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Kinetics study and neural network modeling of degradation of Naphtol Blue Black by electro-Fenton process: effects of anions, metal ions, and organic compound

Chafia Bouasla[a,b,*], Mohamed El-Hadi Samar[a], Hocine Bendjama[c]

[a]*Department of Process Engineering, University Badji-Mokhtar of Annaba, Annaba, Algeria*
Tel. +213 551287948; email: ca.bouasla@yahoo.fr
[b]*Microelectronic and Nanotechnology, Centre for Development of Advanced Technologies, Alger, Algeria*
[c]*Iron and Steel Applied Research Unit, URASM/CSC; P.O. Box 196, Annaba, Algeria*

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ABSTRACT

In the present work, the degradation of azo dye Naphtol Blue Black (NBB) in aqueous solution by electro-Fenton process was investigated. The results indicated that the degradation of NBB by electro-Fenton process followed the second-order reaction kinetics. The experimental results were also modeled by artificial neural network (ANN) with mean squared error of 10^{-5}. This model was developed in Matlab using a feed forward back propagation network; multilayered perceptron. The input variables to the feed-forward neural network were as follows: initial Fe^{3+} concentration, initial pH, concentration of Na_2SO_4, temperature, applied current, and initial dye concentration. The degradation efficiency and rate constant were chosen as the experimental responses or output variables. The findings indicated that ANN provided reasonable predictive performance ($R^2 > 0.99$). Effects of additives such as anions, metal ions, and organic compound on the efficiency and on the rate constant of NBB degradation were also studied under optimum conditions.

Keywords: Degradation; Electro-Fenton; Naphtol Blue Black; Artificial neural network

1. Introduction

Over 100,000 different types of dyes are commercially available [1] and 800,000 tons are produced yearly all over the world. Nearly 50% of these dyes are azo-type dyes [2].

Synthetic azo-dyes are widely used in textile, printing, cosmetic, food colorants, and pharmaceutical industries. Some azo-dyes are also used in laboratories as either biological stains or pH indicators. For example, Naphtol Blue Black (NBB) is an amino acid staining diazo dye used in biochemical research to stain for total protein on transferred membrane blots and in criminal investigations to detect blood present with latent fingerprints.

Advanced oxidation processes (AOPs) offer effective and rapid alternative treatments for textile wastewaters. The AOPs are based on the *in situ* generation of hydroxyl radicals ($^{\bullet}OH$), a highly powerful oxidizing agent, and are effective in treatment of persistent organic pollutants aqueous solutions until their overall mineralization [3].

Electro-Fenton is an advanced electrochemical oxidation process based on the continuous supply of H_2O_2 generated from reaction (1) to a contaminated

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*Corresponding author.

acid solution containing Fe^{2+} or Fe^{3+} as catalyst [4–7]. $^{\bullet}OH$ is then produced in the medium by the Fenton's reaction between ferrous ion and hydrogen peroxide (Eq. (3)). The electro-Fenton process has also been applied to wastewaters containing diverse textile azo dyes by different research groups [8–10]

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (1)$$

$$Fe(OH)^{2+} + e^- \rightarrow Fe^{2+} + HO^- \quad (2)$$

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + H_2O + HO^{\bullet} \quad (3)$$

Artificial neural network (ANN) is an effective tool for modeling complex and non-linear problems in various scientific and technological fields [11]. Artificial neural networks (ANNs), multi-layer perceptron (MLP) particularly, have been widely and effectively applied for process monitoring and control of wastewater treatments. The ANN models have been used for process control of chlorination of wastewater [12], Fenton oxidation [13], sludge hygienization [14], the ANNs also applied to predict the chlorine decay in water distribution [15], to predict the disinfection by-product in chlorination of drinking water [16], to evaluate the performances of water and wastewater plants [17,18].

This paper reports the findings of the degradation of NBB using electro-Fenton process. A kinetic study also was carried out in order to determine the order of reaction.

An artificial neural networks MLP model was developed to predict the efficiency and rate constant of the degradation of the NBB. A comparison between the predicted results of the MLP model and experimental data was also conducted. Besides effects of initial Fe^{3+} concentration, initial pH, concentration of Na_2SO_4, temperature, applied current, and initial dye concentration were examined.

At the next step, the influences of additives such as anions, metal ions, and organic compound on the efficiency and on the rate constant of NBB degradation were also studied under optimum conditions. Comparative mineralization with anodic oxidation and electro-Fenton processes were also conducted.

2. Experimental

2.1. Reagents

NBB (4-Amino-5-hydroxy-3-[(4-nitrophenyl)azo]-6-(phenylazo)-2, 7-Naphthalene disulfonic acid, disodium salt) was purchased from Aldrich (Sigma-Aldrich Corporation, St. Louis, MO, USA). The structure and other chemical information about NBB are given in Table 1 [19].

Ferric sulfate, copper sulfate, manganese sulfate, zinc sulfate, H_2SO_4, H_3PO_4, and HNO_3 were procured from Sigma-Aldrich. Sodium chloride, sodium sulfate, $NaClO_4$, tert-butyl alcohol, and sucrose were commercial products of the purest grade available (analytical grade). All solutions were prepared with distilled water.

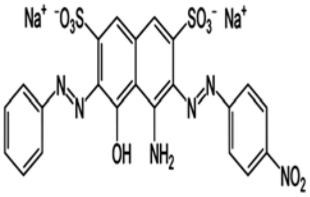
2.2. Electrochemical apparatus and cell

Electrochemical experiments were carried out with an undivided glass cell of 250 mL capacity Fig. 1. In this process H_2O_2 is produced electrochemically via oxygen reduction on the cathode. For this purpose, continuous saturation of air at atmospheric pressure was ensured by bubbling compressed air near the cathode, starting 10 min before electrolysis to reach a stationary O_2 concentration.

The electrolysis is carried out using two electrodes anode platinum (30 cm^2) and a cathode was a 36 cm^2 piece of carbon-felt or graphite (in anodique oxydation). Electrolysis were operated at constant current (*I*) of 20, 80, 150, 300, and 500 mA using a power supply model LD Didactic GMBH.

