Remediation of Spent Caustic in the Wastewater of Oil Refinery by Photo-Fenton Process

Safoora Karimi^a, Aref Shokri^b, Babak Aghel^{c*}

- ^a Department of Chemical Engineering, Jundi-Shapur University of Technology, Dezful, Iran.
- ^b Department of Chemistry, Payame Noor University, Tehran, Iran
- ^c Department of Chemical Engineering, Faculty of Energy, Kermanshah University of Technology, Kermanshah, Iran

*Correspondence should be addressed to Dr Babak Aghel, Email: b.aghel@kut.ac.ir

A-R-T-I-C-L-EI-N-F-O

Article Notes: Received: Jun 07, 2020 Received in revised form: Jun 23, 2020 Accepted: Jun 23, 2020 Available Online: Jul 27, 2020

Keywords:

Biological oxygen demand analysis Box-behnken design Photo-Fenton Process Spent caustic Wastewater

A-B-S-T-R-A-C-T

Background & Aims of the Study: Currently, the advanced oxidation processes have received increasing attention for the treatment of industrial wastewater. In the present study, the photo-Fenton process was used for the remediation of the spent caustic in the wastewater of Kermanshah Oil Refining Company in Iran. The effluent comprising spent caustic is toxic dark brawn with a high level of alkalinity.

Materials and Methods: Diluted wastewater covering the spent caustic from Kermanshah Oil refinery was used in this study in September 2018. In addition, the effects of operative factors, such as the initial concentrations of hydrogen peroxide (H_2O_2) , ferrous ion, and initial chemical oxygen demand (COD), have been investigated. The response surface method and Box-Behnken design of experiments were employed to examine the effects of three independent variables on the response function to obtain the optimum conditions.

Results: Analysis of variance was performed to determine the significance of the effects of independent variables on the response function. Various amounts of variables were optimized for the removal of COD. At optimum conditions (i.e., an H_2O_2 concentration of 600 mg/l, ferrous concentration of 145 mg/l, and initial COD of 300 mg/l), the removal efficiency for COD was 91.5% after 60 min of reaction.

Conclusion: According to the obtained results, the suggested quadratic model demonstrated good correctness. The statistical analysis showed that the model was satisfactory to predict the performance of the process. The wastewater containing spent caustic cannot proficiently be degraded by ultraviolet radiation and hydrogen peroxide (H_2O_2) oxidation separately; however, the photo-Fenton method is verified to be operative and can considerably degrade this pollutant. One of the main disadvantages of this process in the treatment of spent caustic is that the optimum pH is near 3, and a considerable amount of acid is needed to neutralize and acidify the alkalinity of spent caustic.

Please cite this article as: Karimi S, Shokri A, Aghel B. Remediation of Spent Caustic in the Wastewater of Oil Refinery by Photo-Fenton Process. Arch Hyg Sci 2020;9(3):179-188

Background

Some companies, such as refineries and

petrochemicals, are under more severe environmental rules to enhance monitoring and control their wastewater streams. One of the most difficult wastewater streams is created in

Archives of Hygiene Sciences

Volume 9, Number 3, Summer 2020

the process of extracting hydrogen sulfide, mercaptans, and organic acids from hydrocarbon streams. Often diluted caustic (NaOH) solutions are used in the oil refinery industries for the removal of acidic compounds and volatile (organic) sulfur combinations from gaseous streams and liquefied petroleum gas.

The use of caustic leads to the foundation of a waste product referred to as spent caustic (1). Spent caustic is a brown liquid with a sharp odor of sulfur compounds formed by washing sulfur compounds and other contaminants from light hydrocarbon compounds with a solution containing sodium hydroxide. This effluent has high salinity, high alkalinity, high sulfur content, and strong unpleasant odor that should be considered for disposal or purification (2-3).

Some approaches, including physicalchemical techniques or processes of customary oxidation, were used for the treatment of refinery wastewater. Although the oil itself can hold sulfur, the remediation technique is generally applied after the distillation of oil fraction, based on its contact with air, permitting the production of H_2S that is very resistant and corrosive (4).

