

APPROXIMATE ANALYTICAL EXPRESSIONS OF CONCENTRATION  
OF ACETIC ACID AND HYDROGEN PEROXIDE IN BATCH PHOTO-FENTON REACTION

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ABSTRACT

*Mathematical model of the photo-Fenton oxidation process is discussed. This model involves a system of nonlinear equations containing a nonlinear term related to Eley-Rideal-type kinetics. Simple and closed- form of approximate analytical expressions of concentrations of acetic acid and hydrogen peroxide are reported. These analytical results are compared with available experimental and numerical (Matlab program) results. Satisfactory agreement is noted.*

**Keywords:** *Mathematical modeling, photo- Fenton oxidation, hydrogen peroxide, acetic acid.*

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1. INTRODUCTION

Pesticides are commonly used worldwide to face the need for increasing and improving agricultural production [1, 2]. Organic pollution originates from domestic sewage, urban run-off, industrial effluents and agriculture wastewater [3]. Wastewater with organic pollutants contains large quantities of suspended solids which reduce the photosynthetic organisms. Organic pollutants include pesticides, fertilizers, hydrocarbons, phenols, plasticizers, biphenyls, detergents, oils, greases, pharmaceuticals, proteins and carbohydrates. Photochemical and photo catalytic processes have enormous potential for becoming viable alternatives to conventional chemical (AOP) for the treatment of polluted waters and effluents. Currently available photochemical technology permits the conversion of organic pollutants having a wide range of chemical structures into substances that are less toxic and/or more readily biodegradable [4, 5].

Abdul Aziz *et al.* [6] reported that adding H<sub>2</sub>O<sub>2</sub> in a single batch leaves much of it available to attack by hydroxyl radicals, whereas continuously feeding smaller quantities of the reagent to the system would allow the majority of radicals generated to target the organic contaminant. Various studies have been carried out on the heterogeneous photo-Fenton system; In particular, Fe over HY zeolite has been used for the degradation of polyvinyl alcohol [7]. The immobilization of Fe ions also on clays, bentonite and laponite for the oxidation of the azo-dye Orange II has been reported [8]. Similar works have been also described for the degradation of different azo-dyes over iron oxides such as goethite and hematite under non controlled pH conditions [9].

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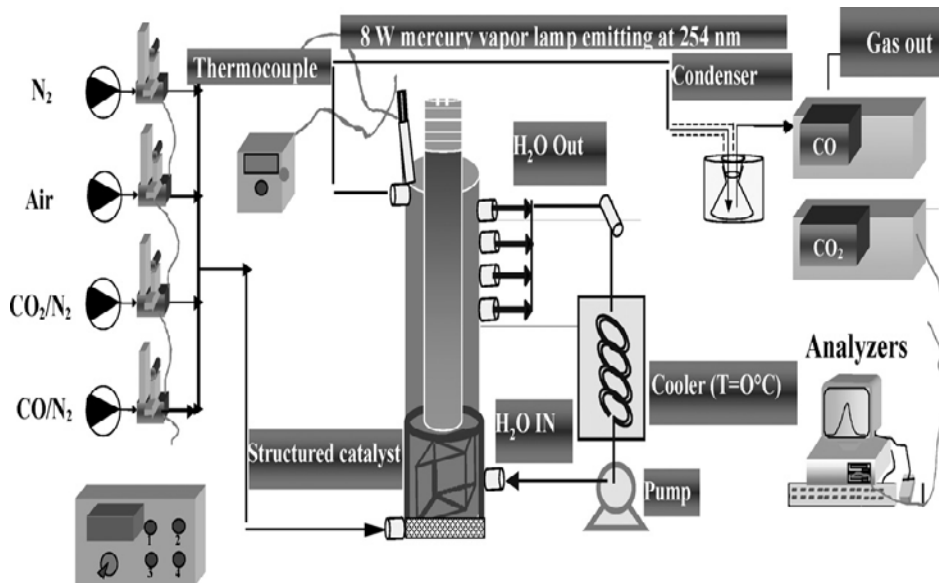
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Nafion has been employed as organic support due to the presence of sulphonic groups allowing the effective anchoring of Fe ions [10]. Photo-Fenton oxidation of phenol was also performed using iron species incorporated over different silica supports [11]. Heterogeneous Fe (III) based photo-Fenton catalyst is often used as suspended particles in the liquid reaction medium [12]. Thus the biggest disadvantage lies in the fact that, after wastewater treatment, separation of catalyst from reaction solution is needed. To avoid this last operation the use of structured catalysts could be a valid solution. Recently, Sannino *et al.* [13, 14] developed a mathematical model of heterogeneous photo-Fenton oxidation of acetic acid on structured catalysts. Also Sannino *et al.* [13] proposed the experimental work for the above model.

