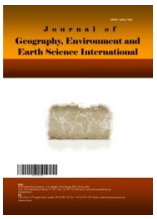

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Multi-way Degradation and Process Optimization of Phenol from Simulated Wastewater System

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Authors' contributions

This work was carried out in collaboration between all authors. Authors PMK and SPB designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors SNP managed the analyses of the study. Author NDW managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

This research was based on the comparative study between microbial, enzymatic and photocatalytic phenol degradation. Different experiments were carried out under three distinct methodologies that seeked to examine which method is more feasible between them through various aspects. For the microbial study, *E. coli* was used for phenol degradation at an optimum condition of *E. coli*. In the enzymatic study, peroxidase was extracted from soybean seed hulls, and it was purified. The purified peroxidase enzyme was applied in phenolic solution at neutral pH. The H_2O_2/UV/TiO_2 scheme was adopted in the photocatalytic treatment of phenol. Maximum phenol degradation was observed in photo catalysis. From this comparative study, a microbial method was found to be more time consuming and an enzymatic method require more steps to perform the experiment while photo catalysis took less time with a more feasible results.

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Keywords: Comparative study; microbial treatment; enzymatic treatment; photocatalytic treatment; first-order reaction kinetics.

1. INTRODUCTION

Recently, considerable attention has been received by many researchers on biodegradation of aromatic compounds due to their toxicity. Among them, phenol and its derivatives are a standard compound in wastewater of many industries such as oil refineries [1], coal refining, petroleum, textiles and pharmaceuticals [2]. It is quite known that the toxicity of phenols towards the whole environment is high and thus has been incorporated in the list of pollutants by the U.S. Environmental Protection Agency [3]. Many researchers are engaged in research on phenol degradation by diverse techniques and methods. The attention is that to investigate which technology will be most feasible, eco-friendly, cost-effective and time saving is the primary goal of the present investigation. The present study compares three methods viz. microbial degradation, enzymatic degradation and photocatalytic degradation.

Until today, many investigators have reported numerous types of microorganisms that remove phenol from wastewater. From the literature reviewed, some microorganisms can consume phenol as a sole source of carbon and energy. These bacterial species include *Streptococcus epidermis* [4], *Escherichia coli, Micrococcus sp., Brucella sp.* [5], *Bacillus subtilis*, *Pseudomonas putida, Acinetobacter calcoaceticus, Bacillus subtilis* [6-8] and *Streptococcus sp.* [8].

Besides, enzymes are applied in biodegradation study of the phenol. Enzymes play a vital role in phenol biodegradation reactions as a biocatalyst [9]. These enzymes include Peroxidase, Chloroperoxidase, Lignin peroxidase, Mn-peroxidase [9] and catalase [10] that isolated from specific plants viz. soybean [11], horseradish, radish [12], and their materials such as seeds [13], leaves [14], stem [15], roots [16]. Tyrosinase and Laccase [9] are obtained from different fungal species.

In recent years, photocatalysis has been developed in wastewater treatment. In this technique, some photocatalysts and their chemically modified transformations were employed for the photodegradation of toxic compounds. The TiO_2 and ZnO were broadly tested as photocatalyst used in this technique [17-20]. Many researchers increase the efficiency of a catalyst by doping with metals such as Ag, Fe, Pr, Co, V under various illumination systems [21]. Some researchers synthesized bimetallic or trimetallic transformations for degradation study [22].

Here, we focus on all related aspects or parameters to select a better, efficient, cost-effective and feasible degradation technique. From the overall primary study, we use *E. coli* for the microbial study while peroxidase extracted from soybean seed hulls and selected for the further process of phenol degradation. Alike we introduced single TiO_2 nanoparticles in phenolic wastewater under both UV and Solar light.

2. MATERIALS AND METHODS

2.1 Materials

All analytical grade and HPLC grade chemicals were purchased from Fisher scientific and Himedia, Mumbai, India. Milli-Q water used for chemical preparations obtained from Milli-Q make of Schimadzu, Japan. *E. coli* microbial culture was used for the study. Soybean seeds were collected from agricultural fields and washed thoroughly with distilled water.