In current decades, several studies have been carried out to develop a better technique for the remediation of spent caustic. Graaff et al. investigated the probability and benefits of a procedure two-step for the biological remediation of sulfide spent caustics in haloalkaline circumstances (5). There are three approaches to the remediation of industrial wastewater, including chemical physical and biological methods. However, they are nondestructive and only transfer contaminants from water to another phase and consequently making secondary pollution (6). Therefore, expensive processes, such as the post-treatment of solid-waste and production of the adsorbent supplies, are required in this regard (7).

The photo-Fenton oxidation is an upgrade of Fenton's reagent with adding an irradiation source. According to the literature, it was reported that the degradation proficiency of the oxidation process enhanced under ultraviolet (UV) lighting, compared to that of the ordinary Fenton reaction. Therefore, the existence of UV illumination in the photo-Fenton method causes the photoreduction of ferric species into ferrous ion (8-9).

Some studies, such as a study carried out by Hsiungsheu et al., investigated the removal of more than 94% of chemical oxygen demand (COD) in wastewater using neutralization and Fenton system considerably reducing the COD and sulfide (10). In a study conducted by Rodriguez et al. on the treatment of caustic wastewater using the electro-Fenton process, 95% of COD was removed at a pH of 4, temperature of 40°C, and iron of 100 mg/l (11).

Abdullah et al. studied synthesized the treatment of spent caustic wastewater using the photo-Fenton oxidation process. They used the response surface method (RSM) for the experiment design of their study (12). Another study carried out by Chen et al., investigated the actual spent caustic wastewater remediation with the COD of 25000 by catalytic and typical wet air oxidation.

Many optimization approaches have been offered in industrial applications. In the traditional optimization approach, the onefactor-at-a-time manner method has many difficulties, such as being time-consuming, expensive, and unsuccessful at both the identification of the interactions among the parameters and prediction studies(13). The alternative to the classical technique is the utilization of statistical and mathematical experimental designs, such as Box-Behnken design (BBD), which was used in the present study.

In the current study, the synthetic wastewater containing spent caustic was treated by the photo-Fenton process. The present study examined the effect of different variables, such as the concentrations of H_2O_2 , concentration of ferrous, and initial COD, on the efficiency of

• Remediation of Spent Caustic in the Wastewater ...

Karimi S et al. / Arch Hyg Sci 2020;9(3):179-188

COD removal using BBD.

Materials & Methods

Materials

The investigated wastewater was the effluent of the spent caustic from Kermanshah Oil Refining Company in Iran after dilution in distilled water with the succeeding properties (Table 1). The features of the spent caustic were not similar at different time points, and the amounts of parameters were not entirely constant. The spent caustic confirmation is greatly variable depending on the procedure condition. The FeSO₄.7H₂O and H₂O₂ solution (30% w/w) were supplied from Merck Company. Supplied manganese oxide (MnO₂) (\geq 99%) was provided by Sigma-Aldrich Company. In addition, distilled water was utilized in all the experiments.

Photo reactor and experiments

The COD content was originated from both inorganic and organic compounds (such as sulfides) in the spent caustic. The COD of the samples was determined by the HACH's COD method utilizing a COD reactor and measured through the standard closed reflux and Colorimetric method [14]. The absorbance of the samples for the COD test was estimated using a spectrophotometer (Agilent 5443) at 600 nm. The pH was adjusted by NaOH or hydrochloric acid (0.1 M) and measured by pH Meter PT-10P (Sartorius Instrument, Germany).

All the experiments were conducted in a one-liter glass photoreactor. The system was

 Table 1) Approximate properties of the studied wastewater (after dilution)

(uter unuter)		
Parameter	Amount	
Sulfide	260 mg/l	
NaOH	1200 mg/l	
COD	900 mg/l	
pН	13.0	
Color	Dark brown	





equipped with a sampling system (Figure 1). A 15W Philips (UV-C) mercury lamp vertically placed at the center of the reactor was utilized as the source of light. The reactor was equipped with a water jacket with an external flow controlled through a thermostat for the adjustment and maintenance of the temperature at 25°C. The solution was mixed with a stirrer for preventing the precipitation of iron ions in the reactor and keeping the solution homogeneous.