To the best of our knowledge, there is no simple analytical expression for steady-state concentrations of acetic acid and hydrogen peroxide for all values of the parameters is derived. The main purpose of this paper is to present the approximate analytical expression for the concentration of acetic acid and hydrogen peroxide for all values of parameters. The main advantage of this analytical method over numerical method is that we can accelerate the convergence rate, minimize iterative times, accordingly save the computation time and evaluate the efficiency. Also, we reported the sensitivity analysis of parameters on the concentration of acetic acid/hydrogen peroxide.

## 2. MATHEMATICAL MODEL

The mathematical model, closely similar to that described earlier [13] was used. Pictorial representation of the catalytic photo-Fenton oxidation is provided in Figure. 1 [14].



**Figure-1:** Laboratory apparatus for the catalytic photo-Fenton oxidation [14].

We assume that the reaction of catalytic oxidation of  $CH_3COOH$  (1) and the photolysis of  $H_2O_2$  (2) in the homogeneous phase is:



The corresponding one-dimensional mass balance equation of acetic acid and hydrogen peroxide, considering transport only by reaction are [13] given as follows:

$$V \frac{dC_1(t)}{dt} = -\frac{K_2 b C_1(t) C_2(t)}{1 + b C_1(t)} W_{LaFeO_3} \quad (3)$$

$$V \frac{dC_2(t)}{dt} = -4 \frac{K_2 b C_1(t) C_2(t)}{1 + b C_1(t)} W_{LaFeO_3} - K_1 C_2(t) V + Q_{H_2O_2} \quad (4)$$

The initial conditions are

$$C_1 = C_{1,0} \text{ at } t = 0 \quad (5)$$

$$C_2 = C_{2,0} \text{ at } t = 0 \quad (6)$$

where  $C_1$  and  $C_2$  are represents the concentration of acetic acid and hydrogen peroxide respectively.  $b$ ,  $W_{LaFeO_3}$ ,  $V$ ,  $Q_{H_2O_2}$ ,  $K_1$  and  $K_2$  denotes the adsorption constant of acetic acid, amount of active phase, solution volume, molar flow rate of  $H_2O_2$  entering the reactor kinetic constant for reaction R1 and R2 respectively.

### 3. APPROXIMATE ANALYTICAL EXPRESSION OF CONCENTRATION OF ACETIC ACID AND HYDROGEN PEROXIDE UNDER NON STEADY CONDITIONS

By solving the Eqns. (3) – (6) using an iterative method, we can obtain the approximate analytical expressions of concentration of acetic acid  $C_1$  and hydrogen peroxide  $C_2$  as follows:

$$C_1(t) = C_{1,0} \exp[-N(1 - e^{-K_1 t}) - LMt] \quad (7)$$

$$C_2(t) = (C_{2,0} + M)e^{-K_1 t} - M \quad (8)$$

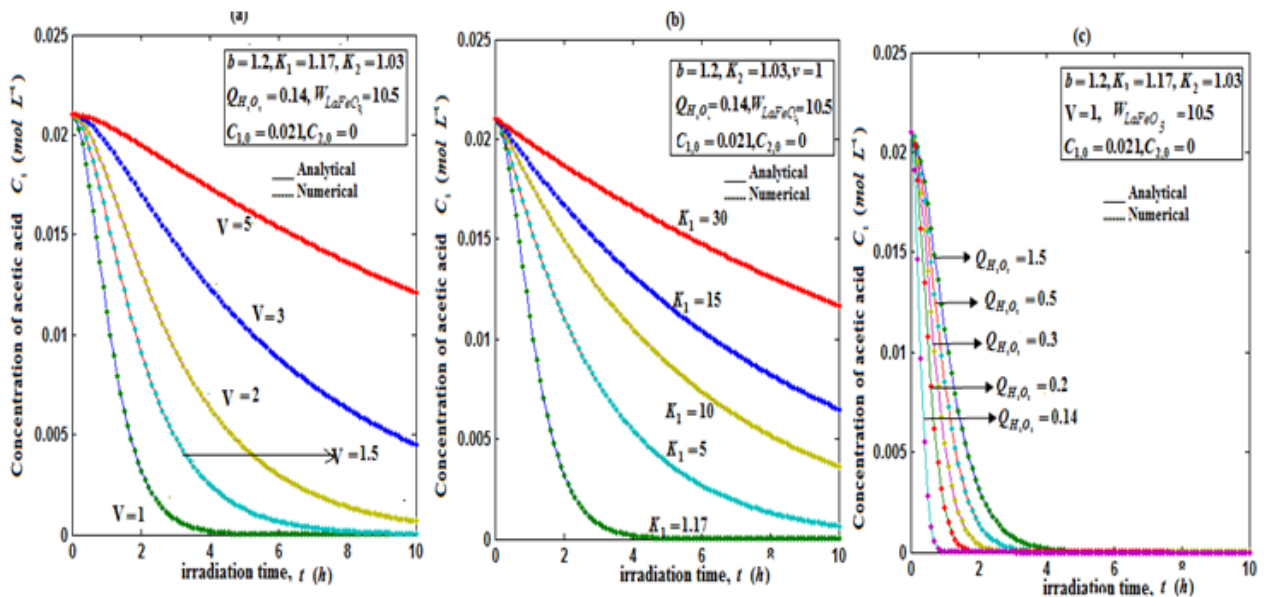
Where

$$L = \frac{-K_2 b W_{LaFeO_3}}{V(1 + bC_{1,0})}, M = \frac{4LC_{1,0} C_{2,0}}{(LC_{2,0} + K_1)} + \frac{Q_{H_2O_2}}{VK_1} \text{ and } N = \frac{-L(C_{2,0} + M)}{K_1} \quad (9)$$

The Eqns. (7) and (8) satisfies the boundary conditions (5) and (6). These equations represent the new approximate analytical expression of the concentration of acetic acid and hydrogen peroxide for all possible values of the parameters  $b$ ,  $W_{LaFeO_3}$ ,  $V$ ,  $Q_{H_2O_2}$ ,  $K_1$  and  $K_2$ . When  $t \rightarrow \infty$  (steady state) and initial concentration of the hydrogen peroxide is zero ( $C_{2,0} = 0$ ), from the Eqns. (7) and (8) we obtain  $C_1(t = \infty) = 0$  and  $C_2(t = \infty) = \frac{Q_{H_2O_2}}{VK_1}$ .

### 4. DIFFERENTIAL SENSITIVITY ANALYSIS OF PARAMETERS

Differential sensitivity analysis is based on partial differentiation of the aggregated model [15]. We have found the partial derivative of concentration of acetic acid/hydrogen peroxide (dependent variable) with respect to the parameters  $b$ ,  $W_{LaFeO_3}$ ,  $V$ ,  $Q_{H_2O_2}$ ,  $K_1$  and  $K_2$  (independent variables). At some fixed experimental values ( $b = 0.021 \text{ mol L}^{-1}$ , ( $W_{LaFeO_3} = 0.083 \text{ mol L}^{-1}$ ,  $V = 1 \text{ ml}$ ,  $Q_{H_2O_2} = 0.038 \text{ mol L}^{-1}$ ,  $K_1 = 1.17 \text{ Lg}^{-1} \text{ h}^{-1}$  and  $K_2 = 1.04 \text{ h}^{-1}$ ) of the parameters, the numerical value of the rate of change of concentration can be obtained. From this value we can obtain the percentage of change in concentration with respect to the above parameters. Sensitivity analysis of the parameters is given in Figure. 2 (f) and Figure. 3 (d).



