Modeling the Fenton depuration of the effluent from a slaughterhouse based on design of experiments

Abstract

In an effort to improve the quality of treated water, the implementation of a new technology referred to as Advanced Oxidation Processes (AOP) is being examined, either alone or in combination with other processes. When working with real conditions there are sometimes changes which involve adjustments of the process, and it is easier to perform such adjustments when it has a reliable mathematical model. The studied scaled design referred to as Fenton treatment, involving the use of a central-composite design (quadratic model) which was tested on the effluent discharge of a slaughterhouse. As a result of our treatability study, we experienced removal efficiencies based on chemical oxygen demand (COD) greater than 85%, while ascertaining that removal process was the result of chemical oxidation and coagulation.

Keywords: central composite design, coagulation, chemical oxidation, fenton reaction, model, slaughterhouse effluent

Introduction

The meat processing industry generates large quantities of waste water with high content of organic matter, which must be removed prior to being discharged. In order to improve water quality and ensure regulatory compliance, Advanced Oxidation Processes (AOP) may be used in combination with other processes as pre or post treatment. It has been reported that Fenton process have removal efficiencies of chemical oxygen demand (COD) greater than 85%. In this work, we have used AOPs based on Fenton process in the depuration of the effluent of a slaughterhouse; in order to improve its quality. Fenton process is based on the oxidative action of free hydroxyl radicals, with a redox potential of 2.8 V₃ produced by Fenton reaction in acid medium. This reaction must not be analyzed alone, because there are others occurring simultaneously, with different reaction constants, so Eq. 1 to 7 are the principal ones:

\[ \text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \cdot \text{OH} + \text{OH}^- \quad K_r=70 \]  

(1)

\[ \cdot \text{OH} + \text{organic matter} \rightarrow \text{final products} \quad K_r \]

(2)

\[ \cdot \text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2^* \quad K_r=3.3\times10^7 \text{M}^{-1}\text{s}^{-1} \]  

(3)

\[ \text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \cdot \text{HO}_2 + \text{H}^+ \quad K_r=0.01 \text{M}^{-1}\text{s}^{-1} \]  

(4)

\[ \text{Fe}^{3+} + \text{HO}_2^* \rightarrow \text{Fe}^{2+} + \text{O}_2 + \text{H}^+ \quad K_r=1.2\times10^8 \text{M}^{-1}\text{s}^{-1} \]  

(5)

\[ \text{Fe}^{2+} + \text{HO}_2^* \rightarrow \text{Fe}^{3+} + \text{HO}^- \quad K_r=1.3\times10^9 \text{M}^{-1}\text{s}^{-1} \]  

(6)

\[ \cdot \text{OH} + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \cdot \text{OH}^- \quad K_r=3.2\times10^8 \text{M}^{-1}\text{s}^{-1} \]  

(7)

When applying this treatment with real wastewaters, sometimes there are changes in its quality and is convenient to have a mathematical model which allows to predict which adjustments are necessary. There are models based on chemical analysis and experimental determination of some parameters but it was decided to work on the development of a statistical model using the software Statgraphics; due to the quantity of substances present in our sampled real effluent and the high number of experimental data available. Taking this in consideration we developed a model for the Fenton treatment of the effluent of a slaughterhouse, with inclusion of the following factors: initial ferrous ion concentration (Fe^{2+}), initial hydrogen peroxide concentration (H₂O₂), initial chemical oxygen demand (COD), and time (t). Based on our analysis, we conducted a kinetic study as a complement.

Materials and methods

Materials

As it has been commented the water quality was a variable throughout this study; this quality is represented by COD, so periodically samples of the effluent were taken at different times at the distal end of the actual wastewater treatment facility (plant), in order to obtain working samples with unique qualities, storing them at 4°C. Some of the working samples were prepared by dilution. For the objective of the study we focused on the COD parameter, of which highest value was 577mg L⁻¹ and flow with an average value of 350m³d⁻¹. In this analysis, we employed ferrous sulphate
(FeSO₄·7H₂O, provided by KEM), titanium oxysulphate (O₂STi. xH₂SO₄, provided by FLUKA Analytical), H₂O₂ (provided by KEM), sulfuric acid, orthophenanthroline and ferrous ammonium sulphate, all chemicals used is analytical grade and purchased from Karal and KEM. In preparing solutions pure water (it is better if we mention type of water like type-II or type-III) was used (conductivity<1μS/cm⁻¹) from a Millipore equipment model Elix 5.