NBB was comparatively degraded in an acidic aqueous medium containing Na_2SO_4 as supporting

Table 1
Chemical information of NBB

Common name	CI no	Other names	λ_{max} (nm)	Mol.wt (g/l)	Structure
Napthol Blue Black	20,470	Acid Black B Amidoblack-10B	617	616.50	

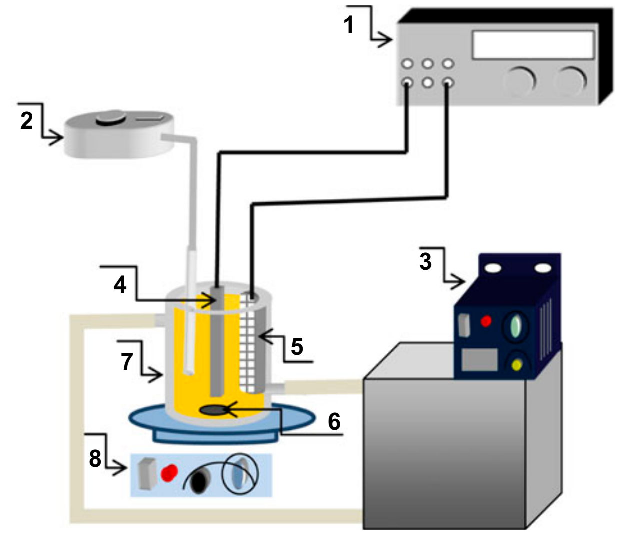


Fig. 1. The schematic view of the undivided lab electrolysis cell system: (1) supply source, (2) air pump, (3) thermostatic bath, (4) carbon-felt cathode, (5) platinum anode, (6) magnet, (7) electrolysis cell, and (8) magnetic stirrer.

electrolyte and H_2SO_4 was added to adjust its initial pH. The solution pH was measured by a pH meter (Eutech Instruments Pte. Ltd., Rajah Crescent, Singapore). The temperature was controlled by a thermostatic bath (TECTRON BIO, SELECTA, Barcelona, Spain). Stirring was applied to the solution using a magnetic stirrer (IKA Labortechnik type RW20).

2.3. Analytical method

The concentration of the dye in the reaction mixture at different reaction times was determined by measuring the absorption intensity at $\lambda_{\max} = 617$ nm under initial pH using a UV–visible spectrophotometer (BOECO S24).

The percentage of NBB degradation efficiency was calculated by using the following Eq. (4):

$$\text{Degradation efficiency} = \frac{C_0 - C_t}{C_0} \times 100\% \tag{4}$$

where C_0 is the initial concentration of NBB and C_t is the concentration of NBB at reaction time.

2.4. Chemical oxygen demand (COD) measurement

COD was measured according to the method presented by Thomas and Mazas [20], using a dichromate solution (Aldrich) as the oxidizer in a strong acid medium. Test solution (2 mL) was transferred into the dichromate reagent and digested at 150°C for 2 h. The optical density for the color change of dichromate solution was determined with a UV–visible spectrophotometer.

3. Results and discussion

3.1. Kinetic study

The degradation of dye by Fenton and electro-Fenton were complicated processes due to the involvement of many side reactions and intermediates. These processes could not be easily depicted by simple reaction kinetics.

Several investigators have found that the Fenton and electro-Fenton reactions for dye degradation follow pseudo-first-order kinetics [21].

Chan and Chu [22] have studied the degradation of the atrazine by Fenton reagent. They showed that the reaction of degradation occurs in two stages and that these steps have a kinetic pseudo-second order.

Bouasla et al. [23] found that the degradation of the azo dye (Acid Yellow 99) by Fenton oxidation process in aqueous solutions occurs in one step and that the reaction kinetics follows a pseudo-second order. These results agree with several studies [24].

From the kinetic study of the Fenton reaction, the reaction order for the degradation of NBB by electro-Fenton will be determined.

The first and second-order kinetics rate constants for the degradation of NBB at different reaction conditions were obtained and the results were summarized in Table 2. It was observed that the regression coefficients obtained for the two models are different. The second-order kinetics shows higher correlation than the first-order kinetics. It can be concluded that the degradation of NBB by electro-Fenton oxidation fits the second-order reaction kinetic of the type:

$$-\frac{dC}{dt} = k_2 C^2 \tag{5}$$

To verify the feasibility of the proposed model, results derived from the model and those from raw data were compared and confirmed. For example, Fig. 2 shows the prediction of NBB degradation by electro-Fenton process with 0.05 mM of Fe^{3+}, for which the prediction curves (models), agrees very well to the data.

3.2. Modeling of experimental results by artificial neural network

3.2.1. Neural network technique

The data processing using the neural network technique started in 1943 with the work of McCulloch

Table 2
The first and second-order kinetic rate constants for the degradation of NBB at different reaction conditions