The amount of 1000 ml of diluted wastewater was utilized in each experiment. The concentration of hydrogen peroxide, ferrous ions, and initial COD were the intended parameters, and it was aimed to decrease the percentage of COD removal. The reaction time was reported as 60 min in all the experiments. The percentage of COD removal was calculated using the following equation:

Removal of $COD(\%) = \left(\frac{COD_0 - COD_t}{COD_0}\right) \times 100$ Equation (1)

Archives of Hygiene Sciences

@ 0

Volume 9, Number 3, Summer 2020

where COD_0 and COD_t are considered the values of COD at the initial and *t* times, respectively. The amount of H₂O₂ remaining in the samples, interfering with the COD test, was removed using MnO₂ powder. The samples were filtered for the separation of MnO₂ powders [15].

Experimental design and statistical analysis

The experimental design was utilized for the optimization of the percentage of COD removal in a scientific way. The impacts of hydrogen peroxide concentration (X_{HP}) , ferrous concentration (X_F) , and initial COD (X_{COD}) on the removal of COD were examined in order to optimize the procedure $X_{HP}X_FX_{COD}$. Table 2 tabulates the input variables $(X_{HP}, X_F, \text{ and } X_{COD})$, along with the associated dimensions and values. The empirical results of the percentage of COD removal are shown in Table 3.

Among all the RSMs, experimental BBD needs a smaller number of experiments (i.e., a total of 15 experiments for three variables) [16]. Based on the design of the experiments, the following model was presented for the response • Remediation of Spent Caustic in the Wastewater...

variable (*COD Removal*, %), as a polynomial equation of the independent variables:

$Res. = b_0 + \sum b_i x_i + \sum \sum b_{ij} x_i x_j + \sum \sum b_{ii} x_i^2 + \varepsilon \text{ Equation (2)}$

where b_0 is a constant number; ε is the remainder of the equation, b_{ij} is a linear interaction between the input variables of x_i and x_j (i = 1, 2 and j = 1, 2, 3j = 1, 2, 3); b_i is the slope of the variable; b_{ii} is the second order of the input variable x_i (i = 1, 2, 3).

Analysis of variance (ANOVA) was utilized to investigate the significance of each variable (i.e., operating parameter) in the polynomial equation (Equation 2) [17]. In ANOVA, a pvalue of 0.05 was considered statistically significant. The p-values of less than 0.0500 determine the importance of model terms. The p-values greater than 0.10, demonstrate that the model terms are not important.

The statistical significance of the secondorder models was defined by F-value. When the estimated F-value is higher than the F-value in Table 4, the p-value will be much less

Variable	T I	Symbol –	Range and level		
variable	Unit		Low (-1)	Middle (0)	High (+1)
Hydrogen peroxide concentration	mg/l	C_{HP}	200	400	600
Ferrous concentration	mg/l	C_F	50	100	150
COD	mg/l	C_{COD}	300	600	900

Table 2) Experimental ranges and levels of independent variables

D	Manipulated variables		Response (%)	
Kun no.	C _{COD}	C _{Ferrous}	C _{HP}	Removal of chemical oxygen demand (%)
1	900	150	400	59.5
2	300	100	200	82.0
3	300	100	600	92.5
4	900	50	400	65.0
5	300	150	400	92.5
6	600	150	200	67.0
7	600	150	600	84.0
8	900	100	200	54.5
9	600	100	400	78.1
10	600	50	600	83.5
11	600	100	400	78.4
12	900	100	600	75.0
13	300	50	400	89.5
14	600	50	200	67.3
15	600	100	400	78.5

Archives of Hygiene Sciences

 \odot

Volume 9, Number 3, Summer 2020

• Remediation of Spent Caustic in the Wastewater...

Karimi S et al. / Arch Hyg Sci 2020;9(3):179-188

Source	Adj SS	DF	MS	F -value	P-value
Model	1887.92	9	209.77	49.63	0.000
X _{COD}	1313.28	1	1313.28	310.7	0.000
$X_{Fe(II)}$	0.66	1	0.66	0.16	0.709
X_{H202}	515.21	1	515.21	121.89	0.000
X_{COD}^2	1.24	1	1.24	0.29	0.612
$X_{Fe(II)}^{2}^{2}$	4.71	1	4.71	1.11	0.34
X_{H202}^{2}	11.36	1	11.36	2.69	0.162
$X_{COD}X_{Fe(II)}$	18.06	1	18.06	4.27	0.094
$X_{COD}X_{H2O2}$	25	1	25	5.91	0.059
$X_{H202}X_{Fe(II)}$	0.16	1	0.16	0.04	0.853
Error	21.13	5	4.23		
Lack of fit	21.05	3	7.02	161.9	0.06
Pure error	0.09	2	0.04		
Total	1909.06	14			
Model Summary					
	S	\mathbb{R}^2	R_{adj}^2	R_{pred}^2	
	2.05593	98.89%	96.9%	82.35%	

