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Published by the Faculty of Engineering, Khon Kaen University, Thailand

Degradation of Penicillin G contaminant in synthesized wastewater by Fenton-like reaction

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Received 21 January 2022
Revised 15 May 2022
Accepted 24 May 2022

Abstract

The aim of this research was to investigate the degradation of Penicillin G (PEN G) in synthesized wastewater via a Fenton-like reaction. Calcium dioxide (CaO_2) was used as an oxidant in the Fenton-like reaction. Factors of the PEN G degradation study such as pH, $FeSO_4$, CaO_2, and reaction time were determined using the Box-Behnken design (BBD). The experimental study was conducted in a 500 mL batch reactor, with 150 ppm initial concentration of PEN G. The results showed that PEN G degradation was optimal (38.67%) at pH 3, ferrous dosage of 0.08 g/L, CaO_2 concentration of 1 g/L, and reaction time of 120 min. The degradation took place in the first 20 min. The reaction time was increased up to 120 min to achieve a pH of 8 in the test solution to meet the industrial effluent standard by the Ministry of Industry, Thailand. The kinetic study indicated second order and the pseudo first order reaction for the degradation in 0-20 min and 20-120 min, respectively. The research results indicated that pH, iron dosage, and CaO_2 content-except reaction time-influenced PEN G degradation as predicted by the BBD. The degradation was substantially quick as well. Fenton-like reaction for a high concentration of PEN G should be used as pre-treatment.

Keywords: Antibiotics degradation, Advance oxidation, Penicillin G, Fenton-like reaction

1. Introduction

Pharmaceutical products, if released into the environment, are considered environmental pollutants. While pharmaceutical products are widely used to treat human, animal, and plant diseases [1], the antibiotics in pharmaceutical products, when leaked into the environment, can cause further health problems in humans and animals. β-lactam antibiotics are the most widely used broad class of antibiotics; they inhibit cell wall biosynthesis in bacterial organisms [2]. A β-lactam antibiotic, Penicillin G (PEN G) was the first antibiotic discovered and used for human bacterial diseases [3]. The β-lactam rings in such antibiotics are a cause for concern [4]. Its indiscriminate use led to PEN G-resistant bacteria, which are resistant to several medical treatments [5]. PEN G, if discharged as effluent, can accumulate in environmental receptors such as soil, sediments, surface water, and groundwater and may ultimately enter the food chain [6]. PEN G can damage microbial ecosystems in the aquatic environment and lead to the development of antibiotic-resistant bacteria. [7].

PEN G is not degraded by conventional activated sludge processes [6, 7]. Therefore, a simple and efficient non-microbial method must be developed for the degradation of PEN G-contaminated wastewater. While several physical and chemical processes have been developed, activated carbon adsorption is the one most extensively used in water and wastewater treatment processes [8, 9] and is applied to remove a wide range of pharmaceutical contaminants. However, the extent of removal of β-lactam antibiotics is affected by their low hydrophobicity. Regarding the chemical characteristics of PEN G, it is water-soluble and thus difficult to filter. PEN G is a huge molecular ($C_{16}H_{18}N_2O_4S$) compound, and it is difficult to perform ion exchange. For wastewater treatment, extraction might not be used as conventional treatment process but mostly used for recovering high value metals such as silver, gold, etc. Advance oxidation processes (AOPs), such as ozonation [10] and photolysis [11], are being increasingly applied for industrial wastewater treatment. Ozonation increases the cost of wastewater treatment and photolysis shows low efficiency in antibiotic removal [12]. Fenton and Fenton-like reactions have been reported to cause rapid degradation of β-lactam rings [13]; however, the process requires high oxidant dosage and low pH (typically pH 2-4) to prevent iron precipitation, which can be expensive for large scale treatment. A Fenton-like reaction can be readily prepared by mixing an appropriate heterogeneous catalyst and CaO_2 in an aqueous solution. A heterogeneous catalyst is beneficial because it can be easily separated from the reaction mixture, e.g., filtration. Therefore, the expensive catalysts can