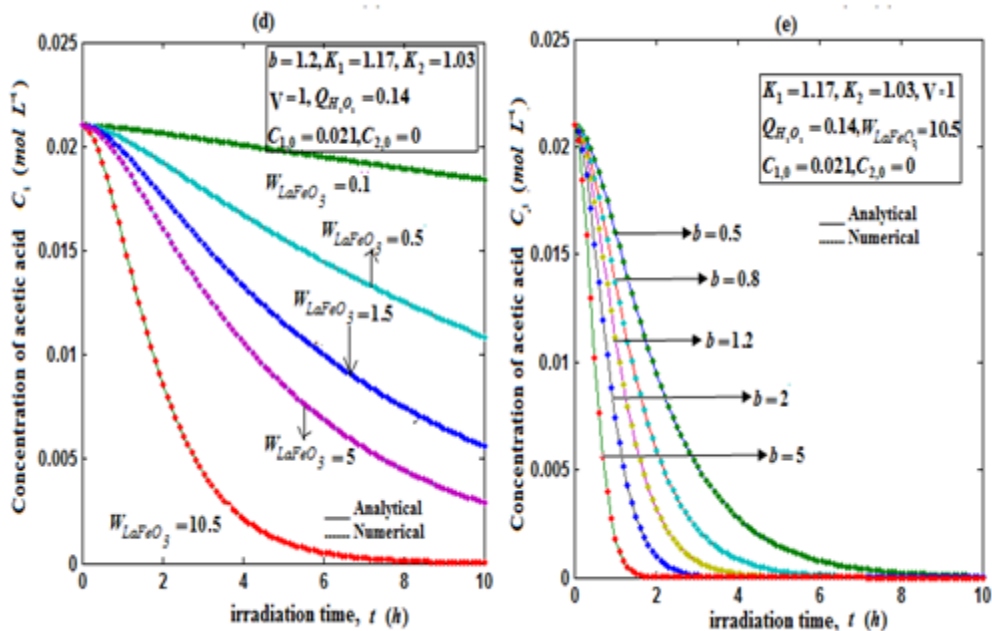


Figure-2: (a - e) Plot of concentration of acetic acid  $C_1$  versus irradiation time  $t$  using Eqn. (7) for various values of parameters  $V, K_1, Q_{H_2O_2}, W_{LaFeO_3}$  and  $b$  respectively.

