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RESEARCH ARTICLE - CHEMICAL ENGINEERING

# Low-Cost Photo-Fenton-Like Process for the Removal of Synthetic Dye in Aqueous Solution at Circumneutral pH

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## Abstract

Fenton-like processes have been widely studied in recent years and are considered promising for organic wastewater treatment. Enhancement of wastewater treatment performance involves the development of economical and environmental aspects of the process. The present work aims to investigate the degradation and mineralization of an organic model compound, namely patent blue V (PBV) in aqueous solution. The process adopted uses the Fenton-like mode enhanced by UV light, using a low amount of reagent at natural pH, which was close to neutral. Some key parameters including UV light, $H_2O_2$ dosage, catalyst amount and initial dye concentration in the homogeneous Fenton-like processes were discussed. The complete degradation of 10 mg/L of PBV was obtained in 1 h with low reagent concentrations (0.98 mg/L and 39.1 mg/L of $Fe^{3+}$ and $H_2O_2$, respectively) at natural pH (6.4). The mineralization was justified through the determination of sulfates, nitrates and calcium formed during oxidation. The reaction obeys the pseudo-first-order and kinetic constants, namely the apparent rate constant, the half-life time and the catalytic efficiency, strongly depend on the catalyst concentration. The reutilization of the generated sludge in the photo-Fenton-like process was discussed. However, in spite of the decrease in the degradation efficiency, the possibility of recycling the catalyst $Fe^{3+}$ as sludge $Fe(OH)_3$ makes the process photo-Fenton-like, cheaper and environment friendly.

**Keywords** Photo-Fenton-like · Degradation · Mineralization · Patent Blue V · Catalyst · Sludge reutilization

## 1 Introduction

Pollution of the aquatic medium by organic compounds such as synthetic dyes poses a serious environmental and health problems affecting directly or indirectly the human life [1, 2]. Particularly, azo dyes and their derivatives products engender high toxicity with carcinogenic and genotoxic effects on aquatic life [3, 4]. Furthermore, these pollutants undergo a very slow biodegradation [5–7]. Statistical investigations reported the disposal of wastewater with significantly high contents of dyes and pigments from several industrial activities (paper, textile, food…etc.) [3, 4]. As a consequence, these molecules find their way to the water resources, either surface or underground, due to the ineffectiveness of conventional wastewater treatment plant methods [8–10]. Since the discovery of the Fenton reaction in 1876 [11], the degradation of organic molecules displays a revolutionary development. The Fenton's reagents clearly improve the efficiency of the removal of organic pollutants, based on the increase in production of free radicals ($HO^{\cdot}$) which comes from the catalytic decomposition of the oxidant $H_2O_2$ [8]. These radicals have a strong oxidation capacity (standard potential of $HO^{\cdot} = 2.80$ V versus standard hydrogen electrode) [12]. The Fenton-like is an economic and profitable process (high-efficiency and non-expensive reagents), easy to use [7, 13, 14] and efficient to mineralize organic

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pollutants [2]. But, it has some inconveniences, such as a medium pH limit (generally, it operates at acidic medium), and causes a secondary pollution by the sludge of iron oxyhydroxide produced during the process [1, 15]. Therefore, researchers have turned to the heterogeneous system that uses transition metal catalysts such as iron [1, 16, 17], copper [16, 18, 19] and others ($Co^{2+}$, $Mn^{2+}$) [20, 21]. However, the yield of this process still remains limited and catalyst stability appears to be another challenge for economic and environmental profitability. This has led some researchers to move toward improving the efficiency of homogeneous Fenton to apply this process in a wide pH range [22, 23].

The principal disadvantage of the Fenton process in wastewater treatment is the increased cost of the process by the continuous loss of catalyst added because it cannot be reused in several cycles [24]. To avoid this main problem, a few works have recently tried to reuse the generated sludge as a source of iron in heterogeneous Fenton process for wastewater treatment [25–27] or as a precursor for the preparation of a heterogeneous Fenton catalyst [28].

The aim of this study is to degrade a synthetic dye molecule that contains aromatic rings in an aqueous medium by photo-Fenton-like process; the reaction was performed with the Fenton reagents ($Fe^{3+}$ and $H_2O_2$) enhanced by a UV source light with medium intensity (125 W), at natural pH (6.4). It should be noticed that the concentrations of reagents used in this work were very low (less than 1 ppm for $Fe^{3+}$ and lower than 40 mg/L for $H_2O_2$). These concentrations of iron respected the amounts imposed by the applicable regulations for the European Union which sets this limit at 2 ppm in wastewater [29]. In order to evaluate the performance of the process, the sludge obtained after the reaction was reused to degrade the pollutant.