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doi: 10.14456/easr.2022.61

be easily and effectively recovered. In Fenton-like reaction, a hydroxyl radical is formed. Hydroxyl radicals can decompose organic compounds into CO_2 and H_2O [14]. Preliminary investigations indicated that simultaneous usage of several reagents resulted in the most effective degradation of pollutants. Some studies have suggested that CaO_2 is more efficient at releasing hydroxyl radicals (OH^-) than H_2O_2 [14, 15]. Among other reagents that can release OH, CaO_2 was selected owing to its relatively low cost. The release of OH^- from CaO_2 is gradual and occurs only in an acidic aquatic environment [16]. Dissolution of CaO_2 in water to obtain H_2O_2 and $Ca(OH)_2$ takes place according to Eq. (1) [17].

$$CaO_2 + 2H_2O \rightarrow H_2O_2 + Ca(OH)_2 \quad (1)$$

Therefore, it seemed reasonable to carry out this experiment using the reagent of Fenton-like reaction.

The main objective of this study was to determine the degradation efficiency of Fenton-like reaction in PEN G contaminated wastewater. The effects of calcium peroxide as an oxidant in Fenton-like process on PEN G; pH, $FeSO_4$, CaO_2, and reaction time were investigated using Box-Behnken design (BBD).

2. Materials and methods

2.1 Materials and reagents

All the chemicals used were of analytical laboratory grade and included: Penicillin G sodium salt ($C_{16}H_{17}N_2NaO_4S$, 96%) (Sigma-Aldrich), hydrogen peroxide (H_2O_2, 30%) (Sigma-Aldrich), calcium peroxide (CaO_2) (Sigma-Aldrich), ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) (Sigma-Aldrich), hydrochloric acid (HCl) (Lab Scan).

2.2 Study background

Studies on optimum conditions were performed for 2 experimental sets of PEN G degradation via Fenton-like reaction using the Box-Behnken (BBD) technique [18-21].

Pre-study was performed with an initial concentration of 50-100 ppm PEN G, and total degradation rapidly took place in the first five minutes. Hence, 150 (mg/L) of PEN G was used in the study.

2.3 Experimental study

The first experimental set was performed under the following condition: pH (3-7), CaO_2 content (1-5 g/L), and ferrous ion (0.04-0.12 g/L). The initial concentration of 150 ppm PEN G was placed in a batch reactor of 500 mL in volume, and pH was adjusted using HCl and NaOH. Ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$), a source of ferrous iron, and calcium oxide (CaO_2) as oxidant was added to the pH-adjusted solution of PEN G. The reaction was conducted at ambient temperature.

Under the experimental setting, the optimum conditions were determined as follows.

- During the first 20 min of reaction, 5 mL of samples were drawn from the reactor at an interval of 5 min and filtered using 0.45-micron filters. Afterward, the samples were drawn at intervals of 10 min and filtered.
- The experiment was terminated after 150 min when there was no further degradation of PEN G.

The results of the first experimental set indicated that the experimental conditions were optimum as the highest degradation efficiency of PEN G was recorded.

The second experimental set was performed under the pH stated above, under the first optimum pH of the first experimental set, and other influencing factors of the (BBD) technique. The procedure for the second experimental set was the same as that of the first experimental set.

2.4 Analysis of PEN G

High-performance liquid chromatography, (HPLC Hitachi Chromaster-5000, Japan) equipped with a 5C18-Ar-II (250 mm×4.6mm ID, COSMOSIL Packed Column), was conducted to analyze PEN G concentration. The mobile phase was solvent A (30% water) and B (70% methanol) with a constant flow rate of 1.0 mL/min during the 15 min analysis. The peaks of PEN G were detected using a UV detector (Hitachi Chromaster 5420 UV/VIS, Japan) at a wavelength of 230 nm.

