Research Article

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

Javier Páramo-Vargas,[1] Manuel I Maldonado-Rubio,[2] Fernando I Gómez-Castro,[3] Juan M Peralta-Hernández[4]

[1]Departamento de Ingeniería Ambiental Universidad Tecnológica, Universidad Tecnológica de Léon, Mexico
[2]Plataforma Solar de Almería-CIEMAT, Spain
[3]Departamento de Ingeniería Química, Universidad de Guanajuato, Mexico
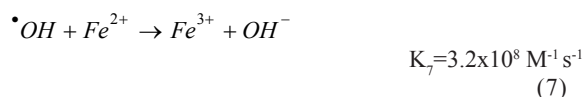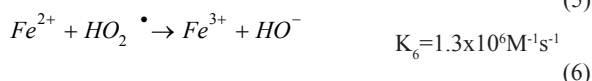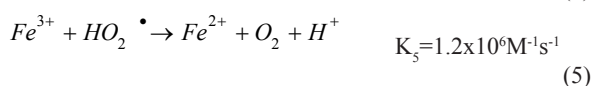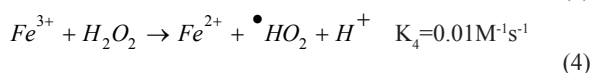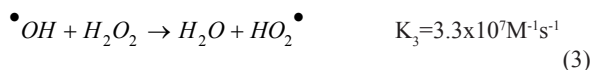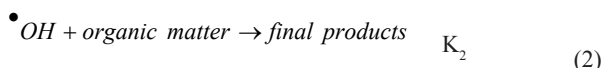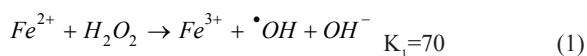[4]Departamento de Química, Universidad de Guanajuato, Mexico

Correspondence: Juan M Peralta-Hernández, Universidad de Guanajuato, DCNE, Departamento de Química, Cerro de la Venada S/N, Pueblito de Rocha, Guanajuato, Gto. CP. 36040, Mexico,
Email jparamo@utleon.edu.mx, juan.peralta@ugto.mx

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.[1,2] 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%.[3,4] 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 V[5] 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.[6,7]

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \quad K_1=70 \qquad (1)$$

$$^{\bullet}OH + organic\ matter \rightarrow final\ products \quad K_2 \qquad (2)$$

$$^{\bullet}OH + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \quad K_3=3.3\times10^7 M^{-1}s^{-1} \qquad (3)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + {}^{\bullet}HO_2 + H^+ \quad K_4=0.01 M^{-1}s^{-1} \qquad (4)$$

$$Fe^{3+} + HO_2{}^{\bullet} \rightarrow Fe^{2+} + O_2 + H^+ \quad K_5=1.2\times10^6 M^{-1}s^{-1} \qquad (5)$$

$$Fe^{2+} + HO_2{}^{\bullet} \rightarrow Fe^{3+} + HO^- \quad K_6=1.3\times10^6 M^{-1}s^{-1} \qquad (6)$$

$$^{\bullet}OH + Fe^{2+} \rightarrow Fe^{3+} + OH^- \quad K_7=3.2\times10^8\ M^{-1}\ s^{-1} \qquad (7)$$

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.[6,8] There are models based on chemical analysis and experimental determination of some parameters[6] 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 $(Fe^{2+})_0$, initial hydrogen peroxide concentration $(H_2O_2)_0$, initial chemical oxygen demand $(COD)_0$ 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 350m^{3}d^{-1}. In this analysis, we employed ferrous sulphate

($FeSO_4 \cdot 7H_2O$, provided by KEM), titanium oxysulphate ($O_5STi \cdot xH_2SO_4$, provided by FLUKA Analytical), H_2O_2 (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<$1 \mu Scm^{-1}$) from a Millipore equipment model Elix 5.