2.2 Microbial Methodology

E. coli bacterial culture was grown on slants of nutrient agar medium for further microbial phenol degradation study and stored at 4°C until further use. Then the minimal salt medium was prepared as (g/L) Na_2HPO_4 33.9, KH_2PO_4 15, NH_4Cl 5, NaCl 2.5, 2 ml of $MgSO_4$ 0.1 M and 0.1 ml of $CaCl_2$ 1 M per liter for actual degrading study [4]. Four consecutive same interval different concentrations of phenolic wastewater were prepared in the range between 250 mg/L to 1000 mg/L in phosphate buffer with pH 7.0. The reaction mixture containing only MSM media and phenol that was used as a control mixture in the microbial study. Similarly, bacterial inoculum was added to the control mixture for further phenol degradation study. Experiments were carried out in a 250 ml conical flask containing 50 ml of MSM media with phenol concentration of above-given range. The mixture was incubated at room temperature (37°C ± 2) on the shaker (100 rpm). Samples were collected and tested at every 24 h time interval for five days.

The samples were centrifuged, and the remaining phenol concentration determined quantitatively by direct UV-visible spectrophotometric method [23]. Optical density was measured at λ_{max} = 269 nm. Remaining concentration of phenol (%) was calculated using following formula:

$$\%\ Phenol\ degradation = \frac{Absorbance\ of\ sample}{Slope\ phenol\ degradation\ (by\ graph)} \quad (1)$$

2.3 Enzymatic Methodology

The experimental procedures of SBP extraction and purification followed with some modifications reported by Liu et al. [24]. The fresh soybean seed hulls was weighed and washed with milli-Q water. These cleaned seeds were soaked in milli-Q water overnight. The soaked seeds were smashed and blended with 500 ml milli-Q water for 10 to 15 min. Then the homogenized mixture was filtered through cheesecloth and after that filtrate of cheesecloth centrifuged at 10,000 rpm for 20 min at 4°C. The collected supernatant was rich in proteins.

The SBP purification process was performed as reported in Liu et al. [24]. The process included three steps. The first step was acetone-ammonium sulphate cooperation precipitation. It comprised both acetone and ammonium sulphate precipitation simultaneously. The volume of acetone taken 0.3 fold of the original amount and solid ammonium sulphate added to form up to 45% saturation. This combination was placed in a refrigerator for 2 h. After that, the mixture was centrifuged for 15 min at 5000 to 7000 rpm. The supernatant and precipitant were collected separately. This 45% saturation was continued to 75% saturation by adding solid ammonium sulphate again with 0.3 fold acetone in the supernatant. The mixture was centrifuged for 15 min at 5000 to 7000 rpm. Only one condition followed that the acetone was pre-stored in a refrigerator and that cooled acetone was added under a cold atmosphere in all our experimental sets. The resulted precipitants were dissolved in milli-Q water to get primary purified SBP. The second step consisted of acetone precipitation alone. The volume of acetone mixed as 1.4 fold separately into the primary purified SBP. The mixture was centrifuged for 15 min at 5000 to 7000 rpm. The resulted precipitant was dissolved in milli-Q water to get secondary purified SBP. The third step included only zinc sulphate precipitation. Before introducing zinc sulphate into the enzyme solutions, the pH was adjusted to eight by HCl or NaOH and then 1.0 mol L^{-1} zinc sulphate solution was mixed to form 0.015 mol/l zinc concentration. The mixture was centrifuged for 15 min at 5000 to 7000 rpm. Lastly, the supernatant was collected and denoted as highly purified SBP enzyme solution [24].

Enzyme assay and protein content were examined after each purification step by the procedures described by Kolhe et al. 2015 [13]. The Reinheitszahl (RZ) values were assayed after each purification steps. The purified SBP stored at 4°C untill the further use of the enzyme. Different concentrations of phenolic wastewater were prepared in the range between 250 mg/L to 1000 mg/L in phosphate buffer with pH 7.0. The reaction mixture contained 50 ml phenolic wastewater, 30 per cent H_2O_2 and enzyme solution. Analyze the initial phenol concentration. The sample was collected after every 1h to examine the residual phenol.

The remaining phenol concentration of each sample was determined quantitatively by the direct UV-visible spectrophotometric method at phenol λ_{max}. The remaining concentration of phenol (%) was calculated by formula 1.