3. Results and discussion

In the first set of the experimental study in which the initial pH range was pH 3-7, PEN G solution with an initial pH of 3 had the highest degradation of 39.54% as shown in Figure 1, indicating that a high level of degradation occurs within an acidic range. The degradation time was 20 min and was mostly constant throughout the experimental time for 120 min. An initial concentration of 150 ppm PEN G was used for the degradation experiment as mentioned above for the pre-study. However, degradation at lower concentrations (50-100 ppm) was evaluated. PEN G was completely degraded in the first five minutes, indicating that the degradation was very fast. Hence, Fenton-like reaction for degradation of PEN G is more effective at lower concentrations.

With regard to the kinetic degradation study, two data sets of PEN G degradation, of 0-10 min and 20-120 min, were considered (see Figure 1). The degradation in 0-20 min was a second-order reaction. The rapid degradation that took place within 20 min was dependent on the concentrations of the two reactants (PEN G and CaO_2 as oxidant), which was high at the beginning of the reaction. However, the degradation in 20-120 min was a pseudo first order reaction. This means that if the concentration of one reactant (i.e. PEN G) was higher than the other reactant (i.e. CaO_2), the transformation of the higher reactant (PEN G) would be very low. The degradation of PEN G was almost constant for 20-120 min but terminated at pH 8.

The second experimental set was performed at a pH range of 2-4 for degradation of PEN G, as presented in Table 1, to find the optimum pH and dosage of CaO_2 (g/L), quantity of iron in solution (g/L), and reaction time (min.).

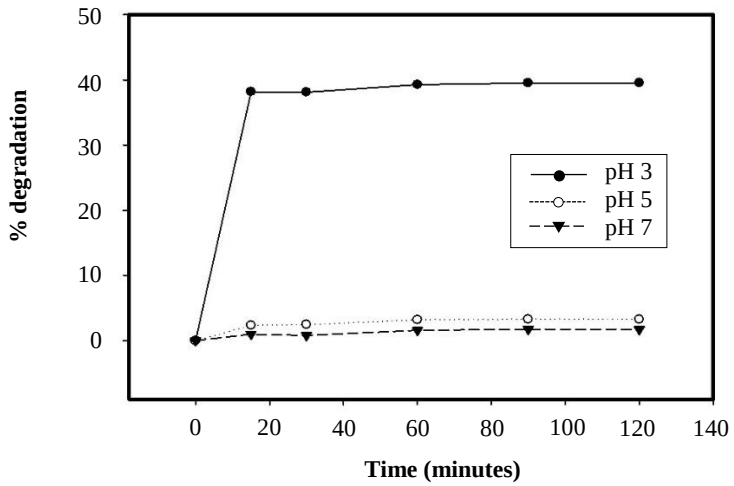


Figure 1 Influence of pH on Penicillin G degradation (CaO_2 dosage 1.15 g/L, ferrous dosage 0.08 g/L, PEN G concentration 150 ppm)

3.1 Influence of pH on Penicillin G degradation

The main effect on PEN G degradation is presented in Table 2. Effects of pH, CaO_2 content, ferrous dosage, and reaction time on degradation of PEN G are presented in Figure 2. The factors in this study include pH, CaO_2 content, ferrous dosage, and reaction time and were designed using BBD. The experimental values of the factors were inputted to BBD to obtain the regression equation presented in Eq. (2). With regard to the optimum condition of PEN G degradation, results showed that the pH ranged from 2 to 3. Precipitation of $Fe(OH)_3$ and decomposition of H_2O_2 caused the pH to increase, hence decreasing PEN G degradation. At low pH, oxinium ions were formed by proton solvation of H_2O_2, causing the continuation of the reaction until pH increased to the value of 8.