Equipment

During tests conductivity, pH and temperature were monitored using a HACH Sension156 portable multiparameter. For chemical oxygen demand determination, a reactor HI839800 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.[9] In experiment conductivity, pH and temperature were monitored using HACH Sension156 portable multiparameter. Chemical oxygen demand (COD) were analyzed on HI839800 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 (COD_t) and the dissolved chemical oxygen demand (COD_d). Taking this into account, each sample was divided into two parts, one taken from the mixed sample, for COD_t and another by filtering through a fiberglass filter Whatman A, for COD_d. COD measurements were in accordance with the Standard Methods.[10] Monitoring of Fe^{2+} was implemented using the phenanthroline method,[10] measuring the absorbance of its orange-red complex with phenanthroline at a wavelength (λ) of 508nm. The measurement of Fe_t involved reduction of Fe^{3+} to Fe^{2+} by using ascorbic acid before the UV-spectrophotometry, and at the end Fe^{3+} was the difference between it and Fe^{2+}. On the other hand, the measurement of the H_2O_2 was also completed by UV-spectrophotometry at a λ of 406nm.[11]

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.

$$RE_t = \frac{COD_o - COD_d}{COD_o} * 100\% \qquad (8)$$

The effects of principal factors: $(Fe^{2+})_0$, $(H_2O_2)_0$, COD_t and time, were studied using a Central Composite Design (CCD) 2^4, with response surface methodology (RSM), involving a total of 52 tests; 16 factorial points, 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.

Table 1 Each one with two replicates and whose design information

Factor	Factor levels				
	-α	-1	0	1	+α
$(Fe^{2+})_0$ (mg L^{-1})	13.9	27.9	41.9	55.8	69.8
$(H_2O_2)_0$ (mg L^{-1})	100	200	300	400	500
COD_t (mg L^{-1})	265.1	355	435.5	503	583.8
time (min)	2.5	5	7.5	10	12.5

Results and discussion

Applying the ANOVA analysis, it was found for the quadratic model, the statistic R^2 of 80.5059 and $R^2_{adjusted}$ 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: $(Fe^{2+})_0$>time>COD_t>$(H_2O_2)_0$. On the other hand Figure 1(B) depicts the response surface for the optimal removal condition of COD for one of the effluents studied (COD_0 of 503mgL^{-1}) at 10min, corresponding to a true sample, not a dilution.

$$RE_t = -20.602 + 1.14238 * (Fe^{2+})_o + 0.102791 * (H_2O_2)_o + 0.138419 * COD_o$$
$$+5.87343 * t - 0.0043153 * (Fe^{2+})_o^2 - 0.000406362 * (Fe^{2+})_o (H_2O_2)_o$$
$$-0.000813263 * (Fe^{2+})_o * COD_o - 0.0222401 * (Fe^{2+})_o * t$$
$$-0.0000252268 * (H_2O_2)_o^2 - 0.0000666185 * (H_2O_2)_o * COD_o$$
$$-0.00462 * (H_2O_2)_o * t - 0.0000277821 * COD_o^2$$
$$-0.00615258 * COD_o * t - 0.0165629 * t^2$$

The data in Table 2 show that the model developed describes properly the Fenton treatment. In the cases which were studied, the variation between COD_d 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 $[Fe^{2+}]_0$ and $[H_2O_2]_0$ those presented as $-\alpha$ and $+ \alpha$ 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 $[Fe^{2+}]_0$ 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 $[Fe^{2+}]_0$ 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 hydroxocomplexes are formed.[12–16] This observation is confirmed throughout different points of the process: a) the presence

