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Sunlight-Assisted Photo-Fenton Degradation of Pesticide in Wastewater: Ecotoxicological Impact on *Nostoc* sp. Algae

Amrita Dutta · Ishita Chakraborty · Debasish Sarkar · Sampa Chakrabarti

Abstract Solar Photo-Fenton reaction, using $FeSO_4$ and H_2O_2, is an effective and energy-efficient advanced oxidation process (AOP) for degradation of pesticides. However, a major environmental concern is whether the net toxicity after the photo-Fenton process is within the tolerance limit of the aquatic plants and animals, since the unreacted pesticide and Fenton's reagent may impart additional toxicity to the treated water. Here, we report the oxidative removal of dichlorvos pesticide in wastewater by solar photo-Fenton reaction along with the residual toxicity analysis of the treated water on an aquatic alga. It was found that at pH 3, dichlorvos, with an initial concentration of 6.9×10^{-5} mol L^{-1}, was observed to be fully degraded within a batch time of 120 min, though the corresponding reduction of chemical oxygen demand (COD) was about 53 % signifying incomplete mineralisation. In order to predict the transient concentration profiles of dichlorvos under different initial concentrations, a four-parameter mathematical model was formulated. Additionally, the resultant toxicity was also examined using a model blue-green alga *Nostoc* sp. Compared to the raw wastewater, the net biomass of chlorophyll-a was found to increase significantly. Respective estimate of the protein concentration also indicated the same trend. Therefore, sunlight-assisted photo-Fenton process may be regarded as an effective and safe technique for the treatment of pesticide-contaminated agricultural wastewater.

Keywords Solar photo-Fenton oxidation · Dichlorvos · Toxicity · *Nostoc* sp. · Chlorophyll-a · Protein

1 Introduction

Uncontrolled application of pesticides and insecticides leads to their deposition in air, water and soil. Agricultural wastewater, often contaminated with organic pesticides, is highly toxic to aquatic biota. Most of these organic compounds are non-biodegradable and have a long half-life period (Karlaganis et al. 2001). These compounds generally reach the surface water bodies directly or indirectly, either through the discharge of agricultural drainage water from treated land or via runoff after application on hard surfaces (Leu et al. 2004). Pesticides may also enter the environment during its manufacture, due to accidental spills and leaks from storage containers. Organophosphate pesticides like 2,2-dichlorovinyl dimethyl phosphate, commonly referred as dichlorvos, are produced in mass and are widely used in the developing countries. Golash and Gogate (2012) have reported that dichlorvos is poisonous if inhaled, swallowed or absorbed through skin and eyes. Due to its fairly good solubility [~10 g L^{-1} (at 20 °C)] in water (WHO 1978, 1994), it is highly mobile in aquatic environment. The half-life of dichlorvos in aqueous

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solutions ranges from 10 to 40 h and is usually around 40 h in acidic conditions.

Conventional remediation techniques, which include flocculation, filtration, and adsorption, have been repeatedly proved to be laborious and futile (Reddy and Kim 2015). In some cases, degradation by-products are found to be more hazardous compared to the original pollutant. Therefore, an efficient remediation technique should ensure complete mineralisation of the pesticide in media (Reddy et al. 2010). Advanced oxidation processes (AOPs) are attractive methods for the treatment of wastewater containing refractory organics, since these processes aim at complete oxidative breakage of organic molecules by generating highly reactive free hydroxyl radicals (·OH) (Espulgas et al. 2002). Many pollutants, including pesticides, pharmaceuticals and dyes can be completely mineralised by AOP, as reported by Chiron et al. (2000), Perez-Estrada et al. (2005) and Lucas and Peres (2006).

Commonly used AOPs are primarily classified into (i) heterogeneous photocatalysis with a wide variety of semiconductor catalysts (TiO_2, ZnO, WO_3, etc.), which is often conjugated with O_3/H_2O_2 dosing, and (ii) homogeneous processings, such as Fenton (Fe^{2+}/H_2O_2) or photo-Fenton reactions ($Fe^{2+}/H_2O_2/UV$ or sunlight)

Solar photo-Fenton process is reported to be one of the most efficient techniques for the treatment of pesticide-contaminated wastewater (Malato et al. 2002; Oller et al. 2006; Maldonado et al. 2007).

The photodegradation of the herbicides *Atrazine* and *Ametryn* with visible light was reported by Rebelo et al. (2007). The respective degradations were observed to be 30 % for *Atrazine* and 63 % for *Ametryn*. Treatment of *Methyl Parathion*-laden wastewater was reported by Chiron et al. (2000). Decomposition of *Fenuron* (1,1-dimethyl-3-phenylurea), a herbicide, was studied by Acero et al. (2002) in batch mode with ozone, UV radiation, and Fenton's reagent. In their study, the maximum conversion was recorded to be around 80 %. Sakugawa et al. (2013) have reported the degradation of three different pesticides at pH 2.8 and 7.2 in pure and natural water using $Fe^{2+}/H_2O_2/UV$-visible light and Fe^{3+}/H_2O_2 UV-visible light oxidation systems. Corresponding results indicate that the spontaneous degradation due to solar illumination by Fe^{3+}/H_2O_2 is higher than that of Fe^{2+}/H_2O_2, both in Milli-Q water and in river water at pH 2.8. In a review article, Ikehata and Gamal (2006) have reported Fenton, photo-Fenton and electro-Fenton processes for the treatment of eight major groups of pesticides.

Irrespective of a wide variety of experimental studies, only a few reports are available on the kinetic modelling of photo-Fenton process in treating pesticide contaminated wastewater. Moreover, all available literature on kinetic modelling is mostly based on simplified pseudo-first/second-order assumption. For example, Oturan et al. (2011) have reported a rate constant about 4.75×10^9 L mol^{-1} s^{-1} based on pseudo-second-order assumption in treatment of *Diuron* using photo-Fenton process. In another study of dichlorvos remediation with Fenton reagent, Lu et al. (1999) have incorporated the concentrations of H_2O_2 and Fe^{2+} in the respective kinetic model, considering an overall pseudo-first-order reaction. The observed rate constant was expressed as a function of $[H_2O_2]$ and $[Fe^{2+}]$ as $k_{obs} = 2.67 \times 10^4 [H_2O_2]^{0.7}[Fe^{2+}]^{1.2}$. A modified first-order approach is reported by Navarro et al. (2011) in pilot-plant solar photo-Fenton treatment of ten different pesticides. The final integrated equation of the following form, $C(t) = ae^{bt}t^c$ (where a, b and c are constant system parameters), was observed to be fairly accurate ($R^2 = 0.99$) in representing the transient concentration profiles of all the different pesticides, which include *Azoxytrobin*, *Cyprodinil* and *Fludioxonil*. From the cited literature, it becomes clear that though the pseudo-first/second-order kinetic models are accurate in representing the transient concentration profiles of different pesticides in Fenton or photo-Fenton treatment, the approach is purely empirical. The simplified kinetic models have no correspondence with the complex, non-elementary reactions that actually take place during the degradation and mineralisation of pesticides in a photo-Fenton process.