Table 1 Experimental design of degradation of PEN G using Box-Behnken Design (BBD)

No.	Initial pH	CaO_2 Dosage (g/L)	Ferrous dosage (g/L)	Time (Minute)	% Degradation
1	2	1	0.08	75	36.89
2	4	1	0.08	75	21.71
3	2	5	0.08	75	32.36
4	4	5	0.08	75	11.74
5	3	3	0.04	30	7.65
6	3	3	0.12	30	21.82
7	3	3	0.04	120	8.20
8	3	3	0.12	120	22.57
9	2	3	0.08	30	32.44
10	4	3	0.08	30	11.18
11	2	3	0.08	120	33.89
12	4	3	0.08	120	13.70
13	3	1	0.04	75	13.99
14	3	5	0.04	75	9.95
15	3	1	0.12	75	32.93
16	3	5	0.12	75	18.27
17	2	3	0.04	75	20.54
18	4	3	0.04	75	7.03
19	2	3	0.12	75	36.79
20	4	3	0.12	75	16.32
21	3	1	0.08	30	37.09
22	3	5	0.08	30	25.22
23	3	1	0.08	120	38.67
24	3	5	0.08	120	28.21
25	3	3	0.08	75	36.96
26	3	3	0.08	75	37.61
27	3	3	0.08	75	36.74

The function of CaO_2 addition was to generate H_2O_2; however, excessive production of H_2O_2 decreased PEN G degradation because OH, which is produced by excessive H_2O_2, could recombine itself or react with H_2O_2 at the same time. In addition, the high content of ferrous ions, which causes OH to increase, increased the degradation of PEN G. However, an excessive number of ferrous ions reduced PEN G degradation because ferrous ions react with OH, which are the products of Fenton reaction. PEN G degradation was also observed to vary with reaction time as shown in Figure 2. Different degradation within the reaction time 0-20 and 20-120 min are presented. Degradation occurred rapidly in the first few minutes, and the pH was stable during the first 10 min (pH=2). The degradation was then maintained at maximum during 20-120 min. PEN G degradation depended largely on the pH of the solution, and the most suitable range of pH was 2-3. The concentrations of iron and hydrogen peroxide were not monitored during the experiments. The degradation rate was mostly constant from 20 min to 120 min, implying that iron concentration was almost stable.

Table 2 Main effect of Penicillin G degradation

Variable	Symbol	Coefficient	P-Value
Constant		37.10	0.000
pH	A	-9.27	0.000
[CaO_2]	B	-4.63	0.002
[Fe]	C	6.78	0.000
Time	D	0.82	0.488
pH*pH	A^2	-6.69	0.002
[CaO_2]*[CaO_2]	B^2	-2.64	0.151
[Fe]*[Fe]	C^2	-14.01	0.000
Time*Time	D^2	-5.94	0.005
pH*[CaO_2]	AB	-1.36	0.507
pH*[Fe]	AC	-1.74	0.398
pH*Time	AD	0.27	0.894
[CaO_2]*[Fe]	BC	-2.65	0.206
[CaO_2]*Time	BD	0.35	0.862
[Fe]*Time	CD	0.05	0.981

$$\text{Percent of Penicillin G degradation} = 9.27 - 34.76A - 4.63B + 6.78C + 0.82D - 5.81A^2 - 13.13C^2 - 5.06D^2 \quad (2)$$