**Results and discussion**

Applying the ANOVA analysis, it was found for the quadratic model, the statistic R² of 80.5059 and R² adjusted of 73.1298, and that the four factors studied were significant. Figure 1(A) depicts the behavior of principal factors, showing that by increasing each one, RE increases, having different levels of influence in the following order of magnitude: (Fe⁰⁰⁰),time→(H₂O₂),. On the other hand Figure 1(B) depicts the response surface for the optimal removal condition of COD for one of the effluents studied (CODₙ₉₅) at 10min, corresponding to a true sample, not a dilution.

\[ RE = -20.602 + 1.14238 \times (t) + 0.102791 \times (H₂O₂) + 0.138419 \times COD + 5.87345 \times t - 0.0043153 \times (t)^2 - 0.0004006362 \times (t)^2 + 0.000813263 \times (t)^2 \times COD - 0.0222401 \times (t)^2 \times COD + 0.0000255268 \times (H₂O₂) - 0.00000666185 \times (H₂O₂)^2 \times COD - 0.000462 \times (H₂O₂)^2 - 0.0000277821 \times COD^2 + 0.00615528 \times COD \times t - 0.0165629 \times t^2 \]

The data in Table 2 show that the model described develops properly the Fenton treatment. In the cases which were studied, the variation between CODₙₙ values obtained and estimated is approximately 6%. These two final result, lead us to conclude that the model obtained is viable for depuration treatment of the effluent studied, by permitting us to manipulate principal variables of the process in function of the water quality represented by COD.

Further analysis of equation (9) was performed in order to establish the maximum removal efficiency to be reached by the Fenton treatment. Equation (9) was codified in the optimization software GAMS, using as lower and upper values for [Fe⁰⁰⁰] and [H₂O₂], those presented as -a and +a in Table 1. First of all, it has been found that the objective function is non-convex, since the characteristics values of its Hessian are -0.0473, -0.0009, 0.000 and 0.0063. Thus, as the time increases, the removal efficiency will also be increased, but the value of [Fe⁰⁰⁰], required will change, as can be observed in Table 3. It can also be observed that as the initial chemical oxygen demand increases, the required [Fe⁰⁰⁰] decreases. It is worth to notice that the required concentration of peroxide to maximize the removal efficiency is always on its minimum value. The removal process, involves chemical oxidation and coagulation, the last one because ferric hydroxo complexes are formed. This observation is confirmed throughout different points of the process: a) the presence

| Table 1 | Each one with two replicates and whose design information |
|---------|--------------------------------------------------------|
| Factor  | Factor levels                                         |
|         | -a          | -1         | 0         | 1          | +u         |
| (Fe⁰⁰⁰), (mg L⁻¹) | 13.9          | 27.9          | 41.9          | 55.8          | 69.8          |
| (H₂O₂), (mg L⁻¹) | 100          | 200          | 300          | 400          | 500          |
| COD, (mg L⁻¹) | 265.1          | 355          | 435.5          | 503          | 583.8          |
| time (min) | 2.5          | 5          | 7.5          | 10          | 12.5          |

**Equipment**

During tests conductivity, pH and temperature were monitored using a HACH Sension156 portable multiparameter. For chemical oxygen demand determination, a reactor H839800 from Hanna Instruments was used and finally, colorimetric measurements were conducted using an UV spectrophotometer Evolution 300UV-Vis (Thermo Scientific). The tests were carried out using a batch reactor of 1 L, with agitation of 350rpm at 23°C, this set up has been reported elsewhere. In experiment conductivity, pH and temperature were monitored using HACH Sension156 portable multiparameter. Chemical oxygen demand (COD) were analyzed on H839800 COD reactor (Hanna instrument).

**Analytical methods**

As it has been mentioned, COD was established as the principal monitoring parameter, with two kinds of COD: the total chemical oxygen demand (CODₙₙ) and the dissolved chemical oxygen demand (CODₙₙ). Taking this into account, each sample was divided into two parts, one taken from the mixed sample, for CODₙₙ and another by filtering through a fiberglass filter Whatman A, for CODₙₙ. COD measurements were in accordance with the Standard Methods.

Monitoring of Fe²⁺ was implemented using the phenanthroline method, measuring the absorbance of its orange-red complex with phenanthroline at a wavelength (λ) of 508nm. The measurement of Fe₄ involved reduction of Fe³⁺ to Fe²⁺ by using ascorbic acid before the UV-spectrophotometry, and at the end Fe³⁺ was the difference between it and Fe²⁺. On the other hand, the measurement of the H₂O₂ was also completed by UV-spectrophotometry at a λ of 406nm.