	$[Fe_2(O_4)_3]$	pH	T (℃)	$[Na_2So_4]$ (mM)	I (mA)	[NBB] (mM)	k_1 (min^1)	R^2	k_2 (mM^{-1} min^1)	R^2	R (%)
1	0.025	2	20	0.5	150	0.05	0.035	0.8	5.25	0.99	95.26
2	0.05	2	20	0.5	150	0.05	0.087	0.81	21.14	0.98	97.5
3	0.1	2	20	0.5	150	0.05	0.059	0.9	14.71	0.97	97.9
4	0.25	2	20	0.5	150	0.05	0.053	0.83	11.31	0.99	97
5	0.05	1	20	0.5	150	0.05	0.038	0.81	2.98	0.95	88.75
6	0.05	2	20	0.5	150	0.05	0.087	0.81	21.14	0.98	97.5
7	0.05	3	20	0.5	150	0.05	0.1282	0.87	8.66	0.98	89
8	0.05	4.5	20	0.5	150	0.05	0.044	0.97	1.5	0.99	66.3
9	0.05	2	20	0.5	150	0.05	0.087	0.81	21.14	0.98	97.5
10	0.05	2	30	0.5	150	0.05	0.21	0.92	66.4	0.95	98.42
11	0.05	2	40	0.5	150	0.05	0.178	0.93	85.96	0.89	99.7
12	0.05	2	50	0.5	150	0.05	0.13	0.94	26.28	0.94	99
13	0.05	2	60	0.5	150	0.05	0.09	0.91	13.38	0.95	98.5
14	0.05	2	20	0	150	0.05	0.065	0.94	8.92	0.96	95.78
15	0.05	2	20	0.25	150	0.05	0.061	0.91	6.39	0.98	96.57
16	0.05	2	20	0.5	150	0.05′	0.087	0.81	21.14	0.97	97.5
17	0.05	2	20	0.9	150	0.05	0.037	0.86	2.41	0.99	90.5
18	0.05	2	20	0.5	20	0.05	0.01	0.93	0.53	0.99	82.5
19	0.05	2	20	0.5	80	0.05	0.02	0.92	2	0.98	91.5
20	0.05	2	20	0.5	150	0.05	0.087	0.81	21.14	0.98	97.5
21	0.05	2	20	0.5	300	0.05	0.087	0.96	3.06	0.94	88
22	0.05	2	20	0.5	500	0.05	0.03	0.77	1.75	0.99	86.5
23	0.05	2	20	0.5	150	0.025	0.034	0.86	6.17	0.98	87
24	0.05	2	20	0.5	150	0.05	0.087	0.81	21.14	0.98	97.5
25	0.05	2	20	0.5	150	0.08	0.18	0.92	29.13	0.98	98.9
26	0.05	2	20	0.5	150	0.048	0.048	0.93	4.31	0.96	99
27	0.05	2	20	0.5	150	0.033	0.033	0.87	2.5	0.98	98.84

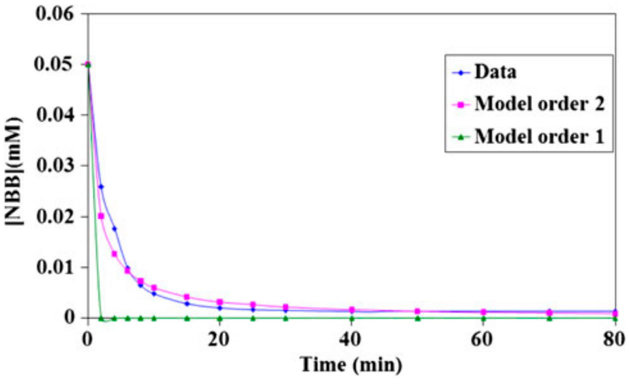


Fig. 2. Degradation kinetic of NBB by electro-Fenton process, the comparison of model and experimental data for second order.

and Pitts [25] who introduced the idea of an artificial neuron.

The topology of an ANN is determined by number of its layers, number of nodes in each layer, and the nature of transfer functions. Optimization of ANN topology is probably the most important step in development of model.

Also in this work, experimental data were modeled by MLP with 3 layers; an input layer, hidden layers, and an output layer. This three-layered feed forward back propagation network consist of 6, 32, and 1 neurons in first, second, and third layers, respectively. MLP was performed in Matlab.

The input variables to the network were as follows: initial Fe^{3+} concentration (mM), initial pH, concentration of Na_2SO_4 (M), temperature, applied current (mA), and initial dye concentration (mM). The degradation efficiency and rate constant were chosen as the experimental responses or output variables. The hyperbolic sigmoid transfer functions have been tested in hidden layer network (6) [26].

$$f(u_i) = \frac{1}{1 + e^{-u_i}} \tag{6}$$

The range of variables studied is summarized in Table 3. The optimal architecture of the MLP (Fig. 3.)

Table 3
Model variable and their ranges

Variable	Symbol	Range
Initial pH	$X_1 = \text{pH}$	2–4
Température (°C)	$X_2 = T$	20–60
Initial Fe^{3+} concentration (mM)	$X_3 = [Fe_2(SO_4)_3]$	0.06–0.12
Concentration of Na_2SO_4 (M)	$X_4 = [Na_2SO_4]$	0.6–1.2
Initial NBB concentration (mM)	$X_5 = [\text{NBB}]$	0.03–0.15
Applied current (mA)	$X_6 = I$	20–500

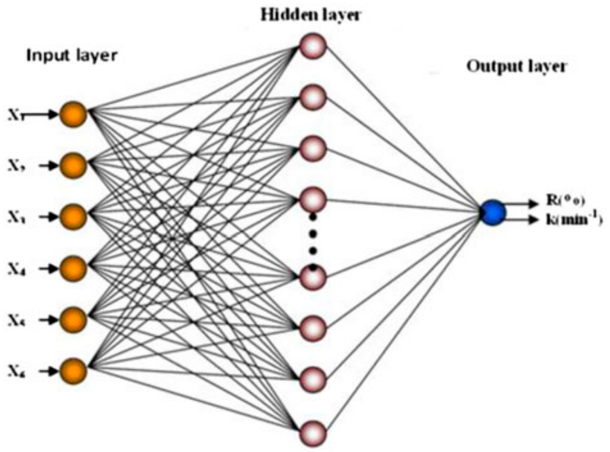


Fig. 3. The MLP optimized structure.

and its parameter variation were determined based on the minimum value of the mean square error (MSE) of the training and validation sets [27].

The MSE was used as the error function. It measures performance of network according to the following equation:

$$\text{MSE} = \frac{1}{Q}\sum_{i=1}^{i=Q}\left(y_{i,pred} - y_{i,exp}\right)^2 \tag{7}$$

where Q is the number of data point, $y_{i,pred}$ network prediction, $y_{i,exp}$ experimental response.

3.2.2. Prediction of the effects of operational variables

The predictions are generally very close to the experimental values, which is a further indicator for the success of the model. The predicted and the experimental performances of the rate constant and percentage of dye removal under different operational parameters are given in Figs. 4 and 5. From this plots it can be seen that obtained results from the proposed model are in good agreement with the experimental data ($R^2 = 0.99$).