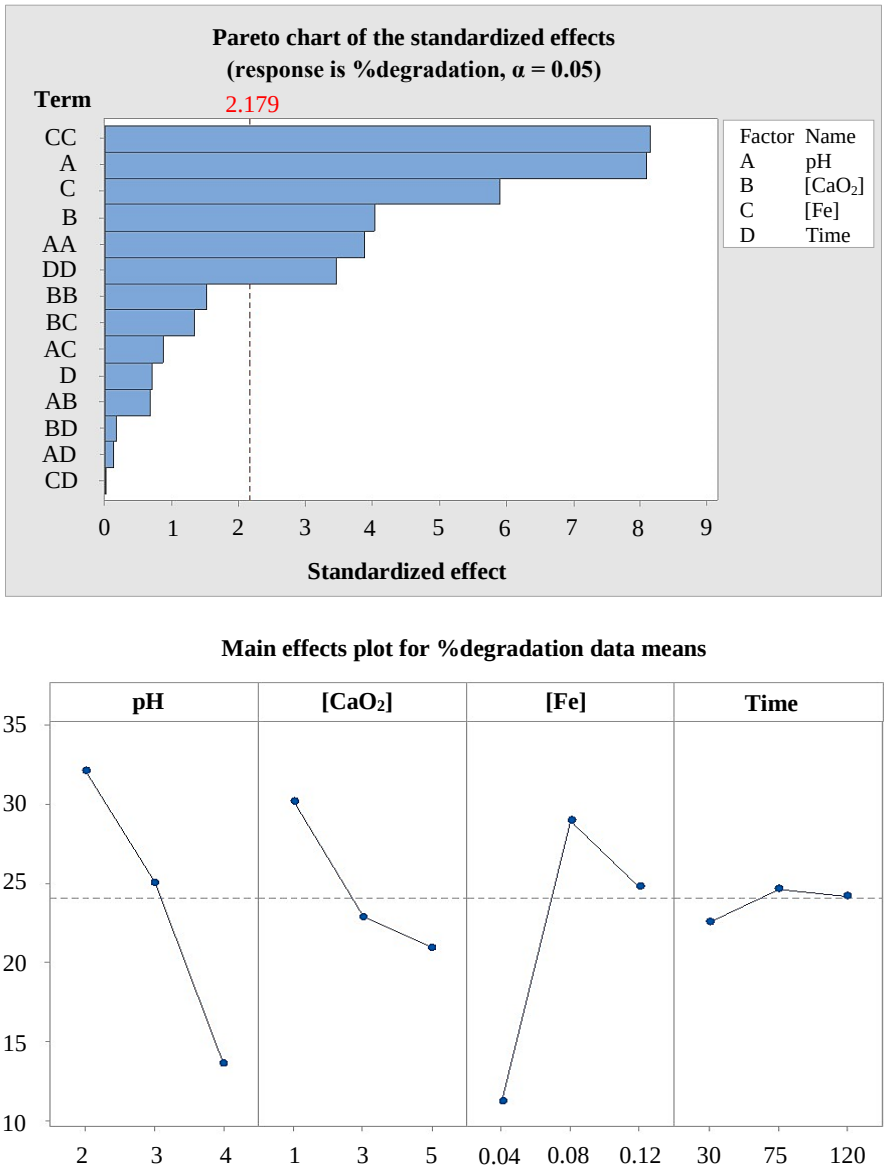


Figure 2 Effect of pH, CaO_2 content, ferrous dosage, and reaction time on degradation of PEN G

To determine the accuracy and reliability of the equation, a normal probability plot was created and is presented in Figure 3. The plot is a straight line, indicating that the experimental data were normal with an R^2=91.43%.