The innovation of this study is to suggest a very cheap process for the removal of organic pollutants. In our knowledge, it is the first time using a very small quantity of catalyst with the reutilization of sludge at circumneutral pH for the degradation of an organic compound.

## 2 Experimental

### 2.1 Reagents and Materials

The patent blue V dye used as a model dye in this study was purchased from *Panreac,* with purity (97%) (molecular weight = 566.66 g/mol, $\lambda_{max} = 631$ nm). Figure 1 shows the chemical structure and UV–Vis spectrum of PBV dye. $FeCl_3 \cdot 6H_2O$, the source of $Fe^{3+}$, was purchased from *Panreac*. Hydrogen peroxide solution (30%) was of analytical grade from *Merck*. Phosphoric acid used for setting the pH of the solution to 3 and NaOH used for $Fe^{3+}$ precipitation were analytical grades purchased from *Panreac*. All chemical reagents were used as received without further purification.

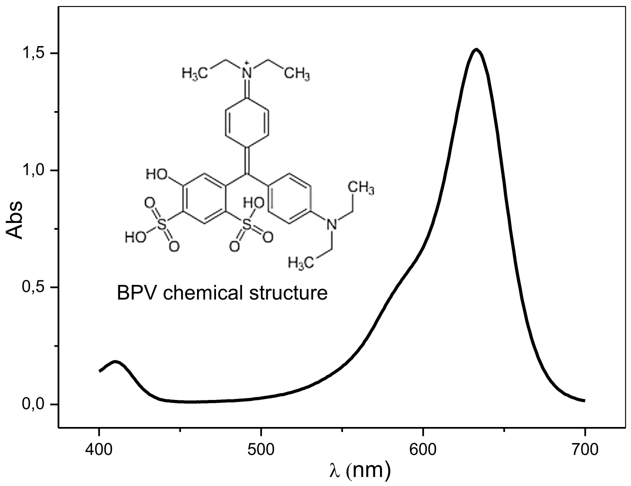

**Fig. 1** UV–visible spectrum and molecular structure of patent blue V

Stocked solutions of dye and $Fe^{3+}$ were prepared using distilled water. All experiments were performed at natural pH (6.4). Only the experiments dealing with sludge reutilisation were done at pH = 3.

### 2.2 Analytical Methods

Aliquots were taken several times and analyzed using a *PerkinElmer* spectrophotometer, allowing the measurement of the UV–Vis absorbance by exploitation of the calibration curve. The maximum absorption wavelength ($\lambda_{max}$) was 631 nm.

The determination of oxidation products such as sulfate $SO_4^{2-}$ and nitrate $NO_3^{2-}$ ions was made by spectroscopy methods as described in the literature [30]. The determination of calcium $Ca^{2+}$ ions was carried out according to the standard method NFT 90-016.

### 2.3 Homogenous Fenton-Like Process

The reaction of the degradation of patent blue V by the photo-Fenton-like system is done in a homogeneous medium, by dissolving a certain amount of iron $Fe^{3+}$ and $H_2O_2$ in an aqueous solution of PBV. The reactions were performed at natural pH (6.4) without any adjustment, with vigorous stirring (250 rd/min), and under UV source light (125 W lamp). The reaction mixture was put in a batch reactor composed of a vertical cylinder form. The time 0 of the kinetics was marked with the addition of the Fenton reagents and turn on the lamps.

To minimize the economic and environmental impact of the process, the sludge produced after the photo-Fenton-like oxidation was reused in successive cycles of reaction. The solution was acidified until pH = 3 by adding phosphoric acid (1 M) at each new run. To precipitate the maximum of $Fe^{3+}$ available in the solution, an amount of NaOH was added at the end of each run. The other parameters were kept unchanged for each run (Fig. 2).

### 2.4 Parameter Effects of UV/Fenton-Like Process

The effects of some parameters such as the dye concentration (PBV), the oxidant concentration ($H_2O_2$) and the catalyst concentration ($Fe^{3+}$) were investigated to optimize the degradation process. The solution was kept at natural pH (6.40), and the dye concentrations used in this study were 5, 10, 20 and 30 mg/L, namely higher than those found in real wastewater. Indeed, due to the rapidity of the Fenton reaction, to clearly observe the degradation kinetics and to obtain usable results, it is preferable to use high concentrations of dye. The concentrations of $H_2O_2$ used in this work ranged between 9.52 and 193.8 mg/L. We report that the selected range must include the theoretical value of $H_2O_2$ calculated (19.58 mg/L) according to the reaction equation of mineralization of PBV. Regarding the catalyst concentration, very low amounts were used, namely in the range 0.5 to 4 mg/L, to minimize the amount of sludge produced.