A summary of results are illustrated in below:

3.2.2.1. Effect of initial Fe^{3+} concentration. The concentration of catalyst (Fe^{3+}) is another important

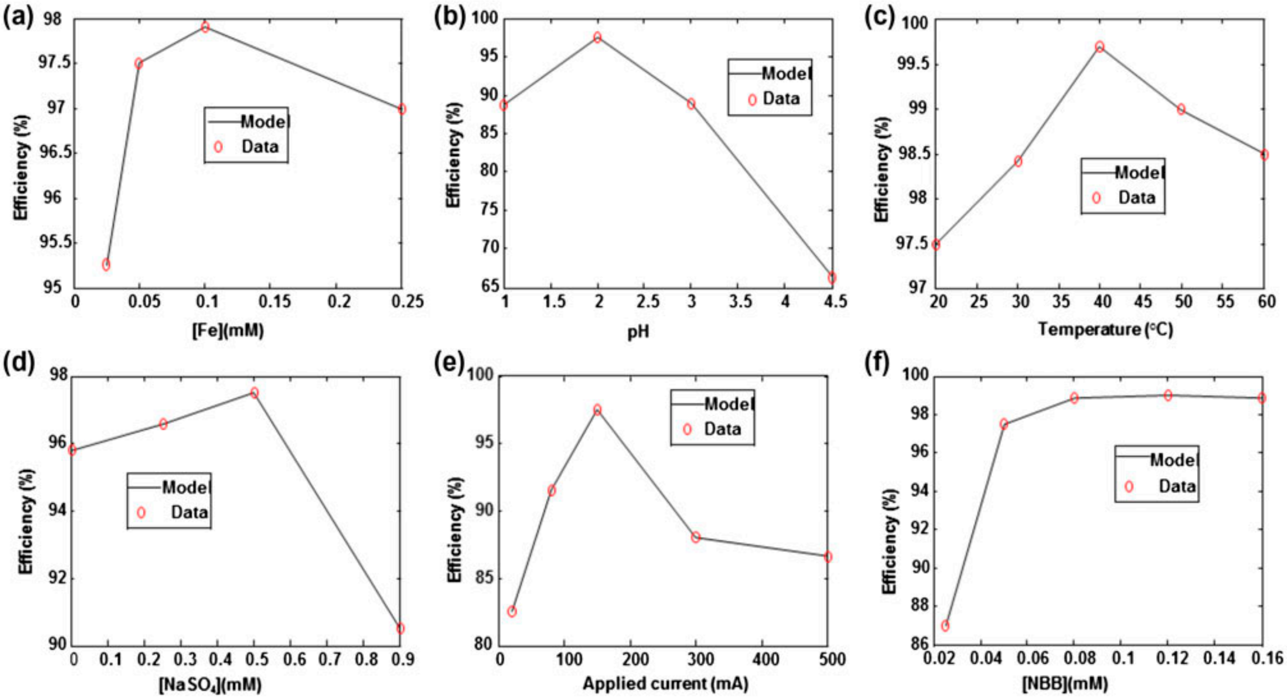


Fig. 4. Simulation and experimental data of the evolution of degradation efficiency. (Initial conditions: $C_0 = 0.05$ mM, $[Na_2SO_4] = 0.5$ M, $T = 20$°C, pH = 2, $I = 150$ mA.)

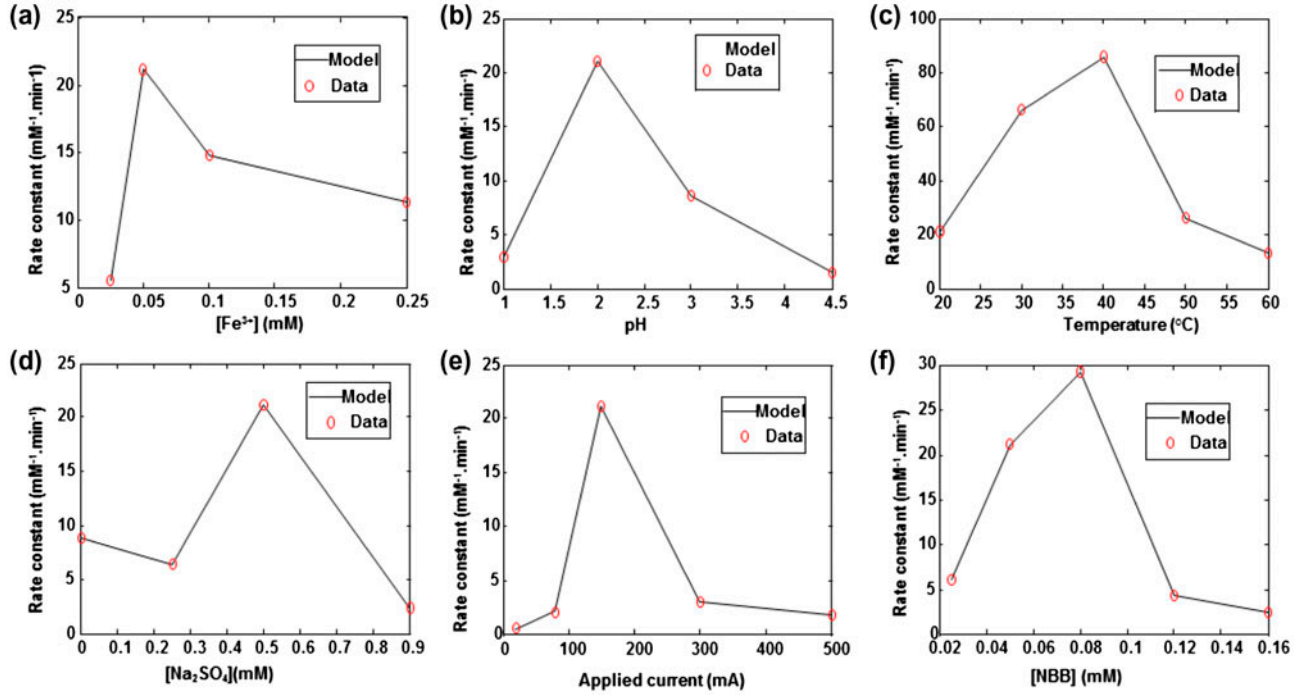


Fig. 5. Simulation and experimental data of the evolution of rate constant. (Initial conditions: $C_0 = 0.05$ mM, $[Na_2SO_4] = 0.5$ M, $T = 20$°C, pH = 2, $I = 150$ mA.)