Table 4) Analysis of variance for presented model of removal of chemical oxygen demand

indicating the importance of the statistical model. The estimated F-value is obtained by dividing the mean squares of regression (including linear, square, and interaction) by the mean squares of the residual as follows (18):

$$F - \text{value} = \frac{MS_{Reg.}}{MS_{Res.}} = \frac{SS_{Reg.}/DF_{Reg.}}{SS_{Res.}/DF_{Res.}}$$
Equation (3)

The regression degree of freedom $(DF_{Reg.})$ is the number of terms minus one. In addition, the residual degree of freedom $(DF_{Res.})$ is the total degree of freedom minus the regression degree of freedom [18]. The design of the experiments was comprised of 15 tests (i.e., 13 tests and 2 replicates at the central point). Table 3 tabulates the percentages of COD removal. All the experiments were randomly conducted for the minimization of the experimental errors.

Results

Design of experiments and analysis of the response variance

Optimal conditions were determined in order

to maximize the removal of COD using the photo-Fenton process. In the current study, the impacts of three independent variables (i.e., H_2O_2 concentration, Fe^{2+} concentration, and initial COD) on the percentage of COD removal (*COD_{rem.}%*) were studied using BBD to obtain desirable conditions. The quadratic relationship was obtained using the least squares method for the determination of the response in terms of the three independent variables as follows:

Equation (4)
$COD \ Removal \ \% = 76.9 - 0.0375 X_{COD} + 0.162 X_{Fe2+}$
$+ 0.0482X_{H202} - 0.000006X_{COD}^{2}$
$-0.000452X_{Fe2+}^2 - 0.000044X_{H202}^2$
$-0.000142X_{Fe2+}X_{COD} + 0.000042X_{COD}X_{H202}$
$+ 0.000002X_{Fe2+}X_{H202}$

Figure 2 illustrates the predicted values of the quadratic model for the percentage of COD removal, compared to the observed values. The calculated values for the percentage of COD removal were obtained using Equation 4.

Table 4 tabulates the findings of ANOVA for the evaluation of the COD removal model.

Archives of Hygiene Sciences

Volume 9, Number 3, Summer 2020



Figure 2) Comparison of experimental and predicted values of COD removal (%)

The total degree of freedom was equal to 1 (15-14=1). As shown in Table 4, the degree of freedom for the model and residual error were reported as 9 and 5, respectively. The calculated F-value was compared to the tabulated F-value as shown in Table 4.

The terms of X_{HP} , X_{COD} , and their squares have a p-value of less than 0.01; therefore, they are distinctly significant. Nevertheless, their squares and term $X_{Fe(II)}$ have great p-values signifying that they are not significant (19). However, the term of the binary interaction • Remediation of Spent Caustic in the Wastewater...

between the variables has a p-value of more than 0.05 indicating that the interaction of variables is non-significant. Moreover, the significance of the lack of fit is more than 0.05, indicating the model's mismatch.

Effects of operating variables

Figures 3-5 depict the effects of hydrogen peroxide (200, 400, and 600 mg/l), Fe^{2+} (50, 100, and 150 mg/l), and initial COD (300,600, and 900 mg/l) concentrations on the removal of COD in spent caustic wastewater. The aforementioned figures illustrated the contour plots of COD removal based on these variables using Equation 4. The contour plots of the COD removal according to hydrogen peroxide, ferrous, and initial COD concentrations are depicted in Figure 3. In addition, the maximum percentage of COD removal was obtained in low values of COD and practically high values of hydrogen peroxide. In the photo-Fenton method, the efficiency of COD removal enhanced with an increase in H₂O₂ concentration.