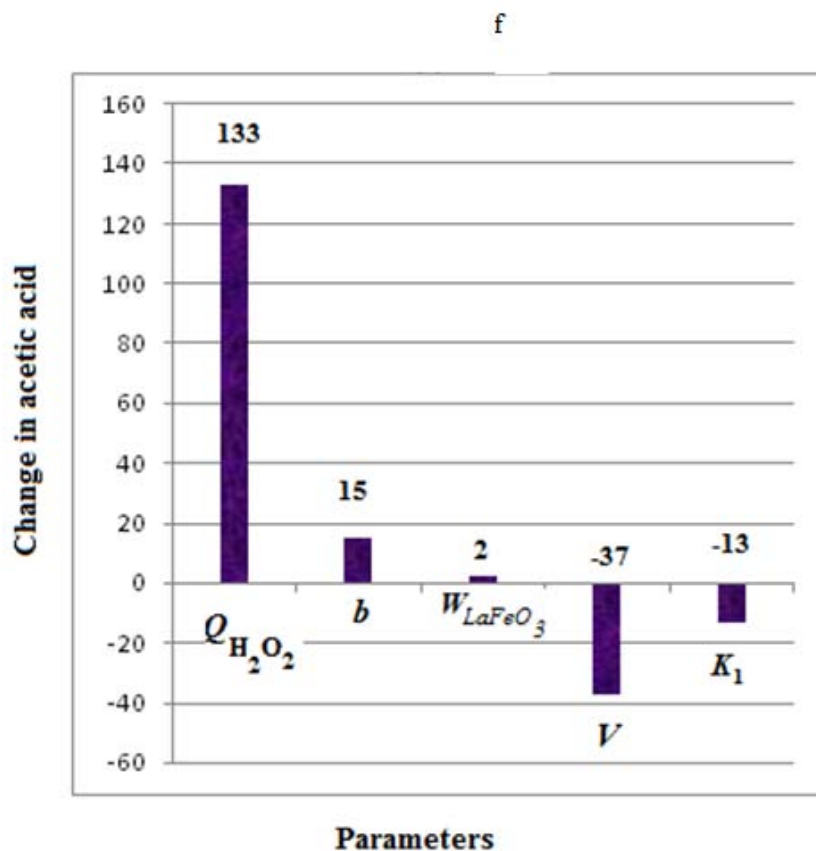
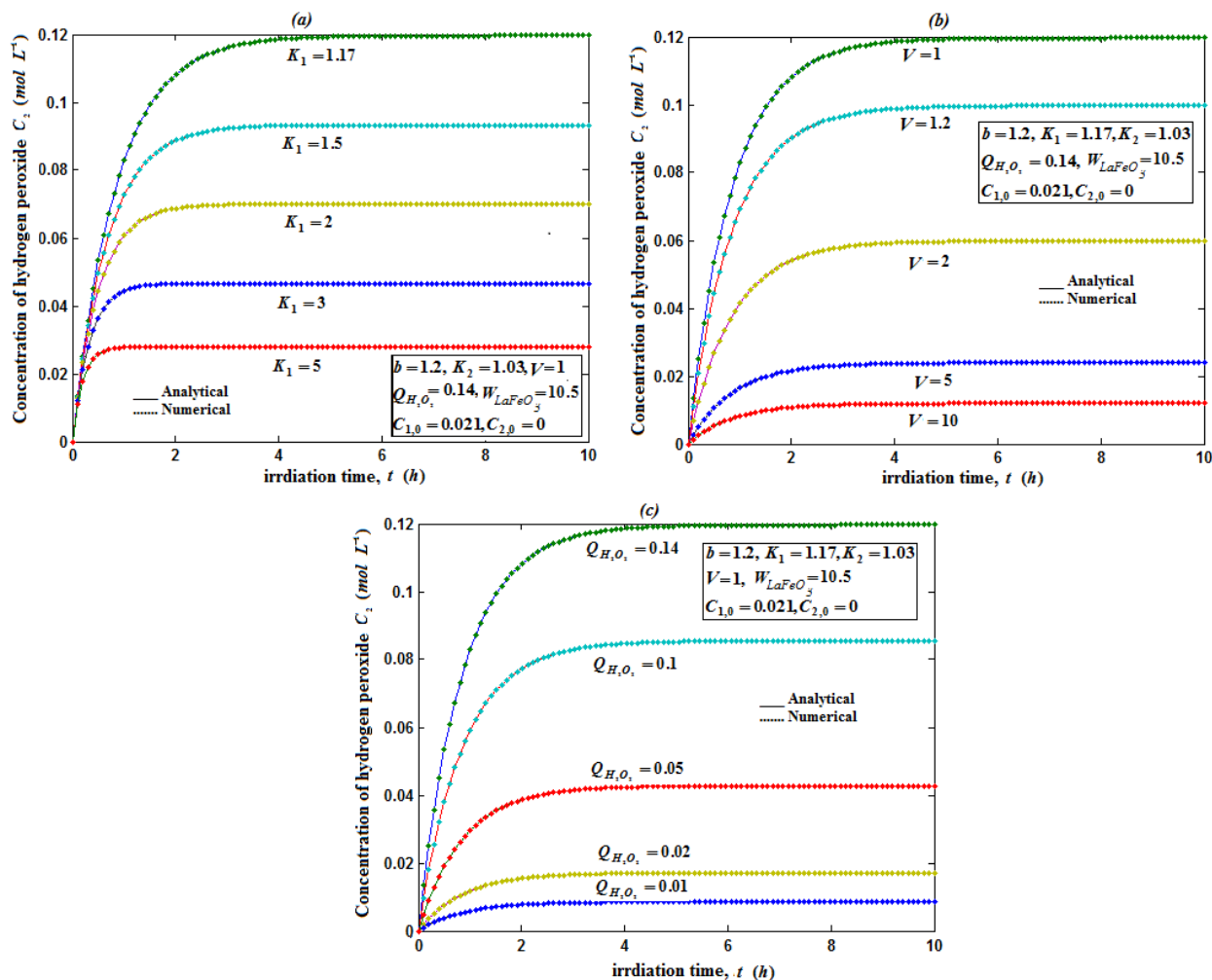
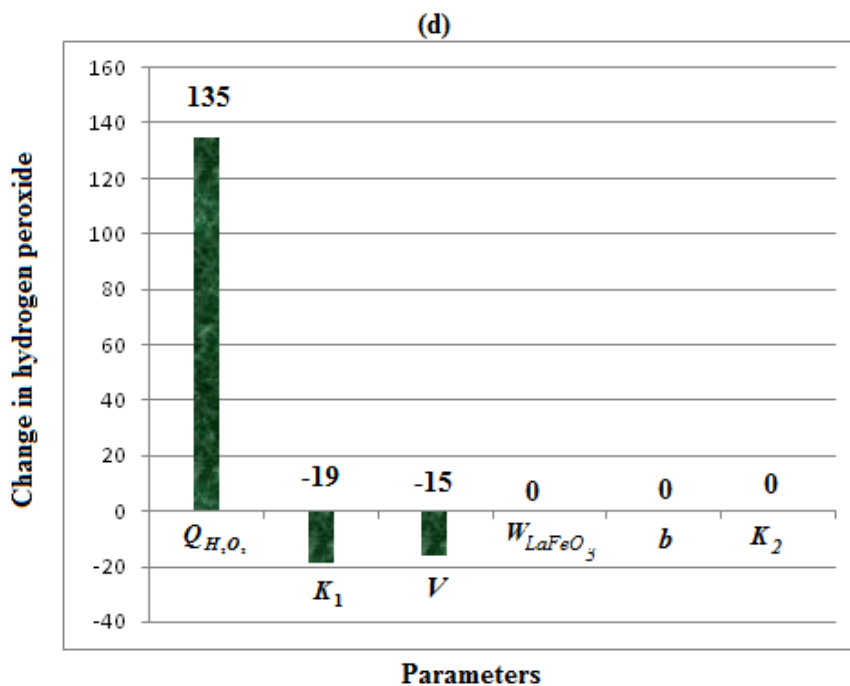