On the other hand, several authors have reported the toxic effects of pesticides and its degradation products as well. Dantas et al. (2003) investigated the efficiency of Photo-Fenton processes for the treatment of wastewater from leather industry, examining the reduction of COD, ammoniacal nitrogen concentration and toxicity. Toxicity in treated wastewaters and possible toxicity of the intermediate stable products was also investigated using *Artemia salina* bioassays. The study reveals a decreasing trend of toxicity with increasing H_2O_2 concentration up to 9 g L^{-1}.

The present work has been undertaken in an attempt to primarily investigate the efficacy of solar photo-Fenton process in remediation of dichlorvos contaminated synthetic wastewater under batch mode with varying parametric conditions of pH, $FeSO_4$ dosage and H_2O_2 dosage. Subsequently, the optimum parametric conditions were evaluated, using the standard response

surface methodology (RSM), in order to maximise the % conversion of target pesticide. A four-parameter mathematical model was formulated to predict the transient concentration profiles of dichlorvos under different initial concentrations. The model was validated under optimum batch condition. Moreover, the toxic effect of the treated wastewater was also studied using Blue Green Algae (BGA), *Nostoc* sp. as biomarker. Growth of chlorophyll-a and a protein test in *Nostdoc* sp. was considered to be the indicative parameters for toxicity.

2 Materials and Methods

2.1 Materials

2.1.1 For Photo-Fenton Degradation Process

Dichlorvos (76 % purity) (molecular formula $C_4H_7Cl_2O_4P$, molecular weight 220.98 g mol^{-1}) was purchased from United Phosphorus Limited, India. Crystalline ferrous sulphate (FeSO$_4$, 7H$_2$O) was purchased from Sisco Research Laboratories Pvt. Ltd., India (Batch No.- T/830449, molecular weight 278.02). For the present study, 0.5 % of FeSO$_4$ solution has been used. Hydrogen peroxide (H$_2$O$_2$, 30 % v/v) was purchased from Merck Specialities Private Limited, India. All solutions were prepared using distilled water. pH of the insecticide solution was adjusted with 0.1 N H$_2$SO$_4$ or NaOH solution. Sodium bi-sulphite (NaHSO$_3$) was purchased from Loba Chemie. A 5.00-N NaHSO$_3$ solution has been used to stop the Fenton reaction at the desired point.

2.1.2 Ecotoxicity Studies

For the eco-toxicity study, *Nostoc* sp. (blue-green algae) was obtained from Vivekananda Institute of Biotechnology, Nimpith, South 24 pgs, West Bengal, India. It was originally supplied in BG-11 medium. Therefore, in the present study, the medium of BG-11 was used everywhere. BG-11 was obtained from Himedia Laboratories Pvt. Ltd, India.

2.2 Analytical Methods

Residual concentrations of dichlorvos were analysed at different time intervals using WATERS 2487 HPLC equipped with a C18 Column (ZORBAX SB-C18 5 μm, 46×150 mm). Acetonitrile and Milli-Q water (50/ 50 v/v for dichlorvos) were used as the mobile phase with a flow rate of 1 mL min^{-1}. Chemical oxygen demand (COD) was determined by the APHA (Rice et al. 2005) standard total reflux method. Reduction of chlorophyll-a in the BGA was estimated by Shimadzu 160A UV–vis spectrophotometer at λ_{max}=663 nm. Chlorophyll-a amount was calculated according to APHA (Rice et al. 2005) standard method. The total protein content in the cellular extract was estimated by Shimadzu UV-1800 spectrophotometer at 280 and 260 nm, respectively.

2.3 Experimental Procedure

Batch experiments of solar photo-Fenton process were performed in a stainless steel box reactor, provided with cooling water circulation to maintain the temperature around 30–32 °C. The reactor was covered with a transparent quartz lid to allow sunlight. Simulated wastewater was prepared by adding dichlorvos into distilled water. Freshly prepared FeSO$_4$·7H$_2$O solution and 30 % w/v H$_2$O$_2$ were added in the synthetic wastewater. Intensity of solar radiation, measured by Metravi 1332 digital Lux meter, was around 60 to 66 kLux (24.12 to 26.53 m W^{-1} cm^{-2}) for all the experimental runs. Samples were withdrawn at different time intervals, and the residual pesticide concentration was analysed by HPLC as described before. The reaction was terminated upon adding 5.00-N NaHSO$_3$ solution.

Initial concentrations of hydrogen peroxide and FeSO$_4$, along with pH, are the key parameters of Fenton oxidation process. For the present work, dosages of H$_2$O$_2$ and FeSO$_4$ were varied in the range of 14 to 58 and 0.072 to 0.36 mmol L^{-1} respectively. For pH, the corresponding range was 3–7. To study the influences of the process parameters on per cent degradation and to optimise the process conditions, a 2^3 simple cubic experimental scheme with triplicate at the central point was employed. However, all steady state experiments were conducted with a fixed initial concentration (=13.3×10^{-5} mol L^{-1}). Response surface methodology (RSM)-based analysis was carried out using the standard Design Expert (version 7.0) package to optimise the process parameters. In the subsequent dynamic study, initial concentration of dichlorvos solution was varied from 6.8×10^{-5} to 37.6×10^{-5} mol L^{-1}. The choice of initial concentration range is consistent with the standard effluent concentration of agricultural wastewater (Lu et al. 1997). As the chosen initial

concentration range is considerably narrow, the optimum process parameters were expected to be conserved in dynamic study.