The discoloration efficiency was determined as follows:

$$\%X = \frac{\left([\mathrm{PBV}]_0 - [\mathrm{PBV}]_t\right)}{[\mathrm{PBV}]_0} \times 100 \tag{1}$$

In which: $[\mathrm{PBV}]_0$ and $[\mathrm{PBV}]_t$ are the initial and the concentrations of dye at any reaction time $t$, respectively.

### 2.5 Kinetic Analysis

The kinetic parameters, namely the apparent rate constant and the half-life time, were determined from the pseudo-first-order model. (Confirmation of the relevance of the model was done by checking the linearization coefficient through the $R$ square.) The model can be written as follows:

$$\frac{[\mathrm{BPV}]_t}{[\mathrm{BPV}]_0} = \exp(-k_{\mathrm{app}}t) \tag{2}$$

It can be expressed by the linear equation:

$$\mathrm{Ln}\frac{[\mathrm{BPV}]_t}{[\mathrm{BPV}]_0} = -k_{\mathrm{app}}t \tag{3}$$

where $[\mathrm{PBV}]_0$ and $[\mathrm{PBV}]_t$ are the initial concentration and the concentration at any given time $t$ of the PBV, respectively, and $k_{\mathrm{app}}$ is the apparent rate constant of the first-pseudo-order reaction. The half-lifetime ($t_{1/2}$) of the sample can be easily calculated from $k_{\mathrm{app}}$ by using the following equation:

$$t_{1/2} = \frac{\ln 2}{k_{\mathrm{app}}} \tag{4}$$

An important parameter of kinetic is the catalytic efficiency which can be calculated by the following formula [31]:

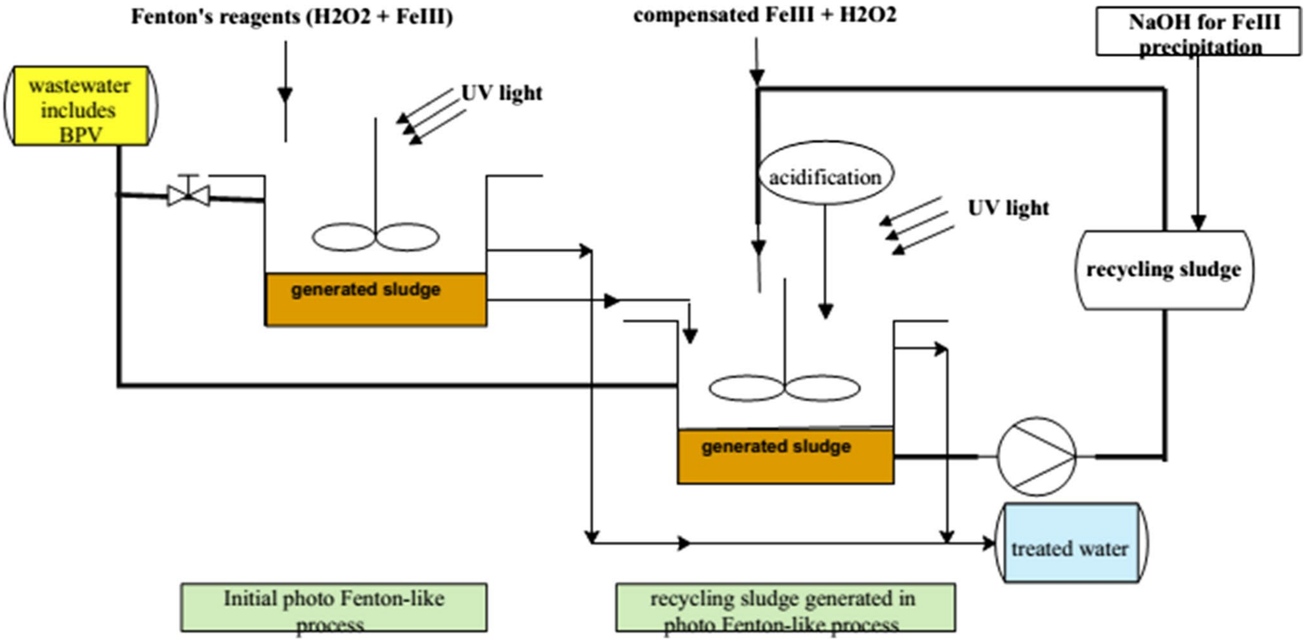

**Fig. 2** Schematic representation of the sludge generated recycling in the photo-Fenton-like process

$$k_c = \frac{k_1 - k_0}{[\mathrm{Fe}^{3+}]^n} \tag{5}$$

where $k_c$, $k_1$ and $k_0$ are the catalytic efficiency, the rate constant with catalyst and the rate constant without the catalyst, respectively. "$n$" is the order of the reaction and $[\mathrm{Fe}^{3+}]$ is the concentration of iron used. Equation (5) can be simplified as follows ($k_0 = 0$ and $n = 1$):