Figure-2: (f) sensitivity analysis of parameters.



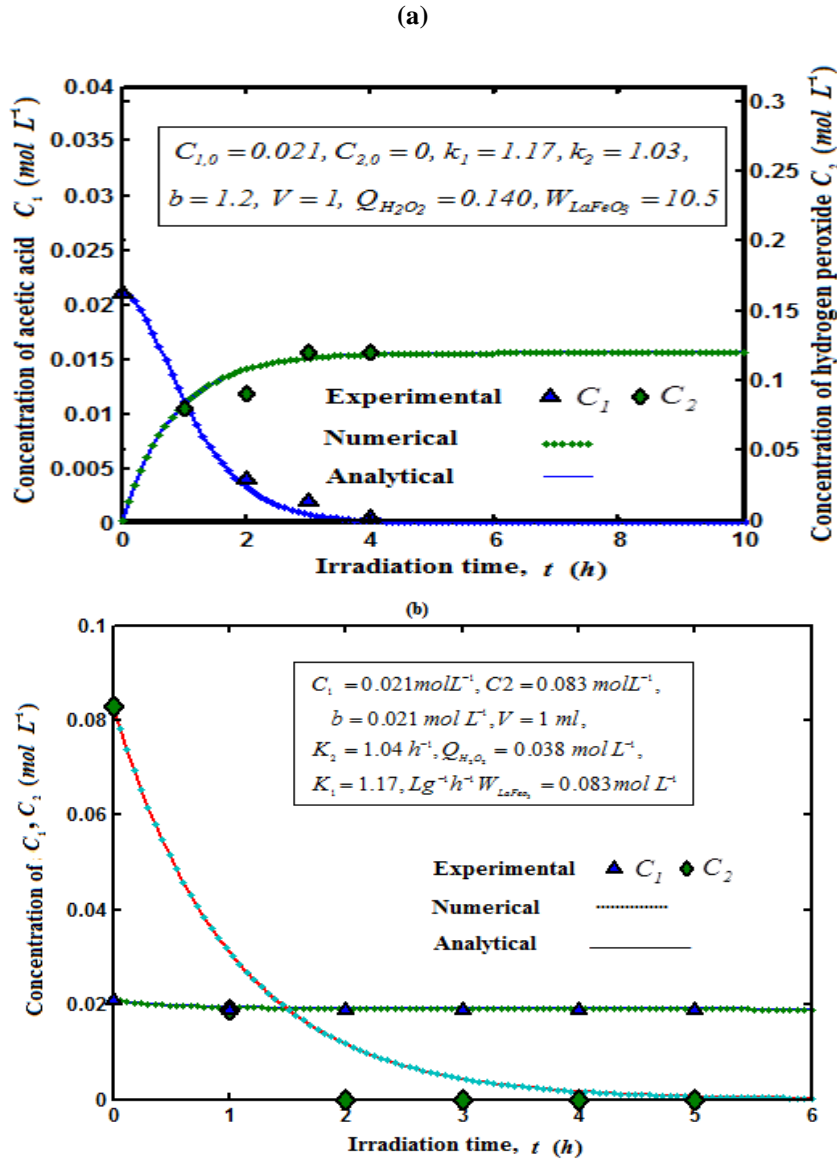
**Figure-3:** (a-c) Plot of concentration of hydrogen peroxide  $C_2$  versus irradiation time  $t$  (h) using Eqn. (8) for various values of  $K_1$ ,  $V$  and  $Q_{H_2O_2}$  respectively.



