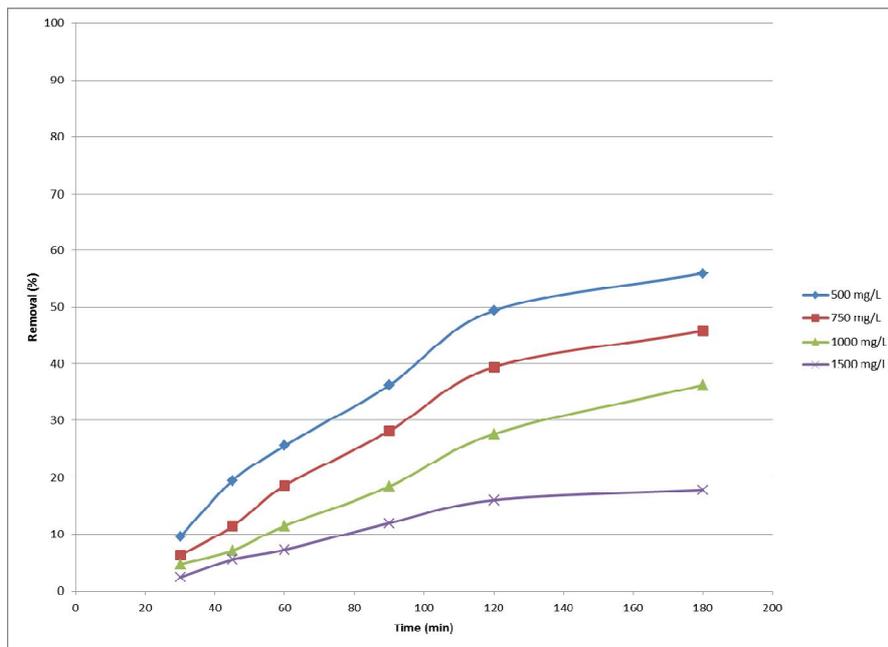


Figure 3 effect of ozonation time on EG removal efficiency (high concentration)

Table 1 effect of pH on EG removal by ozone (low concentration)

T (min)	pH	5	10	20	50	100
120	3	68.14	64.21	59.93	50.39	46.60
	5	79.31	75.41	70.29	63.84	49.96
	7	90.29	86.87	83.09	78.18	65.05
	9	93.31	91.22	90.92	84.44	77.21
	11	99.10	97.66	97.15	91.51	86.12

Table 2 effect of pH on EG removal by ozone (high concentration)

T (min)	pH	500	750	1000	1500
180	3	39.31	29.54	20.88	10.21
	5	43.00	32.21	23.11	12.31
	7	49.39	39.39	27.65	16.07
	9	58.76	51.32	34.12	28.66
	11	67.11	56.33	41.67	36.33

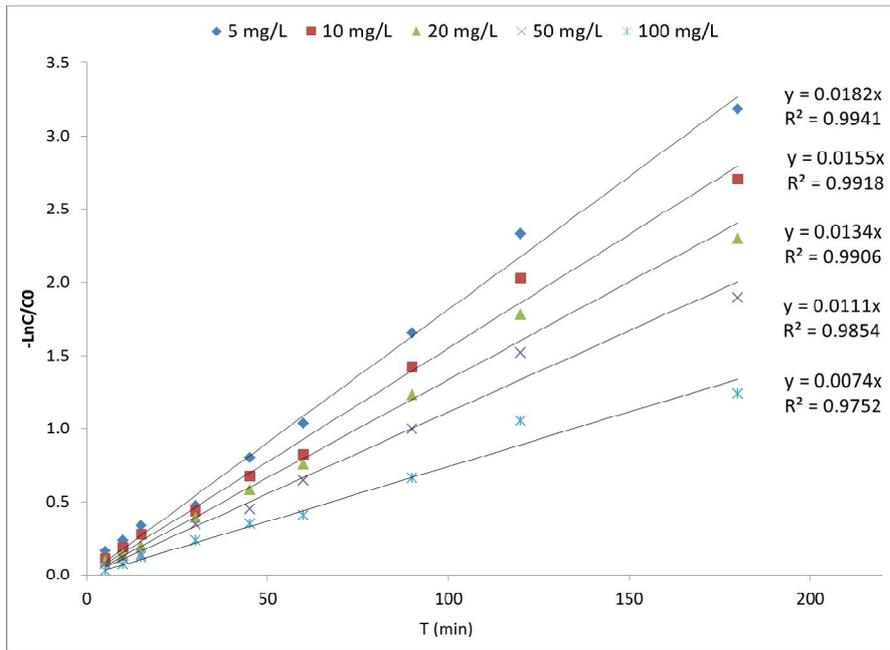


Figure 4 kinetic study of EG oxidation by ozonation (low concentration)

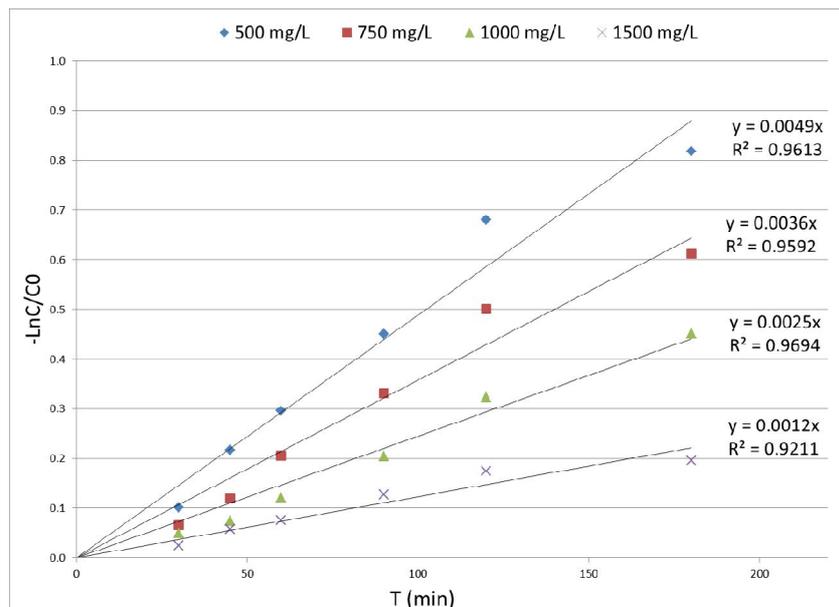


Figure 5 kinetic study of EG oxidation by ozonation (high concentration)

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