$$k_c = \frac{k_1}{[\mathrm{Fe}^{3+}]} = \frac{k_{\mathrm{app}}}{[\mathrm{Fe}^{3+}]} \tag{6}$$

### 2.6 Mineralization Analysis

The PBV mineralization was justified by the formation of sulfates, nitrates and calcium ions according to the PBV theoretical mineralization equation:

$$\begin{aligned} &\mathrm{C_{27}H_{36}CaN_2O_7S_2} + 32\mathrm{H_2O_2} \\ &\quad \rightarrow 26\mathrm{CO_2} + 2\mathrm{H_2O} + 2\mathrm{SO_4^{2-}} \\ &\quad + 2\mathrm{NO_3^{2-}} + \mathrm{CaCO_3} + 96\,\mathrm{H^+} + 88\mathrm{e^-} \end{aligned} \tag{7}$$

Thus, mineralization of 10 mg/L of pollutant was evaluated by the calculation of the concentrations of $\mathrm{SO_4}^{2-}$, $\mathrm{NO_3}^{-}$ and $\mathrm{Ca}^{2+}$.

## 3 Results and Discussion

### 3.1 Effect of UV Light Irradiation

The effect of UV light on the rate of pollutant degradation was investigated by the exposure of an aqueous solution of PBV to UV irradiation; time course of the PBV concentration was monitored. To evaluate the effect of UV on the efficiency of degradation, the results obtained were compared with the degradation of PBV by the Fenton process in the dark.

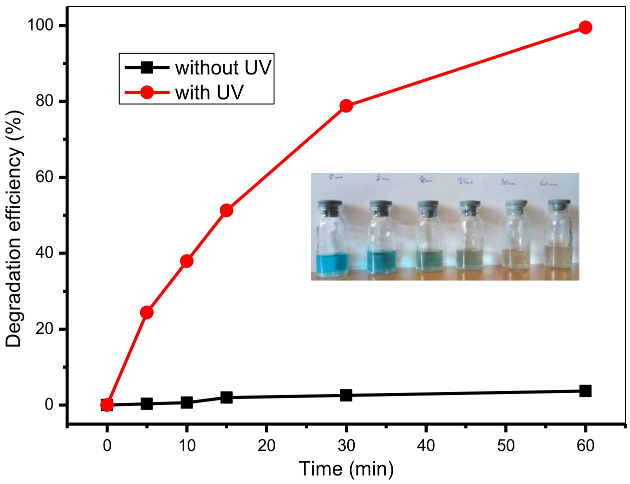

**Fig. 3** UV irradiation effect on the degradation efficiency of the PBV. Reaction conditions, pH = 6.40, $[\mathrm{Fe}^{3+}]_0 = 0.98$ mg/L, $[\mathrm{H_2O_2}]_0 = 78.2$ mg/L and $[\mathrm{PBV}]_0 = 10$ mg/L

As shown in Fig. 3, the degradation efficiency was clearly enhanced by the UV light. In 60 min, the PBV molecules were totally degraded by the Fenton process in the presence of UV light. In contrast, only 3.74% degradation was observed in the presence of the Fenton's reagents but in the dark, showing no significant degradation in the absence of UV light at neutral pH with small amount of catalyst. Bandala et al. [20] found the use of solar light for the degradation of 2,4-dichlorophenoxyacetic acid by Fenton process ($\mathrm{Fe}^{2+}/\mathrm{H_2O_2}$) to be beneficial. Neamtu et al. [32] showed that the degradation rate constant of reactive yellow 84 increased from 0.0875 $\mathrm{min}^{-1}$ in dark to 0.2754 $\mathrm{min}^{-1}$ under UV light in the case of the Fenton process. The use of photochemistry in a homogeneous Fenton process clearly improves the catalytic efficiency and allows to reduce the amount of catalyst [12]. The photons of UV light react with ferrous ions leading to an increase in hydroxyl radicals produced [33]. Moreover, the photoreduction of $\mathrm{Fe}^{3+}$ caused the acceleration of the production of $\mathrm{HO}^{\cdot}$ according to the reaction [32]:

$$\mathrm{Fe}^{3+} + \mathrm{H_2O} + h\nu \rightarrow \mathrm{Fe}^{2+} + \mathrm{HO}^{\cdot} + \mathrm{H}^+ \tag{8}$$