**Figure-3:** (d) sensitivity analysis of parameters. From this figure, it is inferred that the molar flow rate  $H_2O_2$  entering the reactor  $Q_{H_2O_2}$  has more impact than the adsorption constant of acetic acid  $b$  for the variation of the concentration. The remaining parameters accounts for only small changes in concentration.

## 5. VALIDATION OF ANALYTICAL RESULTS WITH EXPERIMENTAL AND SIMULATION RESULTS

To show the efficiency, our approximate analytical results (Eqns. (7) – (8)) are compared with and simulation (Matlab) and experimental results [13] in Figure. (4).



**Figure-4:** Comparison of our analytical results (Eqns. (3) and (4)) with the experimental results [13], and numerical results for the concentration of acetic acid  $C_1$  and hydrogen peroxide  $C_2$ .

A satisfactory agreement is noted. The function pdepe, in Matlab software which is a function of solving the boundary value problems for nonlinear ordinary differential equations is used to solve this equation. The experimental values of the parameters used is given in Table 1. The Matlab program is also given in Appendix A.

## 6. DISCUSSION

Eqns. (3) - (6) are the new and simple approximate analytical expressions of concentrations of acetic acid and hydrogen peroxide for all possible values of the parameters. Figure. 4 (a- b) compares the analytical results with the numerical and experimental results with previous experimental data [13]. Figure. 2 represents the concentration of acetic acid  $C_1$  as a function of irradiation time  $t$ . In Figure. 2 (a-e), the parameters solution volume  $V$ , kinetic constant  $K_1$  and molar flow rate  $Q_{H_2O_2}$  increases the concentration of acetic acid. Also the concentration of acetic acid  $C_1$  decreases slowly from its initial values of concentration and reaches the steady state value zero. Figure. 2 (f), it is observed that the molar flow rate  $Q_{H_2O_2}$  has maximum influence on the concentration of acetic acid  $C_1$ , whereas the remaining parameters  $b$ ,  $W_{LaFeO_3}$ ,  $V$ ,  $K_1$  and  $K_2$  have a very small influence of acetic acid.