Various amounts of Fe^{2+} (range: 50-150 mg/l) were used to reach the optimal concentration. As illustrated in Figure 4, it is



Figure 3) Contour plots of chemical oxygen demand (COD) removal versus hydrogen peroxide and COD concentrations ($pH = 3, T = 25^{\circ}$ C, and t = 60 min)

Archives of Hygiene Sciences Volume 9, Number 3, Summer 2020

Removal of COD(%)



Figure 4) Contour plots of chemical oxygen demand (COD) removal in terms of ferrous and initial COD concentrations ($pH = 3, T = 25^{\circ}$ C, and t = 60 min)



Figure 5) Contour plots of chemical oxygen demand removal versus ferrous and hydrogen peroxide concentrations $(pH = 3, T = 25^{\circ}C, and t = 60 min)$

clear that in the photo-Fenton process, the removal efficiency of COD increased with an increase in the dosage of ferrous ions based on the following equations (20):

$\mathrm{Fe}^{+2} + \mathrm{H}_2\mathrm{O}_2 \rightarrow \mathrm{Fe}^{+3} + \mathrm{OH}^{\bullet} + \mathrm{OH}^{-}$	Equation (5)
$Fe^{+2} + OH^{\bullet} \rightarrow OH^{-} + Fe^{+3}$	Equation (6)

In the photo-Fenton process, the creation of hydroxyl radicals and removal of COD

increased with an increase in the concentration of Fe^{2+} ions from 50 to 100 mg/l. Based on figures 3-5, the increase in the catalyst dosage was partly helpful. However, the catalyst should not be added without any limitations. High amounts of catalyst negatively affected the removal of COD, since the scavenging results might happen (Equations 7-9).



Archives of Hygiene Sciences

Volume 9, Number 3, Summer 2020

Karimi S et al. / Arch Hyg Sci 2020;9(3):179-188

• Remediation of Spent Caustic in the Wastewater...

$H_2O_2 + Fe^{3+} \rightarrow H^+ + FeOOH^{2+}$	Equation (8)
$FeOOH^{2+} \rightarrow HO_2^{\bullet} + Fe^{2+}$	Equation (9)

At the high catalyst amounts, the additional catalyst would consume the produced hydroxyl radical. Higher catalyst quantities would clearly upsurge the treatment cost. Furthermore, the extreme catalyst dosage would result in the production of the high amounts of sludge, which would increase the requirement for the subsequent treatment of sludge.

At a pH of higher than 3, the main fraction of Fe (II) was precipitated as $Fe(OH)_3$, fading the reaction between H_2O_2 and Fe^{2+} . In addition, in alkaline conditions, the removal of COD reduced because the H_2O_2 degrades faster into H_2O and O_2 . Consequently, in the present study, according to the preliminary experiment, pH was fixed at 3 in all the tests and was not optimized.

Optimization of operating conditions

As illustrated in figures 3-5, it is obvious that the percentage of COD removal can be high in some conditions. The values of various variables were achieved using Design-Expert software (version 7.0.0) for the maximization of the percentage of COD removal. Table 5 tabulates the aforementioned optimal values, with the percentage of COD removal. As shown in Table 5, the maximum rate of COD removal was achieved under several conditions, including hydrogen peroxide concentration of 600 mg/l, ferrous concentration of 145 mg/l, and initial COD of 300 mg/l. Under the aforementioned conditions, the maximum rates of COD removal

Table 5) Optimal conditions in the removal of
chemical oxygen demand $(T = 25^{\circ}C \text{ and } t = 60 \text{ min})$

enemieur oxygen demund (1 = 5 0	and v	00 munity
Parameters	Unit	Value
Hydrogen proxide concentration	mg/l	600
Ferrous ion concentration	mg/l	145
COD	mg/l	300
Predicted COD removal	%	95.25
Experimental COD removal	%	91.5

COD: Chemical oxygen demand

 \odot

Archives of Hygiene Sciences

were reported as 95.25% and 91.5% by the model (Equation 4) and experiments with three replications, respectively.

Discussion

As previously mentioned, this study examined the effects of hydrogen peroxide and Fe^{2+} concentrations and initial COD values on the percentage of COD removal from spent caustic wastewater. Figures 3-5 illustrate the contour plots of the percentage of COD removal and aforementioned variables. In addition, the figures were plotted using Equation 4.

Figure 3 depicts a contour plot of the percentage of COD removal regarding H_2O_2 concentration and initial COD. Accordingly, it was observed that the highest percentage of COD removal was achieved when utilizing the mean values for both variables (i.e., H_2O_2 and Fe^{2+} concentration).