### 3.2 Effect of the Dye Concentration

The pollutant concentration is a major parameter in wastewater treatment [34]. In this study, the degradation efficiency for different PBV concentrations by photo-Fenton-like process was investigated. As shown in Fig. 4, the degradation efficiency decreased for increasing the initial concentrations of the pollutant. For 5 and 10 mg/L dye concentration, the PBV molecules were completely degraded (100%), while the degradation efficiency decreased to 73.69 and 64.30% for 20 and 30 mg/L initial dye concentrations, respectively. It should be noted that the concentration of $\mathrm{Fe}^{3+}$ and $\mathrm{H_2O_2}$ was kept constant (0.98 mg/L and 78.2 mg/L) in all experiments. This diminution was therefore due mainly to a low concentration of free radicals produced by the photo-Fenton-like reaction compared to the concentrations of PBV in the solution [6].

### 3.3 Effect of the Oxidant $\mathrm{H_2O_2}$

Hydrogen peroxide $\mathrm{H_2O_2}$ was also among the major parameter in the Fenton process since hydroxyl radicals come from its catalytic degradation. The optimal dose should be selected owing to its cost [32, 35]. Figure 5 shows the degradation efficiency of PBV versus time at a different

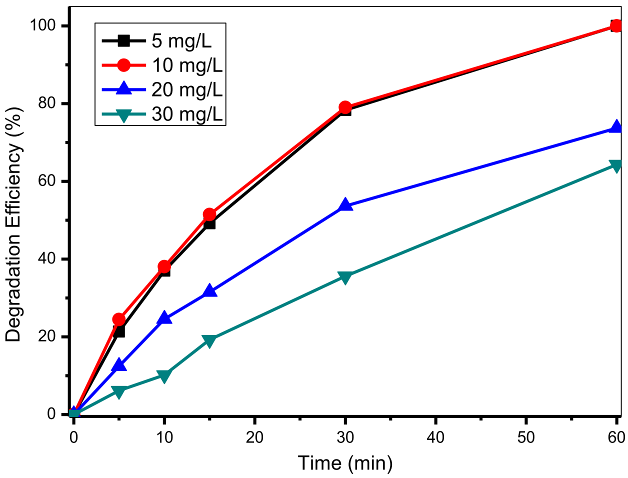

**Fig. 4** Initial dye concentration effect on PBV degradation efficiency. Reaction conditions, pH = 6.40, $[Fe^{3+}]_0 = 0.98$ mg/L and $[H_2O_2]_0 = 78.2$ mg/L

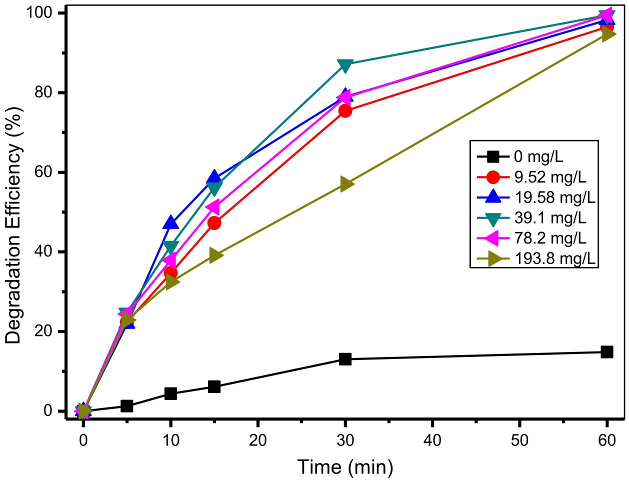

**Fig. 5** Initial $H_2O_2$ concentration effect on PBV degradation efficiency. Reaction conditions, pH = 6.40, $[Fe^{3+}]_0 = 0.98$ mg/L and $[PBV]_0 = 10$ mg/L

concentration of oxidant $H_2O_2$ at natural pH (6.4) and constant iron amount (0.98 mg/L). It can be seen that without $H_2O_2$, PBV degradation did not exceed 10%, while total degradation was observed for 39.1 mg/L $H_2O_2$. The increase in the concentration of oxidant $H_2O_2$ increased the degradation efficiency significantly, due to the increase in hydroxyl radicals $HO^{\cdot}$ formed according to the following reactions [36]:

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\cdot} + H^+ \tag{9}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\cdot} + HO^- \tag{10}$$

$$Fe^{3+} + H_2O + UV \rightarrow Fe^{2+} + HO^{\cdot} + H^+ \tag{11}$$

$$H_2O_2 + UV \rightarrow 2HO^{\cdot} \tag{12}$$

Furthermore, beyond an optimal value, the addition of the amount of $H_2O_2$ has a negative effect on the degradation rate, due to the scavenging effect of free radicals by the excess of $H_2O_2$ as shown in Eqs. (13) and (14) [36, 37]:

$$HO^{\cdot} + H_2O_2 \rightarrow H_2O + HO_2^{\cdot} \tag{13}$$

$$HO_2^{\cdot} + HO^{\cdot} \rightarrow H_2O + O_2 \tag{14}$$

Although, the optimal amount of oxidant is more than the theoretical value calculated by the mineralization reaction, as shown in Eq. (7).

According to the equation, 1 mol of PBV requires 32 mol of $H_2O_2$ for complete mineralization. Theoretically, it must be added 0.576 mM (19.58 mg/L) of $H_2O_2$ to degrade completely 0.018 mM (10 mg/L) of pollutant. To ensure that the PBV is totally removed, the experimental $H_2O_2$ concentration added must be more than the theoretical value [12]. In this study, the optimum $H_2O_2$ amount was 39.1 mg/L, which is therefore more than the theoretical concentration; this might be explained by the fact that a part of the $H_2O_2$ added does not react with the organic molecules. Hence, the optimal dosage of $H_2O_2$ should be determined experimentally [12].

### 3.4 Effect of the Catalyst Dosage

The effect of the catalyst concentration is also among the major parameters in the Fenton-like process [35, 38], because it accelerates the production of free radicals according to the following equations [35]:

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\cdot} + H^+ \tag{15}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\cdot} + HO^- \tag{16}$$

The use of low amounts of $Fe^{3+}$ reduces the cost of wastewater treatment, and thus the load of sludge produced, which is the essential disadvantage in the Fenton process. In this study, the use of a low quantity of catalyst $Fe^{3+}$ was the main objective in the removal of PBV by photo-Fenton-like process. Under UV light, at natural pH (6.4), with 78.2 mg/L $H_2O_2$ concentration, the degradation of PBV was investigated using 0.5, 0.98, 1.96 and 4 mg/L of $Fe^{3+}$. The results obtained are illustrated in Fig. 6, showing that the increase in the $Fe^{3+}$ amount increased significantly the degradation efficiency. The PBV was totally removed in 60, 10 and 5 min with the 0.98, 1.96 and 4 mg/L of $Fe^{3+}$, respectively, while it was only 45% for 0.5 mg/L of $Fe^{3+}$. Consequently, for almost 1 mg/L of iron salt concentration, total degradation was reached within 60 min. This result is of a high economic and environmental significance (allowing to reduce the cost of wastewater treatment and to avoid exceeding the wastewater discharge standard for metals) [29].

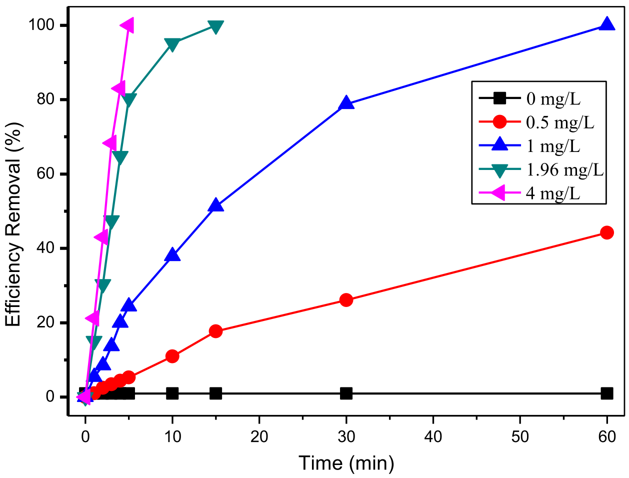

**Fig. 6** Initial $Fe^{3+}$ concentration effect on PBV degradation efficiency. Reaction conditions, pH = 6.40, $[H_2O_2]_0 = 78.2$ mg/L and $[PBV]_0 = 10$ mg/L