The concentration of hydrogen peroxide  $C_2$  versus time  $t$  is shown in Figure. 3. From Figure. 3 (a-c), it is inferred that the concentration of hydrogen peroxide  $C_2$  increases when kinetic constant  $K_1$  and adsorption constant of acetic acid  $b$  decreases whereas the concentration of hydrogen peroxide  $C_2$  increases when  $Q_{H_2O_2}$  increases. Here also the parameter  $Q_{H_2O_2}$  has more influence than other parameters on the concentration of hydrogen peroxide. Also the time taken reaches a steady state value of acetic acid  $C_1$  consumption is

$$t = \frac{1}{K_1} \log \left[ \left( \frac{-4LC_{1,0} C_{2,0}^2}{LC_{2,0} + K_1} + \frac{Q_{H_2O_2} C_{2,0}}{VK_1} \right)^{-1} + \left( \frac{K_2 b W_{LaFeO_3}}{V(1+bC_{1,0})} \right)^{-1} \right].$$

From the Eqn. (4), it is observed that the

concentration of hydrogen peroxide  $C_2$  reaches the maximum value  $\frac{Q_{H_2O_2}}{VK_1}$  when the initial concentration of  $H_2O_2$  is zero. This result is also conformed from the Eqn. (4) for non steady state conditions.

## 7. CONCLUSIONS

A mathematical analysis of a heterogeneous photo-Fenton process using a LaFeO<sub>3</sub> catalyst supported on a monolithic structure was discussed. The model was based on the happening of hydrogen peroxide photolysis and acetic acid oxidation in the heterogeneous phase, assumed first-order and Eley–Rideal-type kinetics, respectively. In this paper the analytical expression of concentrations of acetic acid and hydrogen peroxide are presented. A sensitivity analysis of the parameters from the concentration of acetic acid and hydrogen peroxide are suggested. Our analytical results agree with experimental and simulation data. These analytical results will be useful for the design and processes optimization.

### Appendix-A: Scilab/Matlab program for the numerical solution of Eqn. (6).

```
function pdepe
options= odeset('RelTol',1e-6,'Stats','on');
%initial conditions
x0 = [0.021;0];
tspan = [0,10];
tic
[t,x]= ode45(@TestFunction,tspan,x0,options);
toc
figure
hold on
plot(t, x(:,1))
plot(t, x(:,2))
legend('x1','x2')
ylabel('x')
xlabel('t')
return
function [dx_dt]= TestFunction(t,x)
k1=1.17; k2=1.04;v=1;Q=0.140; b=1.2; W=10;
dx_dt(1)=(-k2*b*W/v)*(x(1)*x(2))/(1+b*x(1));
dx_dt(2)=(-4*k2*b*W/v)*(x(1)*x(2))/(1+b*x(1))-(k1*x(2))+(Q/v);
dx_dt = dx_dt';
return
```

Appendix-B : Nomenclature.

Symbols	Definitions	Numerical Values [13]	Units
$b$	adsorption constant of acetic acid	1.2	$Lmol^{-1}$
$C_1(t)$	CH <sub>3</sub> COOH concentration	-	$mol L^{-1}$
$C_2(t)$	H <sub>2</sub> O <sub>2</sub> concentration	-	$mol L^{-1}$
$C_{1,0}$	CH <sub>3</sub> COOH initial Concentration	0.021	$mol L^{-1}$
$C_{2,0}$	H <sub>2</sub> O <sub>2</sub> initial Concentration	0	$mol L^{-1}$
$r_1$	CH <sub>3</sub> COOH consumption rate	-	$mol h^{-1} g^{-1}$
$r_2$	H <sub>2</sub> O <sub>2</sub> photolysis reaction rate	-	$mol L^{-1} h^{-1}$
$K_1$	apparent kinetic constant for reaction $R_1$	1.17	$h^{-1}$
$K_2$	apparent kinetic constant for reaction $R_2$	1.03 ± 0.01	$h^{-1}$
$Q_{H_2O_2}$	molar flow rate H <sub>2</sub> O <sub>2</sub> entering the reactor (in the case of continuous dosage)	0.140	$mol h^{-1}$
$t$	irradiation time	-	$h$
$V$	solution volume	1	$L$
$W_{LaFeO_3}$	amount of active phase	10.5	$L$
$L = \frac{-K_2 b W_{LaFeO_3}}{V(1+bC_{1,0})}$	rate constant	-12.66	$h^{-1}$
$M = \frac{4LC_{1,0} C_{2,0}}{(LC_{2,0} + K_1)} + \frac{Q}{VK_1}$	Parameter	-0.11965	$mol L^{-1}$
$N = \frac{-L(C_{2,0} + M)}{K_1}$	dimensionless constant	1.2946	None

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