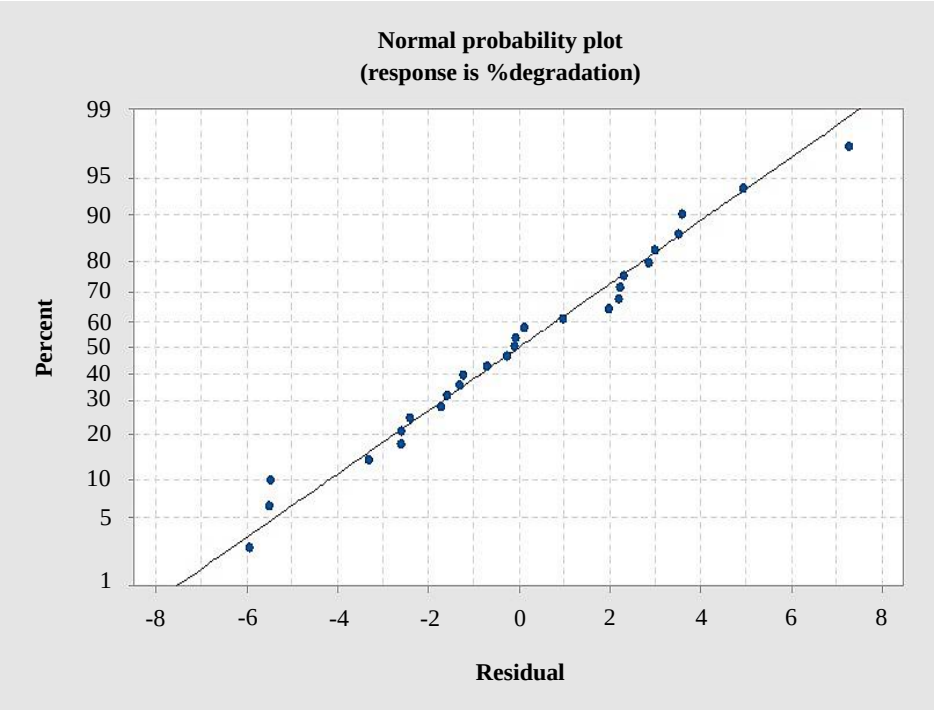


Figure 3 Normal probability plot

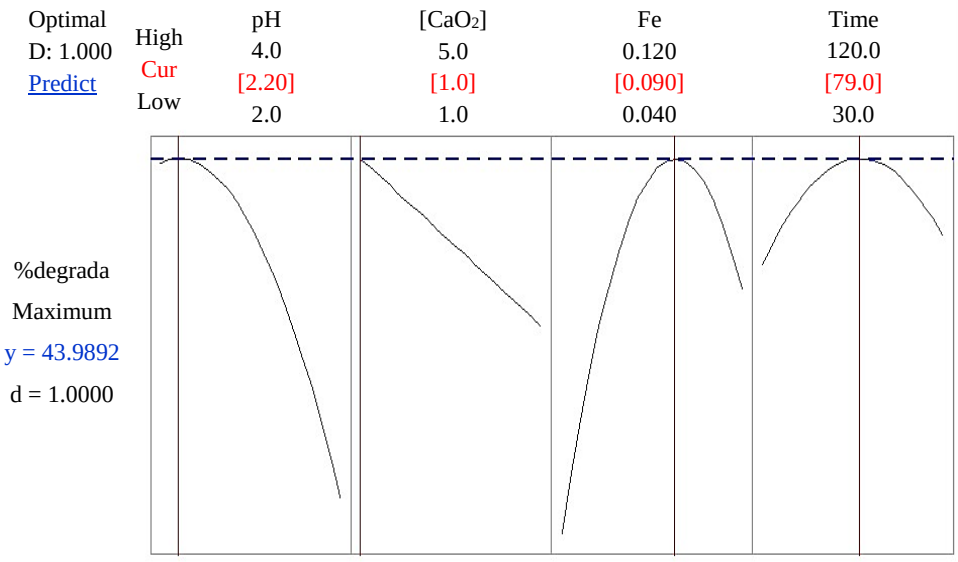


Figure 4 Interaction effect for Penicillin G degradation

The interaction effect of the degradation was observed until there was no further degradation of PEN G. The factors of this PEN G degradation study were designed using BBD as shown in Figure 4. The interactions between CaO_2 content and Fe dosage, pH and Fe dosage, and pH and CaO_2 content were verified to be significant as shown in Figure 5. The generation of H_2O_2 from CaO_2 with Fe ion in the solution follows Eq. (3)-(7) [22-24].