parameter for the electro-Fenton process. The effect of Fe^{3+} concentration on the degradation efficiency and rate constant were investigated in the range of 0.025–0.25 mM, when initial dye concentration was 0.05 mM, pH was 3, temperature was 20°C and applied current was 150 mA. The experimental and predicted values of degradation efficiency and rate constant were plotted vs. Fe^{3+} concentration (Figs. 4(a) and 5(a)). The results presented in Figs. 4(a) and 5(a) show that the degradation efficiency increases from 92.15 to 97.47% (rate constant varied from 5.52 to 21.14 $mM^{-1}min^{-1}$) as a consequence of increasing Fe^{3+} dosage from 0.025 to 0.05 mM within 40 min. Beyond the critical concentrations the rate constant and degradation efficiency of NBB decreased (97.47–95.89%, 21.14–11.31 $mM^{-1}min^{-1}$) with the increasing of the Fe^{3+} concentration. The results indicated that the Fe^{3+} concentration had little effect on the kinetics degradation of NBB by electro-Fenton process. This phenomenon can be explained by:

- The increase in the concentration of Fe^{3+} ions will increase the Fe^{2+} ions by the reduction of ferric ion. Therefore, additional $HO^{\bullet}$ was produced along with the increase of Fe^{2+} concentration.

The influence of higher Fe^{3+} concentration upon the degradation behavior of NBB may be explained by the redox reactions, since $HO^{\bullet}$ radicals may be scavenged by the reaction with the hydrogen peroxide or with another Fe^{2+} molecule as shown below in Eq. (8) [28].

$$Fe^{2+} + HO^{\bullet} \rightarrow Fe^{3+} + HO^{-} \qquad (8)$$

3.2.2.2. *Effect of initial pH.*

The pH is one of the most important factors for the electro-Fenton process. The influence of this parameter was clarified by treating solutions containing 0.05 mM NBB and initial pH between 1 and 4.5 at 150 mA and at 20°C. The final pH does not change and remains equal to the initial pH. As can be seen in Figs. 4(b) and 5(b), the highest electro-Fenton degradation and rate constant were attained under pH 2. It showed that degradation efficiency no more than 66% at pH 4.5 and more than 88% at pH 3.

When pH is below 2: $HO^{\bullet}$ could be consumed by the scavenging effects of H^{+} which will limit the decolorization rate Eq. (9) [29]. The Fenton reaction could be slowed down because hydrogen peroxide can probably be stable by acquiring a proton to form an oxonium ion as $H_3O_2^{+}$ in Eq. (10).

$$HO^{\bullet} + H^{+} + e^{-} \rightarrow H_2O \qquad (9)$$

$$H_2O_2 + H^+ \rightarrow H_3O_2^+ \qquad (10)$$

The oxonium ion makes hydrogen peroxide electrophilic to enhance its stability and presumably to reduce substantially the reactivity with ferrous ion [29].

In addition, for pH above 3, hydrogen peroxides unstable and breaks down into O_2 and H_2O. This instability increases with increasing pH. Similarly, the oxidation potential of the $HO^\bullet$ radical is known to decrease with increasing pH.

3.2.2.3. Effect of temperature. The degradation of NBB by electro-Fenton process was carried at five temperatures (10, 20, 30, 40, and 60˚C) with other tests conditions at $[NBB]_0 = 0.05\,mM$, $[Fe^{3+}]_0 = 0.05\,mM$ and pH = 2.0. The experimental and calculated values of removal are shown in Figs. 4(c) and 5(c). It can be seen that the maximum degradation efficiency (about 88.36%) and rate constant ($85.96\,mM^{-1}min^{-1}$) were achieved at 40˚C and after 70 min.

The degradation efficiency increases from 45 to 89.88% as a consequence of increasing the temperature from 20 to 40˚C within 6 min.

This is because higher temperature increased the reaction rate between hydrogen peroxide and any form of ferrous/ferric iron, thus increasing the rate of generation of oxidizing species such as $HO^\bullet$ radical or high-valence iron species [30].

Beyond the critical temperature, the degradation rate constant of NBB decreased with the increasing of the temperature, this is due to the fact that the solubility of oxygen decreases and at high temperature hydrogen peroxide produced at the cathode undergoes self-decomposition. All these phenomena lead to a decrease of hydroxyl radicals responsible for degradation

3.2.2.4. Effect of electrolyte concentration. To determine the effect of the electrolyte concentration on the degradation of NBB by electro-Fenton process, several electrolysis were carried out in acidic solutions (pH = 2), concentration of NBB (0.05 mM), and varying Na_2SO_4 concentrations in the range of 0–0.9 M at 150 mA. The obtained results are shown in Figs. 4(d) and 5(d). From this plot it can be seen that:

- Obtained results from the proposed model are in good agreement with the experimental data.
- A concentration of Na_2SO_4 equal to 0.25 M, the kinetics of degradation is slower than that achieved at the concentration of 0.5 M.
- The maximum degradation efficiency (97.5%) was obtained with a concentration of 0.5 M Na_2SO_4.

These results can be interpreted by the fact that the increase in the electrolyte concentration increases the conductivity of the solution, promotes electrogeneration of H2O2, and hydroxyl radicals responsible for degradation.

3.2.2.5. Effect of applied current. In order to investigate the influence of applied current on the degradation of NBB by electro-Fenton process, experiments were conducted by varying applied current from 20 to 500 mA. When initial dye concentration was 0.05 mM, Fe^{3+} concentration was 0.05 mM, Na_2SO_4 concentration was 0.5 M, and initial pH value was 2.

It can be seen from Figs. 4(e) and 5(e) that degradation efficiency and rate constant were increased by increasing applied current value from 20 to 150 mA.

This phenomenon can be explained by:

If the amount of $^\bullet OH$ production in the medium is proportional to the increasing H_2O_2 concentration generated when current rises.