Blue Green Algae (*Nostoc* sp.) was used as a biomarker for the measurement of residual toxicity. A 3-day experiment was performed for this purpose. The algal culture was grown in BG-11 medium at pH 7.1. Flasks and media were sterilised in an autoclave at 121 °C and 15 psi for 15 min. Contaminated and treated wastewater samples were separately added to the freshly prepared BG-11 medium. The cultures were grown in 500-mL flasks, containing 200 mL of medium at 30 °C. For the purpose of comparison, an untreated algae sample was grown in the same medium with identical parametric conditions otherwise (control sample). Amount of chlorophyll-a was monitored everyday using spectrophotometry. For biomass study, the algal sample was taken on a filter paper and was dried at 70 °C for 24 h. Weight of the dried sample was measured using a Sartorius make laboratory balance. The absorbance values of the aqueous extracts (with treated as well as control samples), for the purpose of protein content estimation, were measured at 280 and 260 nm using a spectrophotometer. The net concentration of protein was then obtained using the standard formula protein concentration $(mg\,mL^{-1}) = (1.55 \times A_{280}) - (0.76 \times A_{260})$, where A_{280} and A_{260} denote the absorbances at 280 and 260 nm, respectively.

3 Model Formulation

In a standard solar photo-Fenton process, the reactive intermediate of hydroxyl free radical ($\cdot$OH) is formed by sunlight-assisted, iron-catalysed decomposition of hydrogen peroxide. This triggers a series of complex chain reactions. The chain initiation step, described as under, is reported to be rate limiting (Neyens and Baeyens 2003).

$$Fe^{2+} + H_2O_2 + (H^+) \xrightarrow{k_1} Fe^{3+} + HO\cdot + H_2O \quad (k_1 = 70\ mol\ L^{-1}\ s^{-1}) \tag{1}$$
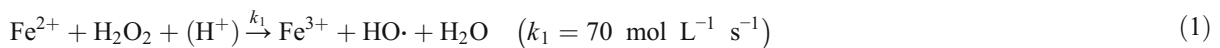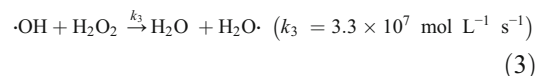
As the initiation step requires a proton, Fenton process is generally recommended under acidic conditions. Hydroxyl ions are well known as extremely potent oxidising agent, which can oxidise a variety of organic compounds through hydrogen abstraction, electrophilic addition or electron transfer reaction (Legrini et al. 1993). Regarding the mechanism of dichlorvos oxidation, it may be noted that the hydrogen abstraction pathway has been established to be dominant using the rigorous GC-MS technique (Evgenidou et al. 2006). Electrophilic addition has insignificant contribution under aqueous condition. Moreover, electron transfer reactions are also limited relative to hydroxyl free radical reactions. Therefore, the degradation is supposed to proceed through hydrogen abstraction from CH_3O- groups of dichlorvos. This leads to immediate oxidation of dichlorvos into desmethyl dichlorvos, which further reacts with hydroxyl free radical forming stable end products (PO_4^{-3}, CO_2, Cl^-, H_2O). The tentative pathway of hydrogen abstraction is presented in Fig. 1 (Evgenidou et al. 2006). In addition to the chain initiation (Eq. 1) and hydrogen abstraction pathways, hydroxyl free radicals undergo a series of side reactions, which includes
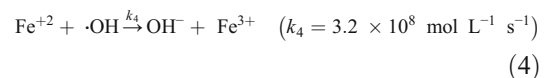
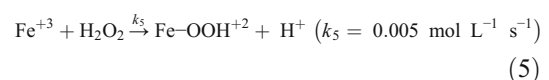1. Recombination into hydrogen peroxide:

$$2\cdot OH \xrightarrow{k_2} H_2O_2 \quad (k_2 = 5.2 \times 10^{-9}\ mol\ L^{-1}) \tag{2}$$
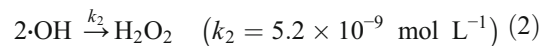
2. Reaction with hydrogen peroxide to form hydroperoxyl radicals (HO_2):

$$\cdot OH + H_2O_2 \xrightarrow{k_3} H_2O + H_2O\cdot \quad (k_3 = 3.3 \times 10^7\ mol\ L^{-1}\ s^{-1}) \tag{3}$$

3. Reaction with Fe^{2+}:

$$Fe^{+2} + \cdot OH \xrightarrow{k_4} OH^- + Fe^{3+} \quad (k_4 = 3.2 \times 10^8\ mol\ L^{-1}\ s^{-1}) \tag{4}$$

4. Reaction with Fe^{+3} to form iron (II) hydroperoxyl radical ($Fe\text{-}OOH^{+2}$):

$$Fe^{+3} + H_2O_2 \xrightarrow{k_5} Fe-OOH^{+2} + H^+ \quad (k_5 = 0.005\ mol\ L^{-1}\ s^{-1}) \tag{5}$$
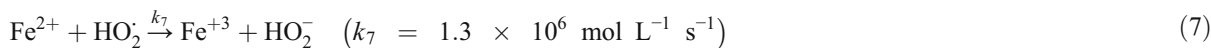
5. Decomposition of iron(II) hydroxyl radical into ferrous iron and hydroperoxyl radical:

Fig. 1 The dominant hydrogen abstraction pathway of dichlorvos

$$Fe-OOH^{+2} \xrightarrow{k_6} HO_2^{\cdot} + Fe^{+2} \quad (k_6 : unknown) \tag{6}$$
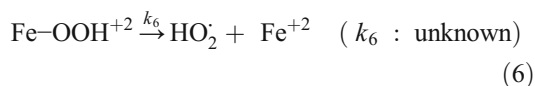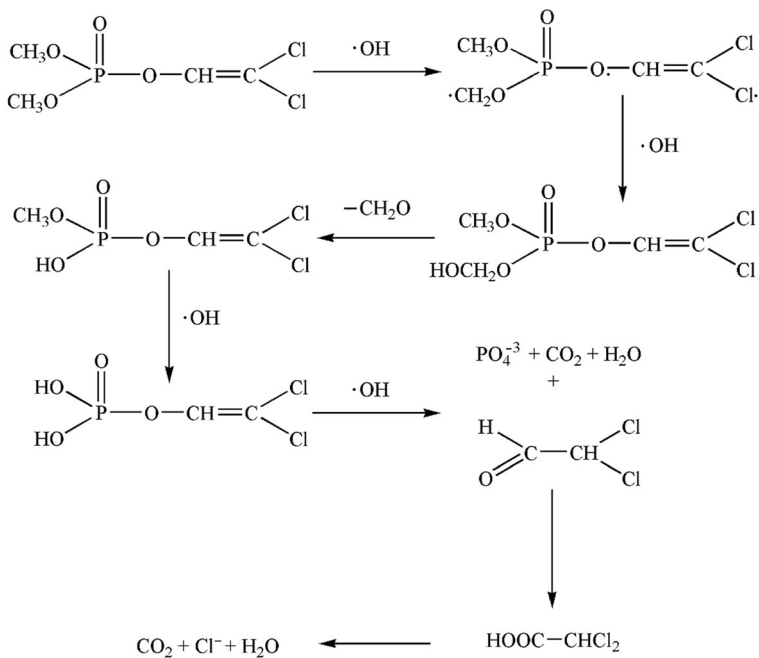
6. Reactions of hydroxyl radical with Fe^{2+} and Fe^{3+} (the rate constants are at pH 3):