In the photo-Fenton process, an extreme increase in the concentration of Fe (II) reduced the efficiency of COD removal because the production rate of primary hydroxyl radicals is very high at high concentrations of Fe²⁺, mostly due to H₂O₂ decomposition (see Equation 10). Consequently, numerous hydroxyl radicals are consumed by side reactions before being utilized for the removal of COD (20–21).

 $H_2O_2 + hv \rightarrow 2^{\bullet}OH$ Equation (10)

Furthermore, the brown turbidity of the solution can result from the high concentration of the ferrous ion. As a result, the absorption of UV light, which is essential for photolysis, is delayed leading to the recombination of OH[•] radicals (Equation 11). This finding has been also reported in multiple other studies (22–23).

 $Fe(OH)^{2+} + hv \rightarrow Fe^{2+} + OH$ Equation (11)

The impact of Fe^{2+} on the removal of COD

Volume 9, Number 3, Summer 2020

• Remediation of Spent Caustic in the Wastewater...

is similar to the effect of H₂O₂ concentration (24). A study carried out by Nueza et al. investigated the treatment of caustic wastewater by the electrochemical process, and 93% of COD was removed (25). In a study conducted by Hawari et al. on the treatment of caustic wastewater, 98% and 99% were reported as COD and sulfide removal at a pH of 1.5, respectively (26). The benefits of the photo-Fenton process were less sludge formation, fewer chemicals, and time obligation but at the consumed power. The cost of power consumption can be reduced by employing sunlight instead of artificial UV light to a larger amount.

Conclusion

In the present study, the spent caustic in the wastewater of Kermanshah Oil Refining Company was treated using the photo-Fenton process. The Box-Behnken system was applied for designing the experiments. In addition, the current study examined the effect of H_2O_2 , Fe^{2+} , and initial COD on the percentage of COD removal. After conducting the tests, the findings were analyzed using ANOVA. The obtained results showed that some operating parameters were significant and effective in the removal of COD.

A quadratic model was presented to analyze the impacts of variables on the percentage of COD removal. At optimum conditions (i.e., hydrogen peroxide concentration of 600 mg/l, ferrous concentration of 145 mg/l, and initial COD of 300 mg/l) and after 60 min of reaction, the removal efficiency for COD was reported as 91.5%. The photo-Fenton process was powerful in the removal of COD. One of the main disadvantages of this process in the treatment of spent caustic is that the optimum pH is near 3, which is not optimized. Furthermore, a considerable amount of acid is required to neutralize and acidify the alkalinity of spent caustic.



Acknowledgements

Kermanshah University of Technology, Kermanshah, Iran, has financially supported the present study.

Funding

The authors would like to acknowledge the financial support of Kermanshah University of Technology for the current study under the ethics code of S/P/T/1187.

Conflict of Interest

The authors declare that they have no conflict of interest concerning the publication of the study.



- 1. Esfahani KN, Farhadian M, Nazar AS. Interaction effects of various reaction parameters on the treatment of sulfidic spent caustic through electrophoto-Fenton. Int J Environ Sci Technol 2019; 16:7165-74. Link
- 2. Alipour Z, Azari A. COD removal from industrial spent caustic wastewater: a review. J Environ Chem Eng 2020; 8(3):103678. Link
- 3. Gareau BJ, Crow B. Ken Conca, governing water: contentious transnational politics and global institution building. Int Environ Agre Polit Law Econ 2006; 6(3):317-20. Link
- Hariz IB, Halleb A, Adhoum N, Monser L. Treatment of petroleum refinery Sulfidic spent caustic wastes by electro coagulation. Separat Purif Technol 2013; 107:150-7. Link
- de Graaff M, Klok JB, Bijmans MF, Muyzer G, Janssen AJ. Application of a 2-step process for the biological treatment of Sulfidic spent caustics. Water Res 2012;46(3):723-30. <u>PMID: 22182680</u>
- Shokri A. Degradation of 4-Nitrophenol from industrial wastewater by nano catalytic Ozonation. Int J Nano Dimens 2016;7(2):160-7. Link
- 7. Shokri A. A kinetic study and application of the electro-Fenton process for the remediation of the

Archives of Hygiene Sciences

Volume 9, Number 3, Summer 2020

aqueous environment containing Toluene in a batch reactor. Russ J Appl Chem 2017;90(3):452-7. Link