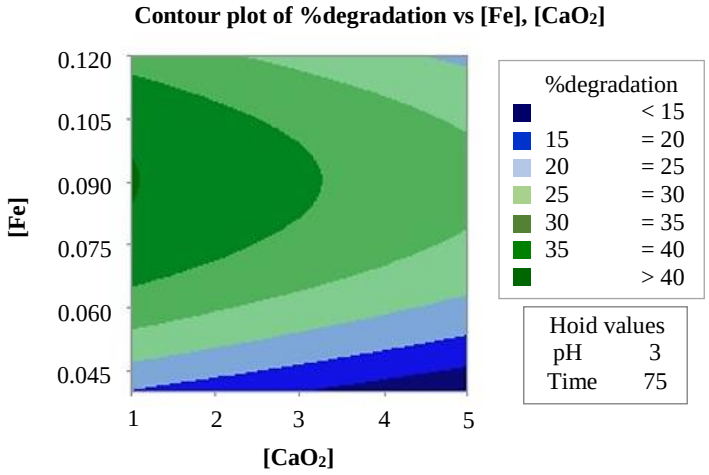
$$CaO_2 + 2H_2O \longrightarrow +2H_2O_2 + Ca(OH)_2 \quad (3)$$

$$2H_2O_2 \longrightarrow 2H_2O + O_2 \quad (4)$$

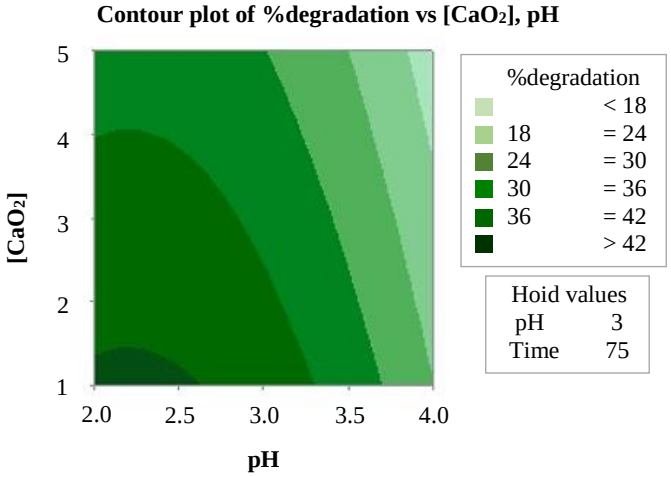
$$2H_2O_2 + H^+ \longrightarrow H_3O_2^+ \quad (5)$$

$$HO^\bullet + H_2O_2 \longrightarrow H_2O + HO_2^\bullet \quad (6)$$

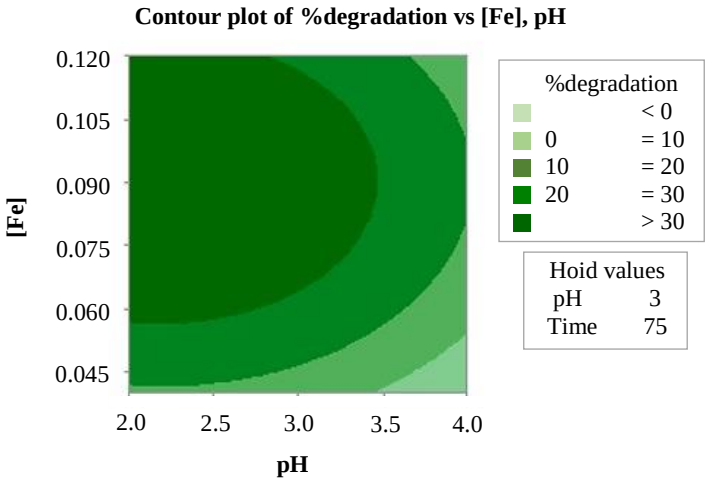
$$HO^\bullet + HO^\bullet \longrightarrow H_2O_2 \quad (7)$$



(a)



(b)



(c)

Figure 5 Penicillin G degradation contour plot

The optimum condition for PEN G degradation based on BBD design was predicted as: pH 2.2, 1 g/L of CaO_2 content, 0.09 g/L of ferrous dosage, and 79 min; the PEN G degradation was 43.99%. The mean of three experiments at those optimal conditions revealed 41.91% of PEN G degradation with an error of 4.73%. The optimal conditions for PEN G degradation (38.67%) in this study were as follows: pH 3, ferrous content of 0.08 g/L, and CaO_2 content of 1 g/L. When the pH of the synthesized wastewater increased to the value of 8, the reaction terminated. The treated wastewater or effluent could be discharged to the receiving water source at that pH because it is within the industrial effluent standard designated by the Ministry of Industry, Thailand.