Higher applied current density means higher applied voltage on the electrochemical system [31]. Also higher electro-regeneration of ferrous ion from ferric ion (Eq. (11)) with increasing current increased the efficiency of Fenton chain reactions [32].

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad (11)$$

The efficiency of electro-Fenton will be less at higher applied current. This is due to the competitive electrode reactions in the electrolytic cell. The discharge of oxygen at anode and the evolution of hydrogen at cathode occur at a higher current. These reactions inhibit main reactions, which lead to decrease in efficiency of E-Fenton [32].

3.2.2.6. Effect of initial concentration of NBB. The pollutant concentration is one of the important parameters in electro-Fenton processes. The variation between experimental and calculated values of degradation efficiency and rate constant under different initial concentration of NBB has been presented in Figs. 4(f) and 5(f). It was observed that the increase in dye concentration decreases the rate constant. An increase of dye concentration from 0.08 to 0.16 mM decreases the rate constant from 29.13 to $2.5\,mM^{-1}min^{-1}$, but the degradation efficiency remained constant.

This phenomenon can be explained by the fact that an increase in the initial concentration leads to an increase of the number of dye molecules and the production of hydroxyl radicals per unit times constant for all initial concentrations of dyes, therefore more the initial concentration of dye increases over the degradation time increases.

3.3. *Effects of additives*

In the present study and under the optimum conditions (Initial conditions: $C_0 = 0.05\,\text{mM}$, $[\text{Na}_2\text{SO}_4] = 0.5\,\text{M}$, $T = 20^\circ\text{C}$, pH = 2, $[\text{Fe}^{3+}]_0 = 0.05$ and $I = 150\,\text{mA}$), the degradation of NBB by electro-Fenton process was investigated in the presence of certain inorganic anions, metal ions, and organic compound.

3.3.1. *Effect of anions*

The influence of various inorganic ions commonly found in natural and industrial waters such as SO_4^{2-}, NO_3^-, Cl^-, and PO_4^{3-} on the electro-Fenton degradation of NBB was examined. We had to choose the nature of the acid to adjust pH and the nature of support electrolyte in order to obtain a smooth treatment.

3.3.1.1. Effect of the nature of the acid used to adjust the pH. To evaluate the influence of these ions, the pH of an NBB aqueous solution by different acids (H_2SO_4, HNO_3, and H_3PO_4) was adjusted. Fig. 6 shows that the degradation efficiency of the NBB dye is higher in solution acidified with H_2SO_4 (97.47%) as H_3PO_4 (94%).

The inhibitory effect of phosphate ions may be due to a complexation and a radical scavenging as shown in Eqs. (12 and 13) [33–37]. Phosphate ions create competition between hydroxyl radicals and organics leading to the inhibition of oxidation.

$$\text{HO}^{\bullet} + \text{H}_2\text{PO}_4^- \rightarrow \text{H}_2\text{PO}_4^{\bullet} + \text{OH}^- \tag{12}$$

$$\text{HO}^{\bullet} + \text{PO}_4^{3-} \rightarrow \text{HO}^- + \text{PO}_4^{2-} \tag{13}$$

According to the complexation effect of phosphate ions may undergo a complex reaction with ferrous and ferric ions, which impedes the reaction causing hydroxyl radicals to be produced. The complexation reactions are shown by Eqs. (14 and 15)

$$\text{Fe}^{2+} + \text{H}_2\text{PO}_4^- \rightarrow \text{FeH}_2\text{PO}_4^+ \tag{14}$$

$$\text{Fe}^{3+} + \text{H}_2\text{PO}_4^- \rightarrow \text{FeH}_2\text{PO}_4^{2+} \tag{15}$$

Nitric acid slightly reduces the degradation kinetics due to a reduction reaction at the cathode Eq. (16).

$$\text{NO}_3^- + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{NO}_2^- + 2\text{OH}^- \tag{16}$$

This reaction is responsible for the loss of electrical efficiency of the system by consumption of a portion of the current delivered. This reduces the efficiency of formation of $\text{HO}^{\bullet}$ radicals.

Degradation efficiencies are in the following order:

$$\text{Ef}(\text{H}_2\text{SO}_4) > \text{Ef}(\text{HNO}_3) > \text{Ef}(\text{H}_3\text{PO}_4)$$

3.3.1.2. Effect of supporting electrolyte species. To investigate the effect of supporting electrolyte species on the electro-Fenton degradation of NBB, many experiments were performed by using Na_2SO_4, NaCl, and NaClO_4 as supporting electrolyte in the same conditions. The obtained results are shown in Fig. 7. As can be seen from this figure, that the kinetic and efficiency of degradation of NBB are almost identical after 60 min electrolysis for supporting electrolytes NaCl and NaClO_4. Over Na_2SO_4, it is clear that the efficiency of degradation obtained is higher (97.5%) after 40 min of contact time. Decrease the efficiency of degradation in the presence of Cl^- ions may be due to their interaction with hydroxyl radicals and $\text{ClOH}^{\bullet-}$ ions react

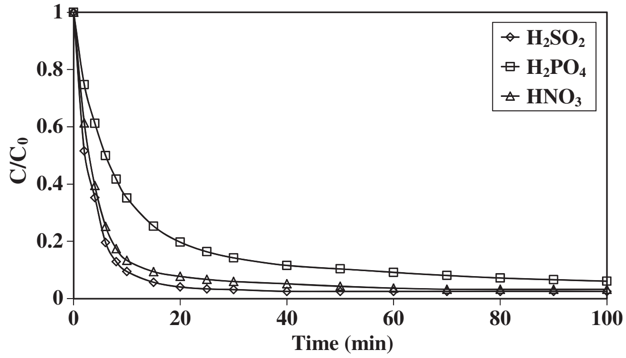


Fig. 6. Effect of the nature of the acid used to adjust the pH on electro-Fenton degradation of NBB $C_0 = 0.05\,\text{mM}$, $[\text{Na}_2\text{SO}_4] = 0.5\,\text{M}$, $T = 20^\circ\text{C}$, pH = 2, $[\text{Fe}^{3+}] = 0.05\,\text{mM}$, $I = 150\,\text{mA}$.