$$Fe^{2+} + HO_2^{\cdot} \xrightarrow{k_7} Fe^{+3} + HO_2^{-} \quad (k_7 = 1.3 \times 10^6 \text{ mol } L^{-1} \text{ s}^{-1}) \tag{7}$$

and

$$Fe^{3+} + HO_2^{\cdot} \xrightarrow{k_8} Fe^{+2} + O_2 + H^+ \quad (k_8 = 1.2 \times 10^6 \text{ mol } L^{-1} \text{ s}^{-1}) \tag{8}$$
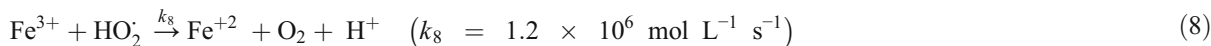
The values of the rate constants shown in Eqs. 1–8 are taken from the review article by Neyens and Baeyens (2003). To develop the overall kinetic model of the present dichlorvos oxidation by photon-Fenton process, it is necessary to represent the hydrogen abstraction pathway through an appropriate rate equation. The tentative reaction pathway, as shown in Fig. 1, includes four hydroxyl radicals, which converts the target pollutant into stable end products. Therefore, in terms of reactants and end products, the reaction may be represented as Fig. 2. The reaction is essentially non-elementary. To simplify the respective kinetic analysis, the rate equation is formulated as

$$-\frac{d[X]}{dt} = k[X]^{\alpha}[\cdot OH]^{\beta} \tag{9}$$

where X represents dichlorvos. The rate constant (k) and stoichiometric coefficients (α and β) are to be determined as adjustable parameters of the present model.

The overall reaction scheme, represented by Eqs. 1–8, includes three stable species (Fe^{2+}, H_2O_2 and X) along
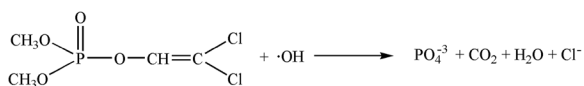

Fig. 2 The non-elementary oxidation scheme of dichlorvos by OH·

with four active intermediates ($-OH$, O_2H, Fe^{3+} and $Fe-OOH^{2+}$). Assuming pseudo-steady state approximation to be valid for the active intermediates, the pertinent kinetic equations for the present system, in addition to Eq. 10 becomes:

$$-\frac{d}{dt}\left[Fe^{+2}\right] = k_1\left[Fe^{+2}\right]\left[H_2O_2\right]$$
$$+ k_4[\cdot OH]\left[Fe^{+2}\right] - k_6\left[Fe-OOH^{+2}\right]$$
$$+ k_7\left[Fe^{+2}\right][\cdot O_2H] \tag{10}$$

$$-\frac{d}{dt}[H_2O_2] = k_1\left[Fe^{+2}\right][H_2O_2] - k_1[\cdot OH]^2 - k_5\left[Fe^{+3}\right][H_2O_2] \tag{11}$$

$$\frac{d}{dt}[\cdot OH] = 0 = k_1\left[Fe^{+2}\right][H_2O_2] - k_1[\cdot OH]^2 - k_3[\cdot OH][H_2O_2] - k[X][\cdot OH] \tag{12}$$

$$\frac{d}{dt}[\cdot O_2H] = 0 = k_3[\cdot OH][H_2O_2] + k_6\left[Fe-OOH^{+2}\right] - k_7 \tag{13}$$
$$\left[Fe^{+2}\right][\cdot O_2H] - k_8\left[Fe^{+3}\right][\cdot O_2H]$$

$$\frac{d}{dt}\left[Fe^{+3}\right] = 0 = k_1\left[Fe^{+2}\right][H_2O_2]$$
$$+ k_4[\cdot OH]\left[Fe^{+2}\right] - k_5\left[Fe^{+3}\right][H_2O_2]$$
$$+ k_7\left[Fe^{+2}\right][\cdot O_2H] - k_8\left[Fe^{+3}\right][\cdot O_2H] \tag{14}$$

$$\frac{d}{dt}\left[Fe\text{-}OOH^{+2}\right] = 0$$
$$= k_5\left[Fe^{+3}\right][H_2O_2] - k_6\left[Fe-OOH^{+2}\right] \tag{15}$$

Equations 9–11 may be viewed as three simultaneous nonlinear, ordinary differential equations of the following form

$$\frac{d[i]}{dt} = f_i\left([j]_1, [j]_2, \dots\dots[j]_7\right) \tag{16}$$

where $[i]=[X], [Fe^{+2}], [H_2O_2]$ and $[j]_1=[X], [j]_2=[Fe^{+2}], [j]_3=[H_2O_2], [j]_4=[\cdot OH], [j]_5=[\cdot O_2H], [j]_6=[Fe^{+3}], [j]_7=[Fe-OOH^{+2}]$. For four active intermediates, as mentioned, four simultaneous algebraic equations of the

form $\varphi_j(\{[j]_k\}_{k=1,7})=0$, where $j=-OH, -O_2H, Fe^{3+}$ and $Fe-OOH^{2+}$ have been formulated (Eqs. 12–15). Therefore, seven equations are available to solve for seven unknown transient variables, $\{[j]_k\}_{k=1,7}$, and the system of equations becomes deterministic. Three primary adjustable parameters, namely k, α and β along with the unknown rate constant k_6, were evaluated via global optimisation of the following objective function:

$$E(Z) = \frac{1}{5}\sum\nolimits_{j=1}^{5}\sum\nolimits_{i=1}^{6}\left(1-\frac{[X]_{ij}^{model}}{[X]_{ij}^{exp}}\right)^2 \tag{17}$$