2.4 Photocatalytic Methodology

The third methodology opted for photocatalytic degradation of phenol. In this study, TiO_2 nanoparticles were used as the photocatalyst while 11 watts of UV lamp was used as illumination for energy. Various concentrations of phenolic wastewater were prepared in the range between 250 mg/L to 1000 mg/L. The pH range kept as 2, 4, 6, 8 and 10 and adjusted with 0.1 M HCl and 0.1 M NaOH solutions. The retention time was 10 h, but samples were collected at every 1h time interval. The reaction mixture contained 50 ml phenolic solution, 30% H_2O_2 and TiO_2 nanoparticles. Analyze the initial phenol concentration. The sample was collected after every 1h to examine the residual phenol.

The remaining phenol concentration of each sample was determined quantitatively by the direct UV-visible spectrophotometric method at phenol λ_{max}. The residual concentration of phenol (%) was calculated by formula 1. The first and second order kinetics study were evaluated from graphs of log concentration versus irradiation time [25].

3. RESULTS AND DISCUSSION

3.1 Microbial Treatment

The phenol degradation performance of *E. coli* strain was examined for different phenol concentrations viz. 250 mg/L, 500 mg/L, 750 mg/L and 1000 mg/L at various time intervals. The per cent phenol degradation was derived based on residual phenol concentration. Fig. 1 shows the effect of phenol concentration indicating that 60.07% phenol degradation was observed at 250 mg/L phenolic concentration at neutral pH after 96 h. As the phenolic concentration increases the phenol degradation decreases. Hence, only 11.75% phenol degradation was observed at 1000 mg/L phenolic concentration at neutral pH after 96 h. Reshma et al. 2014 also used *E. coli* treatment on phenolic wastewater. They obtained 100% phenol degradation for 10 mg/L phenolic solution. We had only 60.07% phenol degradation because 250 mg/L concentration was much more than 10 mg/L concentration. Some bacterial strain may have died at this high phenolic concentration; hence, the *E. coli* bacterial strain did not achieved 100% phenol degradation.

3.2 Enzymatic Treatment

The SBP was extracted from soybean seed hulls by blending it for 10 to 15 min. During the blending of soybean seed hulls, the blended material was lightly warmed, but this was not essential because the SBP activity persisted up to 75°C [11]. A volume of the original enzyme solution was recorded as 530 ml. Table 1 shows the enzyme purification steps and their characteristics. A product of the last purification step having 71.01% recovery and 1.12 RZ value which is near about 1.32 RZ value reported in Liu et al. [24]. This enzyme purification method is more comfortable and cost-effective than other purification methods because it is merely based on only precipitation technique. Total volume, total activity, % recovery, protein content, specific activity, fold purification and RZ value for each step are shown in Table 1.

This purified SBP was introduced in various phenol concentrations viz. 250 mg/L, 500 mg/L, 750 mg/L and 1000 mg/L at various time intervals to evaluate the phenol degradation. The per cent phenol degradation was determined based on residual phenol concentration. Fig. 2 on effects of phenol concentration shows that 62.31% phenol degradation was obtained in 250 mg/L phenolic concentration at neutral pH after 8 h. As in microbial treatment, here also it was observed that as phenol concentration increases the phenol degradation decreases. Hence, only 21.82% phenol degradation was observed in 1000 mg/L phenolic concentration at neutral pH after 8 h but this 21.82% phenol degradation is more as compared to microbial treatment. Pradeep et al. [12] also gave a treatment of SBP on phenolic wastewater. They obtained 72% phenol degradation of 100 mg/L phenolic solution. We had 62.31% phenol degradation in 250 mg/L concentration, which was more.