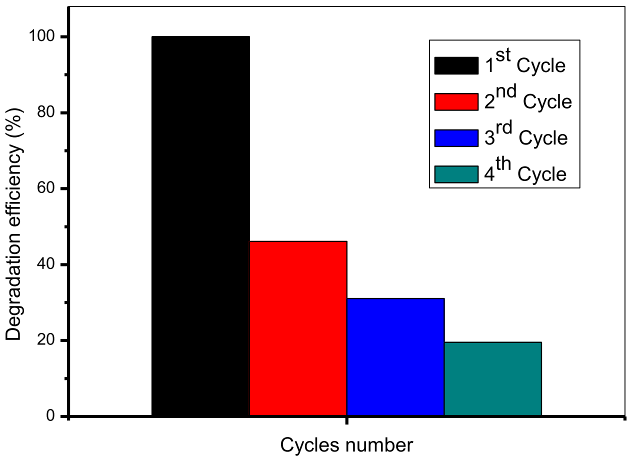

**Fig. 7** Degradation efficiency of PBV over four cycles of reutilization. Reaction conditions, pH (1st cycle) = 6.40, pH (2nd, 3rd and 4th cycles) = 3, $[Fe^{3+}]$ (1st cycle) = 0.98 mg/L, $[Fe^{3+}]_{added}$ (2nd, 3rd and 4th cycles) = 0 mg/L, $[H_2O_2]_0 = 78.2$ mg/L and $[PBV]_0 = 10$ mg/L

Several works report that the $Fe^{3+}$ used in the Fenton system precipitates as $Fe(OH)_3$ at neutral and alkaline medium. Therefore, it decreases the degradation efficiency according to the following equation [24, 26]:

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3 \downarrow \tag{17}$$

Lee and Sedlak [23] report that when the pH is close to the neutral, $Fe^{3+}$ precipitates under its amorphous form, Fe(III)-oxyhydroxides, this complex decomposes the $H_2O_2$ very slowly as a heterogeneous catalyst.

In this work, the efficiency of the Fenton system is clear for the degradation of PBV at pH = 6.4. It can be suggested that the degradation of PBV can be reached by two processes: homogenous system in the presence of $Fe^{3+}$ and heterogeneous process in the presence of $Fe(OH)_3$ species. Additionally, under UV light, $Fe^{3+}$ can be generated according to Eq. (18) [2]:

$$Fe(OH)_3 + h\nu \rightarrow Fe^{3+} + HO^{\cdot} \tag{18}$$

### 3.5 Reuse of Generated Sludge in the Photo-Fenton-Like process

In this study, the reutilization of the catalyst was performed by the reuse of the sludge produced after photo-Fenton-like reaction several times. The degradation efficiency was calculated at the same time of the initial cycle (Fig. 7). The initial catalyst concentration (1st cycle) was 0.98 mg/L, while the concentration of oxidant $H_2O_2$ used at the beginning of each cycle was 78.2 mg/L.

As shown in Fig. 7, the degradation efficiency decreased in the second, third and fourth cycles and became 46, 31 and 19%, respectively. This decrease is mainly due to the decreasing amounts of catalyst available after each cycle, since a certain quantity of $Fe^{3+}$ cannot be recovered by precipitation. Additionally, the degradation products of the pollutant accumulated at each cycle can affect the degradation efficiency. As demonstrated by Gamaralalage et al. [26], the decomposition of $H_2O_2$ can be performed by $Fe^{3+}$ of dissolved sludge and the ferric hydroxide surfaces according to the following reactions:

Homogeneous system

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\cdot} + H^+ \tag{19}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\cdot} + OH^- \tag{20}$$

Heterogenous system

$$\equiv Fe^{3+} - OH + H_2O_2 \rightarrow \equiv Fe^{2+} + H_2O + HO_2^{\cdot} \tag{21}$$

$$\equiv Fe^{2+} + H_2O_2 \rightarrow \equiv Fe^{3+} - OH + HO^{\cdot} \tag{22}$$

### 3.6 Mineralization Study

To get information about the PBV mineralization by the UV/$Fe^{3+}/H_2O_2$ system, sulfates, nitrates and calcium concentrations were determined. These ions are the oxidation products according to Eq. (7) corresponding to the PBV theoretical mineralization. The results obtained are presented in Table 1.