Six experimental data points ($i=1, 6$), spanned over 0–120 min, for five different initial concentrations of dichlorvos were considered to evaluate the normalised sum of the square error. The objective function, E, was minimised to obtain the parameter vector, $Z=[k, \alpha, \beta, k_6]^T$. A step-wise algorithm to simulate the performance of the present batch reactor is outlined below:

1. Input the values of $\{k_i\}_{i=2-5 \text{ and } 7-8}$.
2. Input the time (t_{ut}), up to which the simulation is to be conducted (presently it was set at 120 min based on the transient experimental profile).
3. Input the guess values of $Z=[k, \alpha, \beta, k_6]^T$.
4. Initialisation step: $t=0, [X]=[X]_0, [H_2O_2]=[H_2O_2]_0, [Fe^{+2}]=[Fe^{+2}]_0$ and $[\cdot OH]=[\cdot O_2H]=[Fe^{+3}]=[Fe\text{-}OOH^{+2}]=0$. Additionally, $E(Z)=0$.
5. Select a specific step side (Δt) to solve Eqs. 9–11. For the present study, it was chosen to be 1 s.
6. Solve Eqs. 9–11 using the standard fourth-order Runge–Kutta method to update the transient concentration profiles of three stable species (Fe^{2+}, H_2O_2 and X) from t to $t+\Delta t$.
7. Solve Eqs. 12–15 by multivariable Newton–Raphon technique to update the concentrations of four active intermediates ($-OH$, $\cdot O_2H$, Fe^{3+} and $Fe\text{-}OOH^{2+}$) over the same time interval.
8. If $t+\Delta t=\{t_i^{exp}\}_{i=1,6}$, then also update the objective function, $E(Z)$, according to its definition (Eq. 16).
9. Print $[X]_{t+\Delta t}$ primarily along with the updated concentrations of other species.
10. If $t_{ut}\leq t+\Delta t$, then print $E(Z)$ and go to step 11, else go to step 6.
11. Upgrade Z to $Z+\Delta Z$ according to the well-known sequential simplex technique (Spendley et al. 1962), and go to step 4 unless the respective minimum is achieved.
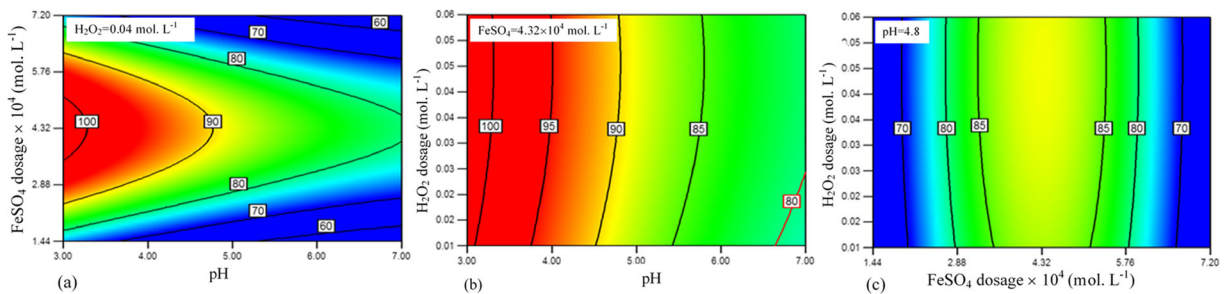
Fig 3 Three different contour plots, representing the variations of % degradation as functions of **a** FeSO$_4$ dosage and pH **b** H$_2$O$_2$ dosage and pH **c** H$_2$O$_2$ and FeSO$_4$ dosages

4 Results and Discussions

4.1 Determining the Optimum Process Conditions

In order to maximise the conversion of dichlorvos, the standard response surface methodology (RSM) was used to determine the optimum values of three process parameters, namely pH, FeSO$_4$ dosage and H$_2$O$_2$ dosage. As mentioned earlier (in Sect. 2.3), the well-known simple cubic design scheme was chosen for the analysis. It was observed that the present system can be best described by multivariable quadratic regression model. After selecting the quadratic model, detail ANOVA was carried out to evaluate the effect of each parameter and their respective interactions. Model's F-value (=27.55) confirms that there is only 0.02 % chance that F-value this large could occur because of noise. It is well-known that R^2 always increases as we add terms to the model, whereas adjusted R^2 statistic often decreases upon adding unnecessary terms. For the present model, proximity of R^2 (=0.97) and adjusted R^2 (=0.96) confirms the presence of significant terms only. Three different contour plots according to the quadratic model are shown in Fig. 3. The figure clearly indicates that the oxidation efficiency of the Fenton reagent monotonically decreases with increasing pH from pH 3. As the initiation reaction is triggered by a proton, pH is expected to influence both the generation of hydroxyl radicals as well as the oxidation efficiency. Moreover, at higher pH (>5), ferrous sulphate gets precipitated as hydroxide (Faust and Hoigne 1990) leading to a reduced mean intensity of solar radiation over the entire reactant volume, which subsequently reduces the per cent degradation. Regarding the effect of H$_2$O$_2$ dosage,

it was observed that for a fixed pH and FeSO$_4$ dosage, per cent degradation increased up to a dosing of 30 mmol L^{-1} followed by a progressive decreasing trend, continued until the highest dosing concentration (=58 mmol L^{-1}). This may be attributed to the scavenging of hydroxyl radical (reaction represented by Eq. 3) at higher H$_2$O$_2$ dosage. Similar observation was reported by Ghaly et al. (2001). FeSO$_4$ dosage was also found to exhibit similar trend like H$_2$O$_2$. Per cent degradation decreased with decrease in the FeSO$_4$ dosage concentration up to a critical value. Any further increase of ferrous sulphate dosage was observed to result in decrease of the per cent degradation. This may be due to the production of a large amount of Fe^{3+}. Fe^{3+} decomposes H$_2$O$_2$ and produces Fe(OH)$^{2+}$ in acidic condition. Tamimi et al. (2008) reported that at higher Fe^{2+} concentration, Fe^{3+} generation from the process of H$_2$O$_2$ decomposition by Fe^{2+} increases progressively, thus making Fe^{2+} unavailable for the main target reaction.

The optimum parametric conditions, to achieve maximum 93.49 % degradation, were estimated by using the steepest accent method, inbuilt in the Design Expert platform. The optimum process parameters are presented in Table 1. It may be noted that the same parameter values were assumed to be conserved in the subsequent dynamic study irrespective of variation in the initial concentration over a narrow range.