Table 1. Purification steps and their characterization of SBP

Steps	Total volume (ml)	Total activity (U/ml)	Recovery (%)	Protein content (mg/ml)	Specific activity (U/mg)	Fold purification	RZ value
Original enzyme solution	530	6.091	100	2.325	2.62	1	0.19
Acetone-ammonium sulphate cooperation precipitation	100	5.451	89.49	0.847	6.44	2.46	0.47
Acetone precipitation	10	4.847	79.58	0.461	10.51	4.01	0.83
Zinc sulphate precipitation	10	4.325	71.01	0.257	16.83	6.42	1.12

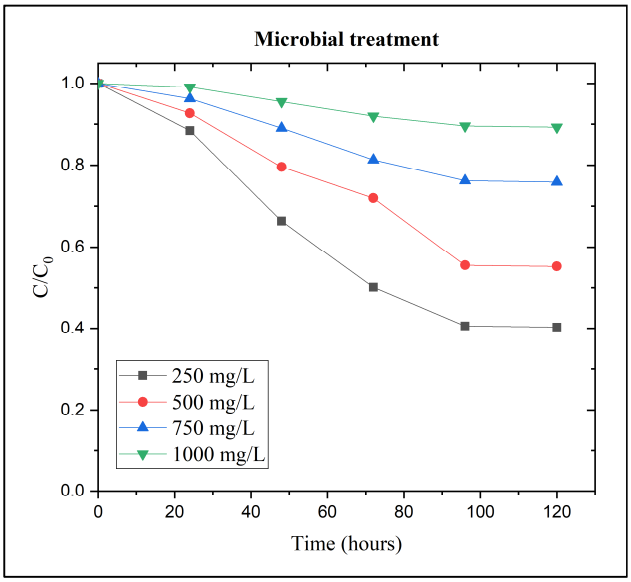

Fig. 1. Phenol degradation by microbial treatment for different concentration of the phenol

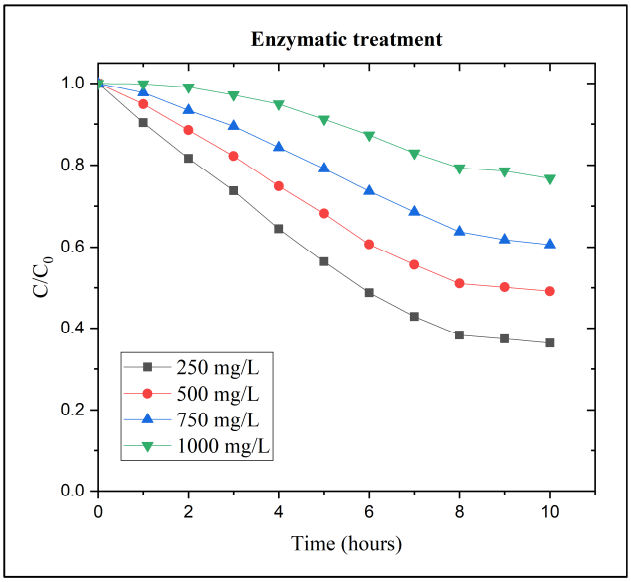

Fig. 2. Phenol degradation by enzymatic treatment for different concentration of the phenol

3.3 Photocatalytic Treatment

3.3.1 Effect of pH condition

Some properties of photocatalysts are highly pH dependent. Hence phenol degradation at different pH was carried out under UV light. In this treatment, TiO_2 nanoparticles were used as a photocatalyst. These nanoparticles were introduced at different pH (2-10) conditions to examine the phenol degradation. It is clearly seen that in Fig. 3, the basic conditions are unfavorable while acidic conditions are favorable for the photocatalytic degradation of phenol. In acidic medium, from pH 2 to pH 6 phenol degradation increases and after pH 6 it decreases. The higher phenol degradation was observed with 63.08% at pH 6. The optimal pH condition was found to be acidic.

Phenol has a pKa value of 9.95 and can be charged positively or negatively under the pH

range studied; i.e., the attraction and interaction between both photocatalyst and phenol will be diverse with the solution pH. Moreover, as the pKa value of phenol is 9.95, it has negative charge above pH 9.95 ≈ 10 and referred as phenolate anions but the conversion of phenolate anions commences when solution pH in between 6 to 8 [26]. Conversely, in highly acidic condition phenol gets a positive charge while in weak acidic and neutral condition phenol molecules exist primarily in their non-ionic form. Additionally, the maximum $OH^{\bullet}$ radicals are produced in the pH range of 6 to 7 [27], due to this reason rate of phenol degradation is higher in this pH range. These hydroxyl radicals are formed from some photocatalytic oxidative and reductive reactions. They have a capacity to directly break down an aromatic ring of phenol molecule and transmute them into the final products which are CO_2 and H_2O through various intermediates, because they are extremely strong, non-selective oxidants [28].