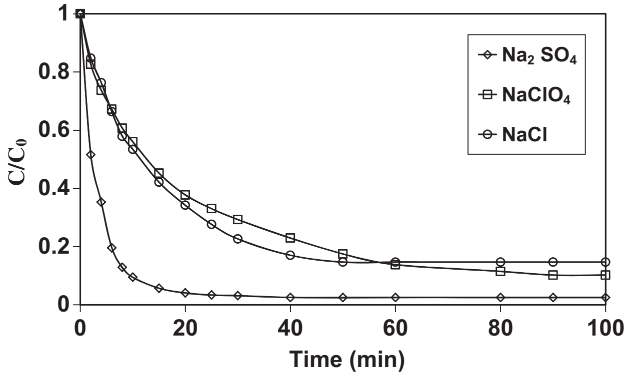


Fig. 7. Effect of supporting electrolyte species on electro-Fenton degradation of NBB. $C_0 = 0.05\,\text{mM}$, $[\text{Na}_2\text{SO}_4] = 0.5\,\text{M}$, $T = 20^\circ\text{C}$, pH = 2, $[\text{Fe}^{3+}] = 0.05\,\text{mM}$, $I = 150\,\text{mA}$.

with Fe^{2+} as shown in Eqs. (17 and 18) and formation of ion pairs ($FeCl^{+}$, $FeCl_2^{\bullet}$) which are more difficult to produce hydroxyl radicals [23,35–41].

$$HO^{\bullet} + Cl^{-} \rightarrow ClOH^{\bullet -} \tag{17}$$

$$ClOH^{\bullet -} + Fe^{2+} \rightarrow HO^{-} + Cl^{-} + Fe^{3+} \tag{18}$$

3.3.2. Effect of metal ions

The Fenton reaction could be catalyzed by several metal ions such as (Fe^{2+}, Co^{2+}, Ag^{+}, Cu^{2+}, Mn^{2+},...) [42–43]. The degradation of NBB dye was investigated in the presence of four different metal ions: Fe^{3+}, Cu^{2+}, Mn^{2+}, and Zn^{2+}). The experiments are carried out under similar conditions. The results presented in Fig. 8 show that the kinetic degradation is low in the presence of Cu^{2+} and Zn^{2+}. Over Fe^{3+}, it is clear that the efficiency of degradation obtained is higher (97.5%) after 40 min of contact time. A similar behavior is observed for Mn^{2+}. The minimum efficiency of about 96% was achieved with Zn^{2+} after 70 min of contact time.

This phenomenon can be explained by

The Cu^{+} ion can be formed from the reduction of Cu^{2+} with $HO_2^{\bullet}$ by reaction (19) with $k = 5.0 \times 107\,M^{-1}\,s^{-1}$ and/or with organic radicals $R^{\bullet}$ by reaction (20) [44]:

$$Cu^{2+} + HO_2^{\bullet} \rightarrow Cu^{+} + H^{+} + O_2 \tag{19}$$

$$Cu^{2+} + R^{\bullet} \rightarrow Cu^{+} + R^{+} \tag{20}$$

Then, the Cu^{2+}/Cu^{+} couple can contribute to the production of OH in the bulk from the Fenton-like reaction (21) with $k = 1.0 \times 10^{4}M^{-1}s^{-1}$ [45–46].

$$Cu^{+} + H_2O_2 \rightarrow Cu^{2+} + HO^{\bullet} + HO^{-} \tag{21}$$

Mn^{3+} with higher standard reduction potential accepts electrons faster than Cu^{2+} Eq. (22), thus regeneration of Mn^{2+} to react with hydrogen peroxide for producing hydroxyl radicals will also be faster compared to the other system (Cu^{2+}, Fe^{2+}) Eq. (23) [47–48].

$$Mn^{3+} + e^{-} \rightarrow Mn^{2+}, E^{\circ} = 1.51\ V/NHE \tag{22}$$

$$Fe^{3+} + e^{-} \rightarrow Fe^{2+}, E^{\circ} = 0.77\ V/NHE \tag{23}$$

Degradation efficiencies are in the following order

$$Ef(Fe^{3+}) = Ef(Mn^{2+}) > Ef(Cu^{2+}) > Ef(Zn)$$

3.3.3. Effects of organic compound (tert-butyl alcohol and sucrose)

In the present study and under the optimum conditions, the degradation of NBB was investigated in the presence of different concentrations of sucrose ranging from 15 to 75 mM. The obtained results were presented in Fig. 9. It was observed that the degradation efficiency and rate constant decreased with the increase in sucrose concentration. For sucrose concentrations equal to 15, 45, and 75, the degradation efficiencies are 86, 85, and 80%, respectively, against by the degradation efficiency of the dye in the absence of sucrose is equal to 97.5%.

In order to investigate the effect induced from the addition of tert-butyl alcohol, the electro-Fenton degradation of NBB at 0.05 mM in the presence of 0–6 mM of tert-butyl alcohol was performed. From Fig. 10 and it was clear that tert-butyl alcohol is a strong inhibitor of degradation NBB process by electro-Fenton. For tert-butanol concentrations equal to 1,

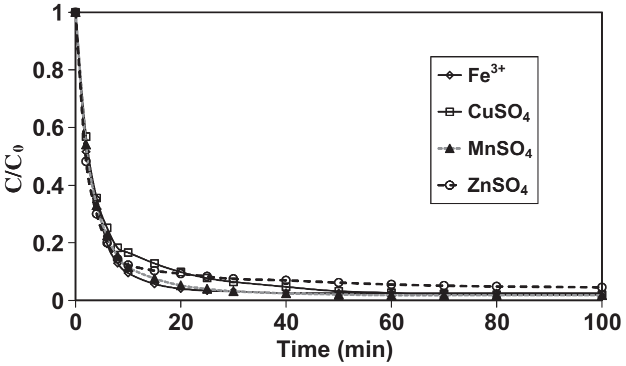


Fig. 8. Effect of Metal on electro-Fenton degradation of NBB. $C_0 = 0.05$ mM, $[Na_2SO_4] = 0.5$ M, $T = 20$°C, pH = 2, $[Fe^{3+}] = 0.05$ mM, $I = 150$ mA.