3.2 Degradation of Penicillin G by different reactants

The use of CaO_2 as the reactant in Fenton-like reaction and the direct use of H_2O_2 in the degradation of PEN G were compared. PEN G degradation via the direct use of H_2O_2 was 80.53%, but 38.76% via the use of CaO_2, indicating that the use of CaO_2 seemed inferior to the direct use of H_2O_2. Under the Fenton-like reaction, pH increased during degradation up to pH 8 at 120 min reaction time; the increasing pH resulted in a lower degradation efficiency. However, when directly using H_2O_2, H_2O_2 must continually be replenished, whereas in the Fenton-like reaction, CaO_2 is added to the solution only once at the beginning owing to its ability to maintain its oxidation capacity for a relatively long time. Another advantage of CaO_2 is its availability and low cost. Furthermore, the reaction product which is calcium hydroxide in solid phase can easily be removed compared with the hydrogen peroxide in liquid form.

In addition, the combined processes seemed to be the best solution for the treatment of wastewater containing antibiotics. The utilization of CaO_2 as an oxidant enabled the reaction to take place in a wider pH range until the pH value got to 8. Although the use of H_2O_2 as an oxidant in the Fenton reaction resulted in better degradation of PEN G, the reaction required a pH 2-3; thus, further treatment of the effluent to adjust the pH to meet the industrial effluent standard is needed, for example, the separation of $Fe(OH)_2$ prior to discharge to the environment. The efficiency of Fenton-like reaction for PEN G degradation was low, but the reaction was very fast; hence, it should be used for pre-treatment. The effluent for pre-treatment can be further treated via the Fenton-like reaction because the rapid degradation of the low concentration of PEN G takes place in the first 5 min as stated in the pre-study. The degradation of PEN G using Fenton-like reaction consist of the first reactor for the high concentration of PEN G followed by the second reactor for the low concentration of PEN G; however, further research study is required.

4. Conclusions

The degradation of PEN G via the Fenton-like reaction was investigated in this study. The factors in the study included pH, CaO_2 content, Fe dosage, and reaction time. The effects of these factors on PEN G degradation were determined and analyzed using the Box-Behnken design (BBD). Results showed that the reaction time was not significant owing to the rapid Fenton-like reaction, which caused most of the degradation in the first 5 min. The interaction effects between CaO_2 content and Fe dosage, pH and CaO_2 content, and pH and Fe dosage on the degradation of PEN G were significant. The experimental results revealed that the optimal conditions were pH 2.2, 1 g/L of CaO_2 content, 0.09 g/L of Fe dosage, and 79 min, and the degradation of PEN G under these conditions was 41.91% and the leaching of iron was below 0.4 mg/L. However, at pH 2.2, the effluent cannot be discharged to the water source. Therefore, it is recommended that optimal conditions, such as pH 3, 0.8g/L of ferrous dosage, and CaO_2 of 1 g/L, be adopted because the pH of the effluent under these conditions was 8, which meets the industrial effluent standard, designed by the Ministry of Industry, Thailand and can be discharged to the water source. Under the same reaction condition, the price of CaO_2 (1.15 g) was 1.5 Bahts (or 0.05 US $) per experiment, whereas that of H_2O_2 (4 mL) was 5.7 Bahts (0.19 US$) per experiment.

5. Acknowledgements

The authors wish to acknowledge the Department of Chemical Engineering, Faculty of Engineering, Khon Kaen University for the financial support for this research. The authors are also grateful for the Project, the Establishment of the Faculty of Engineering at Chaiyaphum Rajabhat University, and for granting leave of absence to Wiparat Nisapai to pursue a Ph.D study. In addition, the authors are grateful for the invaluable supports in terms of facilities and scientific equipments.

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