Table 1 The optimum parameter values at fixed initial concentration of 13.3×10^{-5} mol L^{-1}

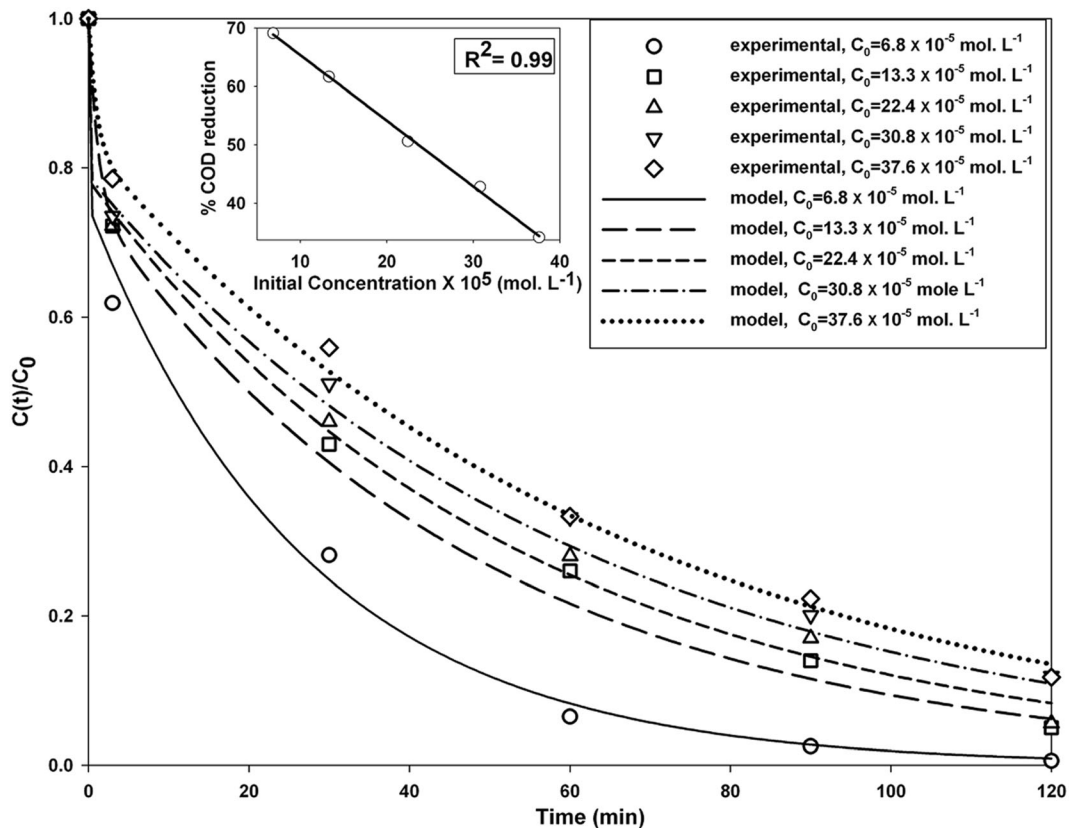| pH	H$_2$O$_2$ dosage (mol L^{-3})	Fe$_2$SO$_4$ dosage (mol L^{-3})
3	0.03	4.3×10^{-4}

Fig 4 Transient concentration profile of *Dichlorvos* in dimensionless form under optimum operating conditions (FeSO$_4$ dosage 4.3×10^{-4} mol L^{-1}, H$_2$O$_2$ dosage 0.04 mol L^{-1} and pH 3). *Insert* shows the trend of COD reduction (in %) with the initial concentration at $t = 120$ min

4.2 Dynamic Analysis Under Optimum Process Conditions

The dynamic study was performed at the optimum process conditions, though the initial concentration of dichlorvos was varied from 6.8×10^{-5} to 37.6×10^{-5} mol L^{-1}. Dimensionless concentration profiles [C $\frac{(t)}{C_0 \text{vs.t}}$], for five different initial concentrations, along with the respective model predictions are shown in Fig. 4. For all the different plots, the standard deviation $\left[= \frac{1}{(5 \times 6 - 1)} \sqrt{\sum_{i=1}^{5} \sum_{j=1}^{6} \left([X]_{ij}^{\exp} - [X]_{ij}^{\text{model}} \right)^2} \right]$ was found to be 0.02, which clearly represents the gross validity of the proposed four-parameter model. The adjusted values of the parameter vector (**Z**), leading to minimum deviation between the experimental data and the model predictions, are given in Table 2. As the simplified reaction (Eq. 9) is a representative chemical equation for an originally non-elementary reaction pathway (Fig. 1),

the optimum values of the stoichiometric coefficients (α and β) did not match with the respective numbers of the participating reactants. However, the rate constant (k) was found to be pretty large, which indicates the degradation to be entirely dependent on the production rate of hydroxyl free radial. Accordingly, the initiation reaction (represented by Eq. 1) may be identified as the rate limiting step, not only for the Fenton part but also for the entire reaction scheme under the preview of the present study. Additionally, it may be noted from Fig. 4 that all the transient concentration profiles actually consist of two characteristically different segments. Over the first 3 min, a massive decrease of dichlorvos con-

Table 2 Elements of the optimum parameter vector (**Z**)

k (mol L^{-1})$^{-3.21}$ s^{-1}	α dimensionless	β dimensionless	k_6 s^{-1}
3.2×10^5	0.76	3.45	12.3

Table 3 Comparison of the present study with the reported literature in terms of kinetic model