**Design of experiments**

Basically, we were focused on the development of a viable model. Target response was established as the removal efficiency of COD (RE), which was calculated through Eq. 8.

\[ RE = \frac{COD_o - COD_d}{COD_o} \times 100\% \]

The effects of principal factors: (Fe⁰⁰⁰), (H₂O₂), COD, and time, were studied using a Central Composite Design (CCD) ²⁴, with response surface methodology (RSM), involving a total of 52 tests; 16 factorial replicates, 8 axial points and 2 central points; each one with two replicates and whose design information is presented in Table 1. Once obtained the model, was validated by applying to a couple of real samples.

**Citation:** Páramo-Vargas J, Maldonado-Rubio MI, Gómez-Castro FI, et al. Modeling the Fenton depuration of the effluent from a slaughterhouse based on design of experiments. MOJ Eco Environ Sci. 2017;2(2):52–55. DOI: 10.15406/mojes.2017.02.00018
of flocs which at the end are measured as settled solids (approximately 30 mL L⁻¹), b) the difference between CODᵧ and CODₓ in each test, having a relation CODᵧ/CODₓ between 0.20 to 0.40, c) the large and rapid decline concentrations of Fe²⁺, Fe₃⁺ and Fe⁴⁺ indicates that iron is removed from the solution. In order to confirm these points, a kinetic study was conducted at (Fe²⁺), of 55.8 mg L⁻¹, (H₂O₂), of 200 mg L⁻¹, pH of 3 and for a total of 60 minutes. The process occurred too quickly and it was divided in two parts for explaining it, procedure referred in other investigations, as is presented in Figure 2. Figure 2(a) depicts the kinetic in the first two minutes and Figure 2(B) depicts the kinetic from 2.5 to 60 min. In both cases a kinetic model of second order was used, having high correlations, with R² of 0.9806 and 0.9951 respectively. We experienced a relation CODᵧ/CODₓ, which decreased throughout the process from 0.45 to 0.27 (Figure 3).

**Figure 1A** Depicts the behavior of principal factors, showing that by increasing each one, RE increases, having different levels of influence in the following order of magnitude: (Fe²⁺) > time > CODₓ > (H₂O₂). **Figure 1B** Depicts the response surface for the optimal removal condition of COD for one of the effluents studied (CODₓ of 503 mg L⁻¹) at 10 min, corresponding to a true sample, not a dilution. **Figure 2A** Depicts the kinetic in the first two minutes. **Figure 2B** Depicts the kinetic from 2.5 to 60 min. In both cases a kinetic model of second order was used, having high correlations, with R² of 0.9806 and 0.9951 respectively. We experienced a relation CODᵧ/CODₓ, which decreased throughout the process from 0.45 to 0.27.

**Figure 3** Depicts the behavior of the different forms of iron, showing the removal of total iron from the solution, confirming coagulation. **Table 2** Describes properly the fenton treatment

| Type of sample          | COD₀<sub>0</sub> (mg L⁻¹) | Fenton treatment | CODᵧ estimated by model (mg L⁻¹) | CODᵧ rea (mg L⁻¹) |
|-------------------------|---------------------------|-----------------|---------------------------------|------------------|
| Effluent from local facility | 503 | 89.2 | 83.7 |
| Effluent from local facility | 581 | 108.4 | 115.9 |

**Table 3** Describes properly the fenton treatment

| CODₓ (mg L⁻¹) | REₓ max | (Fe²⁺)ₓ (mg L⁻¹) | (H₂O₂)ₓ (mg L⁻¹) | t(min) |
|---------------|---------|------------------|------------------|--------|
| 265.1         | 98.756  | 64.022           | 100              | 15     |
| 355           | 98.473  | 42.666           | 100              | 20     |
| 435.5         | 98.838  | 27.35            | 100              | 23     |
| 503           | 98.465  | 13.259           | 100              | 26     |
| 583.8         | 98.537  | 13               | 100              | 38     |

**Conclusion**

The model developed for the depuration treatment of the effluents from the slaughterhouse is viable for use under real conditions as a method for adjusting of the process when changes the water quality. By using this model is becomes possible to acquire design and operation information, ensuring water with high and stable quality. The removal efficiencies of COD obtained greater than 85%, are based on chemical oxidation and coagulation process, showing that it is viable for use in depuration of this effluent and others of similar origin.