- 8. Mohadesi M, Shokri A. Evaluation of Fenton and photo-Fenton processes for the removal of pchloronitro-benzene in aqueous environment using Box-Behnken design method. Desal Water Treat 2017;81(1):199-208. Link
- Shokri A. Removal of acid red 33 from aqueous solution by Fenton and photo Fenton processes. J Chem Health Risks 2017;7:119-31. Link
- Sheu SH, Weng HS. Treatment of olefin plant spent caustic by combination of neutralization and Fenton reaction. Water Res 2001;35(8):2017-21. <u>PMID:</u> <u>11337849</u>
- Rodriguez N, Hansen HK, Nunez P, Guzman J. Spent caustic oxidation using electro-generated Fenton's reagent in a batch reactor. J Environ Sci Health A Tox Hazard Subst Environ Eng 2008;43(8):952-60. <u>PMID: 18569308</u>
- 12. Abdulah SS, Hassan MA, Noor ZZ, Aris A. Optimization of photo-fenton oxidation of sulfidic spent caustic by using response surface methodology. J Environ Sci 2011;25(4):231. Link
- Chen C. Wet air oxidation and catalytic wet air oxidation for refinery spent caustic degradation. J Chem Soc Pak 2013;35(2):244-50. <u>Link</u>
- 14. Shokri A. The treatment of spent caustic in the wastewater of olefin units by ozonation followed by electrocoagulation process. Desal Water Treat 2018; 111:173-82. Link
- 15. El-sousy K, Hussen A, Hartani K, El Aila H. Elimination of organic pollutants using supported catalysts with hydrogen peroxide. Jordan J Chem 2007;2(1):97-103. Link
- 16. Ahmadi M, Rahmani K, Rahmani A, Rahmani H. Removal of benzotriazole by Photo-Fenton like process using nano zero-valent iron: response surface methodology with a Box-Behnken design. Polish J Chem Technol 2017;19(1):104-12. Link
- 17. Rumky J, Ncibi MC, Burgos-Castillo RC, Deb A, Sillanpa M. Optimization of integrated ultrasonic-

Fenton system for metal removal and dewatering of anaerobically digested sludge by Box-Behnken design. Sci Total Environ 2018;645:573-84. <u>PMID:</u> 30032079

- Montgomery D. Design and analysis of experiments. New Jersey: John Wiley; 2001. Link
- 19. Buyukada M. Prediction of photo catalytic degradation and mineralization efficiencies of basic blue 3 using TiO₂ by nonlinear modeling based on Box-Behnken design. Arab J Sci Eng 2016; 41(7):2631-46. Link
- 20. Shokri A. Investigation of UV/H₂O₂ process for removal of Ortho-Toluidine from industrial wastewater by response surface methodology based on the central composite design. Desal Water Treat 2017; 58:258-66. Link
- 21. Trovo AG, Hassan AK, Sillanpa M, Tang WZ. Degradation of Acid Blue 161 by Fenton and photo-Fenton processes. Int J Environ Sci Technol 2016; 13(1):147-58. Link
- 22. Ebrahiem EE, Al-Maghrabi MN, Mobarki AR. Removal of organic pollutants from industrial wastewater by applying photo-Fenton oxidation technology. Arab J Chem 2017;10(2):S1674-79. Link
- 23. Clarizia L, Russo D, Di Somma I, Marotta R, Andreozzi R. Homogeneous photo-Fenton processes at near neutral pH: a review. Appl Catal B Environ 2017;209:358-71. Link
- 24. Nitoi I, Oncescu T, Oancea P. Mechanism and kinetic study for the degradation of lindane by photo-Fenton process. J Ind Eng Chem 2013;19(1):305-9. Link
- 25. Nunez P, Hansen HK, Rodriguez N, Guzman J, Gutierrez C. Electrochemical generation of Fenton's reagent to treat spent caustic wastewater. Separat Sci Technol 2008;44(10):2223-33. Link
- 26. Hawari A, Ramadan H, Abu-Reesh I, Ouederni M. A comparative study of the treatment of ethylene plant spent caustic by neutralization and classical and advanced oxidation. J Environ Manage 2015; 151:105-12. <u>PMID: 25546845</u>

Archives of Hygiene Sciences

Volume 9, Number 3, Summer 2020