Pollutants (pesticide, insecticide, herbicide, etc.)	Remediation technique	Kinetic model	Rate constant and other kinetic parameters	Reference
Azoxystrobin, cyprodinil, fludioxonil, kresoxim-methyl, hexaconazole, tebuconazole, triadimenol, and pyrimethanil (fungicides), primicarb (insecticide) and propyzamide (herbicide)	Photo-Fenton treatment under natural sunlight	Modified first-order kinetics: $C(t)=ae^{bt}fa$, b and c model parameters, b is similar to rate constant	$a \Rightarrow [1.27, 18.15]$ $b \Rightarrow [-0.65, 0.14]$ $c \Rightarrow [-0.63, -0.39]$	Navarro et al. 2011
Dichlorvos	Fenton treatment	Pseudo-first-order overall rate equation: $\frac{d[X]}{dt} = k_{obs}[X]$ where $[X]$: dichlorvos concentration in M	$k_{obs}=2.67 \times 10^4 \times [H_2O_2]^{0.7}[Fe^{2+}]^{1.2}$	Lu et al. 1999
Diuron	Photo-Fenton process	Pseudo-second-order overall rate equation	$k_{obs}=(4.75 \pm 0.20) \times 10^9$ L mol^{-1} s^{-1}	Oturan et al. 2011
Dichlorvos	Photocatalytic degradation with TiO$_2$ and ZnO	Langmuir–Hinshelwood model: $-\frac{dC}{dt} = \frac{k_r K C_0}{1+K C_0}$ where C_0 is the initial concentration of dichlorvos and K represents equilibrium adsorption constant of dichlorvos and k_T is the limiting reaction rate	$k_T=4.29$ mg L^{-1} min^{-1} and $K=0.02$ mg^{-1} L^{-1} for the TiO$_2$ and $k_T=7.34$ mg L^{-1} min^{-1} and $K=0.03$ mg^{-1} L^{-1} for the ZnO.	Evgenidou et al. 2005
Dichlorvos and dimethoate	Photocatalytic degradation with TiO$_2$	Pseudo-first-order overall rate equation	$k_{obs}=0.103$ min^{-1} for dichlorvos and 0.048 for dimethoate (TiO$_2$=100 mg L^{-1})	Evgenidou et al. 2006
Methomyl	Photo-Fenton process (H$_2$O$_2$, Fe^{2+}, UV)	Pseudo-first-order overall rate equation	$k_{obs}=0.175$ min^{-1}	Tamimi et al. 2008
Dichlorvos	Photo-Fenton process	Hydrogen abstraction pathway of dichlorvos coupled with multiple reactions of photo-Fenton system. The primary non-elementary degradation reaction of dichlorvos: $-\frac{d[X]}{dt} = k[X]^{\alpha}[\cdot OH]^{\beta}$	$k=3.2 \times 10^5$ (mol L^{-1})$^{-3.21}$ s^{-1} $\alpha=0.76$ and $\beta=3.45$ (dimensionless)	Present study

Fig. 5 The transient growth pattern of chlorophyll-a of *Nostoc* sp. in fresh, treated and untreated water samples (treatment condition: initial concentration of dichlorvos=13.3×10^{-5} mol L^{-1}, FeSO$_4$ dosage 4.3×10^{-4} mol L^{-1}, H$_2$O$_2$ dosage=0.04 mol L^{-1}, pH 3 and sunlight intensity= 66.8 kLux)
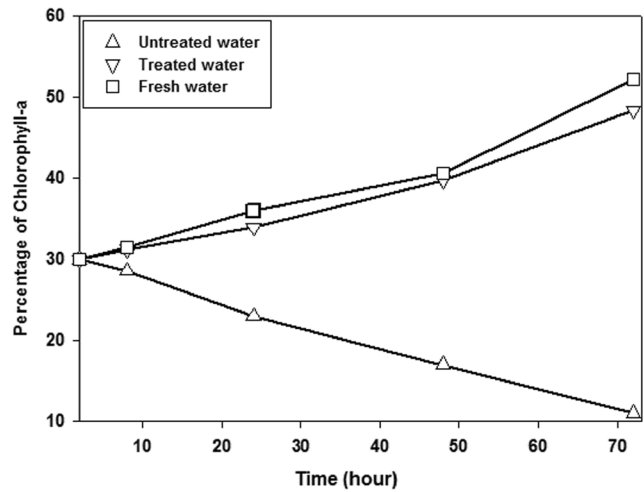
centration was observed for all the different initial concentrations. However, the rate of reaction $\left[=-\dfrac{dC(t)}{dt}\right]$ progressively decreased beyond 5 min, before levelling off at around 120 min. This may be attributed to the increased recombination rate of hydroxyl free radicals into H$_2$O$_2$ (Eq. 2), as well as elevated consumption of the same in pertinent side reactions (Eqs. 3 and 4). Though the present rate model cannot be directly compared with that of reported studies on different pesticides because of varied assumptions, still an overall comparative analysis was carried out, as shown in Table 3. It may be noted that the popularly used pseudo-first-order models, irrespective of high R^2 value, often lead to wrongly predicted minimum concentration values

(Navarro et al. 2011). Therefore, even from an empirical standpoint, biphasic models are generally recommended. Other than that, a modified first order approach, as proposed by Hoerl (1954), has been also used to predict the kinetics of photo-Fenton process. The model was observed to be fairly accurate for different pesticides. However, it is simply a curve-fitting approach, without any physical basis. This is justified in terms of positive values of parameter b in the integrated profile equation: $C(t)=ae^{bt}t^c$, which is supposed to be the negative of the rate constant $(=-k)$. On the other hand, Lu et al. (1999), in Fenton treatment of dichlorvos, have proposed a bifactor rate constant (k) and were able to relate it to the observed overall rate constant through linear regression. k was found to be 2.67×10^4 min^{-1} M^{-2}, and the
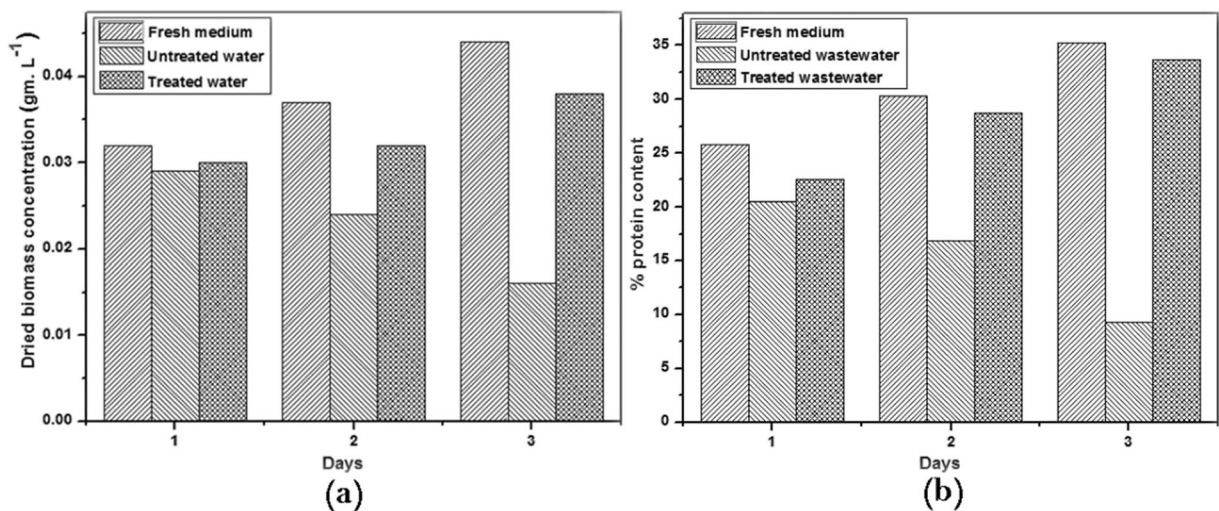