The concentrations of sulfates, nitrates and calcium ions increased from the beginning of irradiation time. Then, it can be noted that the release of $SO_4^{2-}$ became quasi-stationary; this is probably due to the transformation of certain sulfates released into radical ions. These radicals take part in the oxidation reaction. However, the nitrate ions $NO_3^-$ decreased at the end of the reaction. Indeed, only nitrates were monitored, while nitrogen is probably released initially as ammonium

**Table 1** Monitoring of the sulfates, nitrates and calcium concentrations determined during the PBV degradation by photo-Fenton-like process

| Irradiation time (min) | $SO_4^{2-}$ concentrations (mg/L) | $NO_3^-$ concentrations (mg/L) | $Ca^{2+}$ concentrations (mg/L) |
|---|---|---|---|
| 0 | 0 | 0 | 0 |
| 15 | 65.882 | 0.75 | 64.128 |
| 30 | 59.361 | 1.027 | 112.224 |
| 60 | 58.883 | 0.527 | 88.176 |

**Table 2** Kinetics parameters calculated at several catalyst concentrations

| $Fe^{3+}$ concentrations (mg/L) | $k_{app}$ | $t_{1/2}$ | $K_c$ | $R^2$ |
|---|---|---|---|---|
| 0 | 0 | – | 0 | – |
| 0.5 | 0.0043 | 70.0070 | 0.0086 | 0.9929 |
| 0.98 | 0.0226 | 13.3199 | 0.0231 | 0.9969 |
| 1.96 | 0.1323 | 2.2753 | 0.0675 | 0.9451 |
| 4 | 0.1933 | 1.5573 | 0.0483 | 0.9493 |

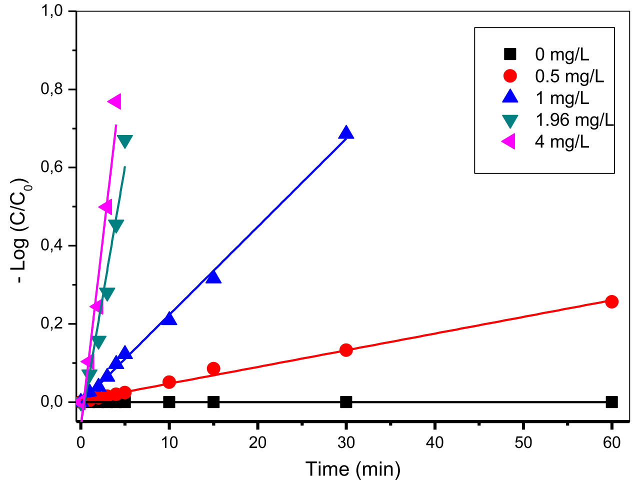

**Fig. 8** Kinetics of the PBV degradation for different catalyst concentrations

ions which oxidize to nitrate ions thereafter [39, 40], as well as the involvement of nitrogen in other forms, such as $NO_2^-$ or of the transformation of $NO_3^-$ into $NO_2^-$. The calcium can be produced by the following reaction:

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca^{2+} + 2HCO_3^- \quad (23)$$

### 3.7 Kinetics Study of the Photo-Fenton-Like Reaction

To determine the kinetic parameters, such as the rate constant, the half-lifetime and the catalytic efficiency for pollutant oxidation, − log C/Co was plotted versus time for the different $Fe^{3+}$ concentrations (Fig. 8). This model was considered by several workers [41, 42]. Table 2 shows the different kinetic parameters values obtained:

As shown in Fig. 8, the PBV degradation by the photo-Fenton-like process follows a pseudo-first-order kinetic law, which was confirmed by the linearization coefficient $R^2$ ($>0.9$). The apparent rate constant values presented in Table 2 increased for increasing catalyst amount, while the half-lifetime decreased very quickly at the beginning of the reaction. This means that significant amounts of pollutant degraded in the first minutes, because the HO˙ has a significant capability to attack organic molecules rapidly [36]. The catalytic efficiency calculated versus the catalyst concentration shows a significant effect until the concentration of 1.96 mg/L, while beyond this amount the value of $K_c$ hardly changes. The increase in the catalyst concentration above the optimum value does not induce a significant increase in the catalytic efficiency, due to the increased formation of complexes $Fe(OH)_3$ and the scavenging effect of $Fe^{3+}$ [31].

## 4 Conclusion

This work attempts to evaluate the Fenton-like process enhanced by UV light using minute Fenton reagent concentrations of 0.98 and 39.1 mg/L for $Fe^{3+}$ and $H_2O_2$, respectively. The main disadvantage of the Fenton reaction is its pH limitation (acidic pH 3), while in this study, high degradation efficiency (100% in 60 min) was obtained at natural pH (6.40) when the process was enhanced by the UV light.

To remedy the generated sludge problem after the Fenton reaction, we have tried to reuse it without any activation in several successive reaction cycles, and the results obtained confirm the possibility of the reuse of this sludge in spite of yield reduction. Thus, it reduces the cost process by reducing the amount of catalyst. This result is of major economic and environmental significance.

The mineralization of the organic pollutant (PBV) was justified by the monitoring of sulfates, nitrates and calcium formation according to the theoretical mineralization equation.

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