3.3.2 Effect of catalyst load

To examine the effect of TiO_2 nanocatalyst dosing on the phenol degradation, several experiments were carried out at catalyst loading from 1 to 4 g/L with 250 mg/L pollutant concentration. Fig. 3 indicates that the increase in the amount of nanocatalyst loading also increases the rate of phenol degradation up to a particular catalyst dose of 3 g/L. This increased rate of degradation may be due to the higher surface area. Nevertheless, after 3 g/L amount of catalyst loading the degradation rate starts declining. As the catalyst load increases, the experimental solution becomes turbid and resulting in UV rays getting scattered leading to a decrease in reaction rate [29]. The maximum phenol degradation at 3 g/L of catalysts dose was considered as an optimum condition for further study.

3.3.3 Effect of H_2O_2 and TiO_2 ratio

An oxidizing agent is another aspect of the photocatalytic oxidation process. Other experimental sets were performed for the study of the impact of various rates between H_2O_2 and catalyst load as 2:1, 1:1 and 1:2. Fig. 4 shows that a maximum phenol degradation was recorded at 1:2 ratio. It happens obviously because half the quantity of H_2O_2 as on catalyst dose was enough for phenol degradation. The H_2O_2 used only an oxidizing agent in a reaction medium. There is no use of a double quantity of H_2O_2 in the reaction mixture. Because in an excess amount of H_2O_2 reacts with those hydroxyl radicals which are responsible for degrading the pollutant molecule [30]. While the same quantities of H_2O_2 and catalyst load, also not well for the degradation because there is no sufficient amount of catalyst in the mixture. This phenomenon was reported earlier in 2001 by Ghaly et al. [30]

3.3.4 Effect of phenol concentration

TiO_2 nanoparticles applied in various phenol concentrations viz. 250 mg/L, 500 mg/L, 750 mg/L and 1000 mg/L at various time intervals to evaluate the phenol degradation. The per cent phenol degradation was determined based on residual phenol concentration. As initial phenol concentration increases, the rate of phenol degradation decreases from 250 mg/L to 1000 mg/L. This happens due to the competitive adsorption on the active sites of photocatalyst between the hydroxide radicals and phenol molecules [31]. Fig. 4 on effect of phenol concentration shows that 68.39% phenol degradation obtained in 250 mg/L phenolic concentration at neutral pH after 8 h. As in microbial treatment, here also seen that the phenolic concentration increases the phenol degradation decreases. Hence, only 28.46 % phenol degradation observed in 1000 mg/L phenolic concentration at neutral pH after 8 h, but this 28.46% phenol degradation is more than in microbial treatment. Pradeep et al. [12] also gave a treatment of SBP on phenolic wastewater. They obtained 72% phenol degradation of 100 mg/L phenolic solution. We had 68.39% phenol degradation in 250 mg/L concentration, which was more.

3.3.5 Degradation rate kinetics

The kinetic study of photodegradation of phenol was investigated for UV/H_2O_2/TiO_2 system. A model with a higher value of correlation coefficient (R^2) considered as more applicable. The equation for first and second order kinetics is shown below.

First order reaction kinetics: $\log(qe - qt) = \log qe - Kf 2.303t$ (2)

Second order reaction kinetics: $\left(\frac{t}{qt}\right) = \left(\frac{1}{Ksqe^2}\right) + \left(\frac{1}{qe}\right)t$ (3)

Where q_e and q_t are the amounts of phenol degradation (mg g^{-1}) at equilibrium time and at

time t (min), respectively. K_f is the rate constant of first-order reaction (min^{-1}) which can be obtained from the slope of log (qe-qt) versus time plot. Also, a rate constant of pseudo-second-order K_s reaction (g mg^{-1} min) can be obtained from t/qt versus t plot. For the phenol, first-order reaction kinetic was fitted than second-order reaction kinetics first order having a maximum value of R^2. Besides the apparent first-order rate constants decreased with the increase of initial phenol concentrations [32]. Hence, kinetic constant based on phenol degradation by UV calculated for a first-order reaction. Table 2 shows a description of first-order reaction kinetics.