Fig. 6 a Change of oven-dried biomass over 3 days in control, untreated and treated samples. **b** Change of total protein content over 3 days in control, untreated and treated samples

representative kinetic equation was expressed as $-\frac{d[X]}{dt} = 2.67 \times 10^4 [H_2O_2]^{0.7} [Fe^{2+}]^{1.2} [X]$. Similar studies on different pesticides, reported by Tamimi et al. (2008) and Evgenidou et al. (2006) any many other, are all based on pseudo-first-order assumption. The rate equation for *Diuron* oxidation by hydroxyl radical, as reported by Oturan et al. (2011), was found to follow a second-order kinetics. Corresponding rate constant was evaluated to be $(4.75 \pm 0.20) \times 10^9$ L mol^{-1} s^{-1}, which is much higher than that of the present study $[=3.2 \times 10^5 (mol \ L^{-1})^{-3.21} s^{-1}]$. However, the overall order of the present investigation was determined to be $n = \alpha + \beta = 4.21$. Accordingly, the lower value of rate constant is expected to be compensated by more than twofold higher exponent term attached to the concentration function.

In addition to the transient concentration profile, mineralisation of dichlorvos was measured in terms of reduction in chemical oxygen demand (COD). Per cent reduction of COD, defined as $\left[= \frac{COD \ (t=0) - COD(t=120 \ min)}{COD \ (t=0)} \times 100 \right]$, was observed to decrease in a linear fashion ($R^2 = 0.99$) with increasing initial concentration, as shown in inset of Fig. 4. However, the per cent degradation after 120 min was considerably higher compared to the corresponding per cent reduction of COD. For example, for an initial concentration of 13.3×10^{-5} mol L^{-1}, the degradation was as high as 96 %, whereas the reduction of COD was only 62 %. The difference clearly confirms the presence of some stable intermediates/products that are oxidisable and present in the reaction system, and may be even after complete degradation of the primary pollutant. These intermediates/products may have some residual toxicity that can affect the aquatic lives if discharged to the surface water body. Therefore, the net toxicity of treated water was examined using a blue-green alga, *Nostoc* sp. as the biomarker. The indicating parameters chosen were the degradation of chlorophyll-a and total cellular protein content.

4.3 Growth of Chlorophyll-a

Blue Green Algae is regarded as a good toxicity marker for polluted water (Bringmann and Kuhn 1980). In the present study, the algae *Nostoc* sp. was used for residual toxicity analysis. In order to investigate the residual toxicity level of the treated wastewater, experiments were carried out by growing this algal species in fresh, treated and untreated water samples under optimum parametric conditions. Except the fresh sample, the initial concentration level in treated and untreated samples was fixed at 13.3×10^{-5} mol L^{-1}. It is well known that the toxicity has negative influence on the photosynthetic ability of the algae (Firat and Cetin 2009). Therefore, the growth of chlorophyll, which is the major photosynthetic pigment, is expectedly suppressed in untreated water sample. Figure 5 represents the transient growth pattern of chlorophyll-a over a duration of 72 h, for all the three water samples. The figure clearly indicates decreasing trend of chlorophyll in untreated sample (30 to 11 % over 72 h), whereas in treated sample, the growth is comparable to that in fresh water. After 72 h, the treated sample exhibited a chlorophyll growth from 30 to 48 %. In the case of fresh water, the 72-h growth was recorded to be 52 %, which is only 4 % higher than that of treated sample. In addition to the chlorophyll growth, toxicity study was further extended with the same *Nostoc* sp. to the pattern change of oven-dried biomass amount and per cent protein content over 3 days. In Fig. 6a, b respectively, the growths of cultivated algal biomass and per cent protein content have been compared for untreated, treated and control media. It may be noted that for all these experiments, the initial concentration of dichlorvos was fixed at 13.3×10^{-5} mol L^{-1}.

In the absence of dichlorvos, the growth-inhibiting pollutant, both biomass growth (from 3.2×10^{-2} to 4.4×10^{-2} g L^{-1}), and protein content were observed to increase significantly (38 %) over a period of 3 days. Simultaneously, in untreated waste sample, both the marker variables were recorded to decrease over the same time interval, indicating the toxic effect of dichlorvos on the growth of the biomarker, *Nostoc* sp. Decrease in biomass was from 2.9×10^{-2} g L^{-1} (day 1) to 1.6×10^{-2} g L^{-1} (day 3), whereas the protein content was reduced by 60 %. The results clearly indicate the effectiveness of the present solar photo-Fenton technique in reducing the overall toxicity of dichlorvos contaminated wastewater.

5 Conclusion

Sunlight-assisted Fenton's process effectively degrades dichlorvos pesticide in simulated agricultural wastewater. Using RSM, optimum process parameters under batch mode were found to be 4.3×10^{-4} mol L^{-1} of FeSO$_4$ dosage and 0.03 mol L^{-1} H$_2$O$_2$ dosage at pH 3

under an average sunlight intensity of 66 kLux (26.53 mW cm^{-2}). The maximum per cent degradation achieved under the scope of the present study was around 95 %. However, corresponding removal of COD was limited to 86.6 %, which clearly signifies the presence of oxidisable intermediates. Additionally, a four-parameter mathematical model was proposed and validated, which has exhibited a close proximity of predicted trend relative to the experimental data (standard deviation=0.02). Toxicological status of the wastewater, before and after the treatment, was examined relative to freshwater. It was observed that the life process of the blue-green alga, *Nostoc* sp., was inhibited in the untreated wastewater, as indicated by the degradation of chlorophyll-a and protein over 3 days. However, the algae could sustain in the treated wastewater, as tested in terms of net chlorophyll-a and protein contents. Therefore, the study clearly establishes the novelty of solar photo-Fenton process in treatment of agricultural wastewater, particularly in the light of economic feasibility and toxicological effects.

Compliance with Ethical Standards

Conflict of Interest   The authors declare that there is no conflict of interest.

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