**Acknowledgements**

Financial support from PRODEP-UGTO-PTC-472 and UGTO under the Project 007/2015, and 778/2016, is acknowledged.
Conflict of interest
The author declares no conflict of interest.

References
1. Frenkel VS, Cummings GA, Mailacherryu KY. Food-processing wastes (Review). Water Environ Res. 2016;88(10):1395–1408.
2. Oller, S Malato, JA Sánchez-Pérez. Combination of advanced oxidation processes and biological treatments for wastewater decontamination-a review. Sci Tot Environ. 2011;409(20): 4141-4166.
3. Ein-Mozaffari F, Mohajerani M, Mehrvar M. An overview of the integration of advanced oxidation technologies and other processes for water and wastewater treatment. Int J Eng. 2009;3(2):120–146.
4. Kabaşlı I, Arslan T, Arslan-Alaton I, et al. Organic matter and heavy metal removals from complexed metal plating effluent by the combined electrocoagulation/Fenton process. Water Sci Tech. 2010;61(10):2617–2624.
5. EJ Ruiz, C Arias, F Brillas, et al. Mineralization of Acid Yellow 36 azo dye by electro-Fenton and solar photo electro-Fenton processes with a boron-doped diamond anode. Chemosphere. 2011;82(4):495–501.
6. Wu Y, Zhou S, Qin F, et al. Modeling the oxidation kinetics of Fenton’s process on the degradation of humic acid. Journal of Hazardous Materials. 2010;179(1-3):533–539.
7. Neyens E, Baeyens J. A review of classic Fenton’s peroxidation as an advanced oxidation technique. J Hazard Mat. 2003;98(1-3):33–50.
8. Liu H, Li XZ, Leng YJ, et al. Kinetic modeling of electro-Fenton reaction in aqueous solution. Water Res. 2007;41(5):1161–1167.
9. Paramo Vargas J, Chavez EI, De la Rosa C, et al. Treatment by advanced oxidation processes for an effluent of an anaerobic digester from a slaughterhouse. Sust Environ Res. 2015;25(4):195–205.
10. American Public Health Association AWWA. Water Environment Federation. Standard Methods for the examination of water and wastewater. 20th edition. Washington, USA: American public health association; 1998.
11. Peralta-Hernández JM, Meas-Vong Y, Rodríguez FJ, et al. Comparison of hydrogen peroxide-based processes for treating dye-containing wastewater: Decolorization and destruction of Orange II azo dye in dilute solution. Dyes and Pigments. 2008;76:656–662.
12. Deng Y. Physical and oxidative removal of organics during Fenton treatment of mature municipal landfill leachate. J Hazard Mat. 2007;146(1-2):334–40.
13. Kang YW, Hwang KY. Effects of reaction conditions on the oxidation efficiency in the Fenton process. Water Res. 2000;34(10):2786–2790.
14. Lau IWC, Peng W, Herbert HPF. Organic removal of anaerobically treated leachate by Fenton coagulation. J Environ Eng. 2001;127:666–669.
15. Paramo-Vargas J, Camargo AME, Gutierrez-Granados S, et al. Applying electro-Fenton process as an alternative to a slaughterhouse effluent treatment. J Electroanal Chem. 2015;754:80–86.
16. Zhang H, Wu X, Li X. Oxidation and coagulation removal of COD from landfill leachate by Fered-Fenton process. Chem Eng J. 2012;210:188–194.
17. J Páramo-Vargas, S Granados, MI Maldonado-Rubio, et al. Peralta-Hernández. Up to 95% reduction of chemical oxygen demand of slaughterhouse effluents using Fenton and photo-Fenton oxidation. Environ Chem Lett. 2016;14:149–154.
18. Méndez-Díaz J, Sánchez-Polo M, Rivera-Utrilla J, et al. Advanced oxidation of the surfactant SDBS by means of hydroxyl and sulphate radicals. Chem Eng J. 2010;163:300–306.
19. Üstün GE, Solmaz SKA, Morsünbül T, et al. Advanced oxidation and mineralization of 3-indole butyric acid (IBA) by Fenton and Fenton-like processes. J Hazard Mat. 2010;180:508–513.

Citation: Páramo-Vargas J, Maldonado-Rubio MI, Gómez-Castro FI, et al. Modeling the Fenton depuration of the effluent from a slaughterhouse based on design of experiments. MOJ Eco Environ Sci. 2017;2(2):52–55. DOI: 10.15406/mojes.2017.02.00018