of flocs which at the end are measured as settled solids (approximately 30mLL^{-1}), b) the difference between COD_d and COD_t in each test, having a relation COD_d/COD_t between 0.20 to 0.40, c) the large and rapid decline concentrations of Fe^{2+}, Fe_t and Fe^{3+} indicates that iron is removed from the solution.[17] In order to confirm these points, a kinetic study was conducted at $(Fe^{2+})_0$ of 55.8mgL^{-1}, $(H_2O_2)_0$ of 200mgL^{-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,[18,19] 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 R^2 of 0.9806 and 0.9951 respectively. We experienced a relation COD_d/COD_t, which decreased throughout the process from 0.45 to 0.27(Figure 3).
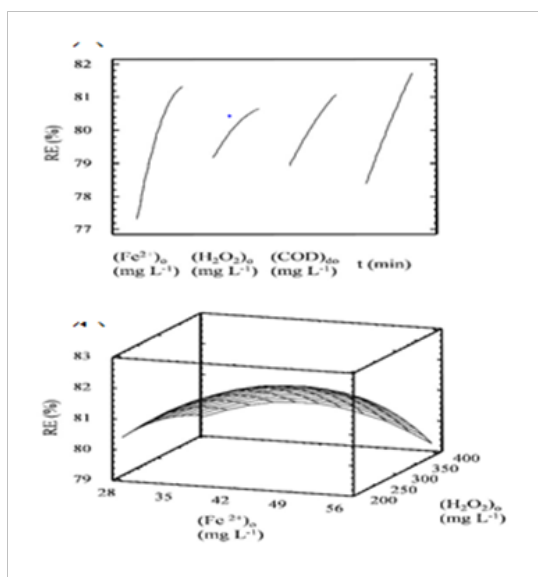

Figure 1A Depicts the behavior of principal factors, showing that by increasing each one, RE increases, having different levels of influence in the following order of magnitude: $(Fe^{2+})_0$>time>COD_t>$(H_2O_2)_0$.

Figure 1B Depicts the response surface for the optimal removal condition of COD for one of the effluents studied (COD_0 of 503mgL^{-1}) at 10min, corresponding to a true sample, not a dilution.
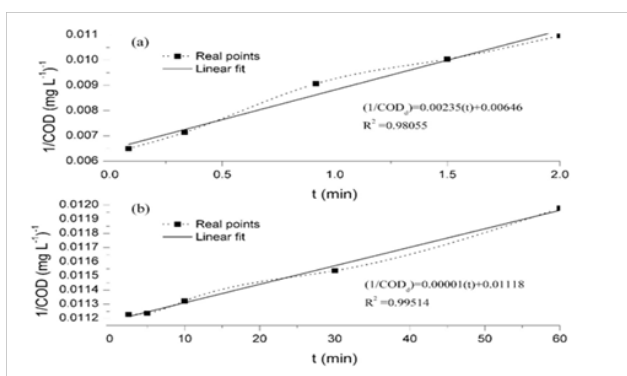

Figure 2A Depicts the kinetic in the first two minutes.

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 CODd/CODt, which decreased throughout the process from 0.45 to 0.27.
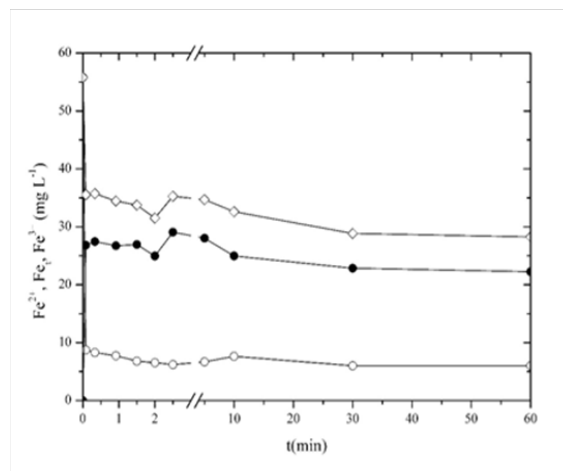

Figure 3 Depicts the behavior of the different forms of iron, showing the removal of total iron from the solution, confirming coagulation.

Table 2 Describes properly the fenton treatment

| Type of sample | DQO$_0$ (mg L^{-1}) | Fenton treatment | |
		COD$_d$ estimated by model (mg L^{-1})	COD$_d$ rea (mg L^{-1})
Effluent from local facility	503	89.2	83.7
Effluentfrom local facility	581	108.4	115.9

Table 3 Describes properly the fenton treatment

COD$_0$ (mg L^{-1})	RE$_t$ max	(Fe^{2+})$_0$(mg L^{-1})	(H$_2$O$_2$)$_0$ (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.

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Conflict of interest

The author declares no conflict of interest.

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