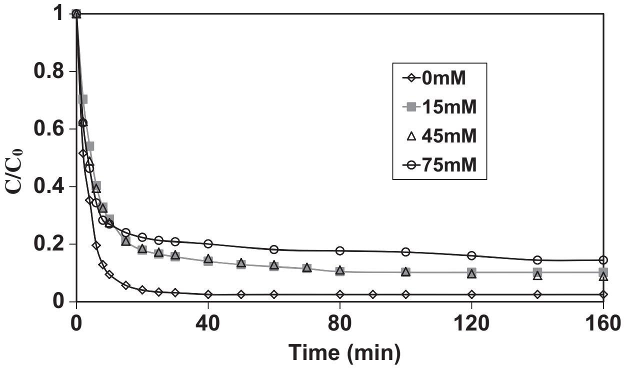


Fig. 9. Effect of sucrose addition on electro-Fenton degradation of NBB. $C_0 = 0.05$ mM, $[Na_2SO_4] = 0.5$ M, $T = 20$°C, pH = 2, $[Fe^{3+}] = 0.05$ mM, $I = 150$ mA.

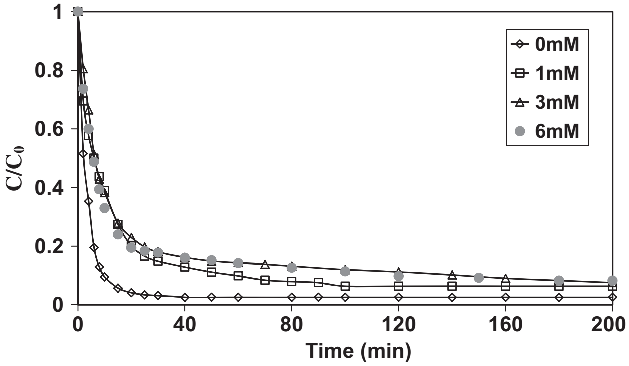


Fig. 10. Effect of tert-butyl alcohol on electro-Fenton degradation of NBB. $C_0 = 0.05$ mM, $[Na_2SO_4] = 0.5$ M, $T = 20$ °C, pH = 2, $[Fe^{3+}] = 0.05$ mM, $I = 150$ mA.

3, and 6, the degradation efficiencies are 87, 84, and 84%, respectively; the same phenomenon is observed with sucrose. This phenomenon can be explained by the fact that the t-butanol and sucrose in competition with the NBB dye.

3.4. Mineralization of NBB by various oxidation processes

Fig. 11 shows the comparative DCO decay found for a 0.05 mM NBB dye solution when it is degraded at 150 mA, pH 2, and at 20°C by simple anodic oxidation with a graphite cathode and electro- Fenton with cathode of carbon-felt.

The results show that the electro-Fenton process is more efficient than the anodic oxidation process. The reduction of COD with the electro-Fenton process is rapid because 50% of the dye was mineralized during at 60 Minutes of contact time. By against with anodic oxidation the reduction of COD is relatively very low (20% at the same contact time).

The small reduction of COD, may be due that the quantity of hydroxyl radicals generated by the anodic oxidation process is not sufficient than that formed in the electro-Fenton process.

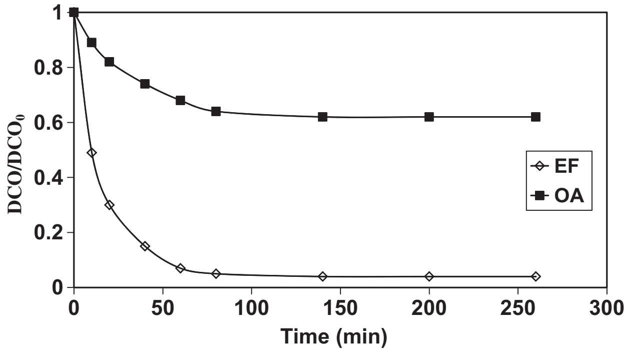


Fig. 11. Mineralization of NBB by various oxidation processes. $C_0 = 0.05$ mM, $[Na_2SO_4] = 0.5$ M, $T = 20$ °C, pH = 2, $[Fe^{3+}] = 0.05$ mM, $I = 150$ mA.

4. Conclusion

In this study, the degradation of NBB was investigated by using the electro-Fenton process. The results showed that the electro-Fenton process for NBB was found to follow pseudo-second-order kinetics.

The ANNs model was successfully used to describe the complex nonlinear behavior of NBB degradation with the range of experimental conditions adopted.

This model was developed in Matlab using a feed forward back propagation network (MLP) with 6, 32, and 1 neurons in first, second, and third layers, respectively. The findings indicated that ANN provided reasonable predictive performance ($R^2 > 0.99$).

The optimal values of the operating parameters during the oxidation of the acid yellow dye by Fenton process were found to be pH = 2, $[Fe^{3+}]$ = 0.05 mM, $[NBB]_0 = 0.05$ mM, $[Na_2SO_4]$=0.5 M, $T = 20$ °C, and $I = 150$ mA.

The efficiency and rate constant of electro-Fenton degradation were found to decrease in the following order of acids $(H_2SO_4) > (HNO_3) > (H_3PO_4)$ and supporting electrolyte species $Na_2SO_4 > NaCl > NaClO_4$. This inhibition may be due to a complexation and a radical scavenging.

The presence of metal ions in an aqueous solution decreases the efficiency of the degradation of NBB in the following order Ef (Fe^{3+})=Ef (Mn^{2+})>Ef (Cu^{2+})>Ef (Zn).

The electro-Fenton degradation of NBB decreased in the presence of t-butanol and sucrose. The slight decrease is a clear indication that the t-butanol and sucrose in competition with the NBB dye. Comparative mineralization with anodic oxidation and electro-Fenton processes was also studied under optimum conditions. The results show that the electro-Fenton process is more efficient than the anodic oxidation process.

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