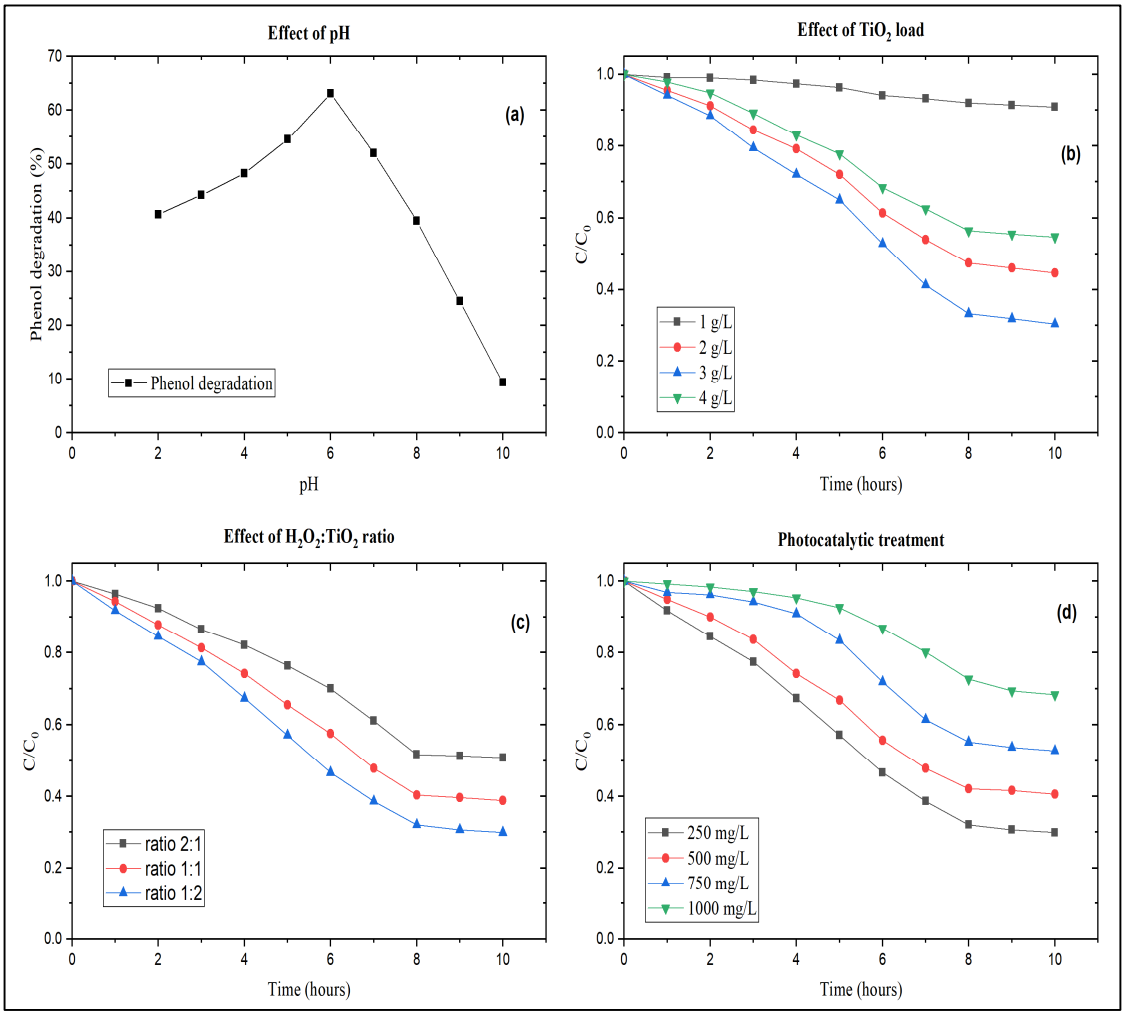

Fig. 3. (a) Phenol degradation at various pH conditions, (b) Effect of TiO_2 nanoparticles loading on phenol degradation, (c) Effect of H_2O_2:TiO_2 nanoparticle ratio on phenol degradation and (d) Effect of different phenolic concentration on phenol degradation under UV light

Table 2. Description of first-order reaction kinetics

Substrate	Concentration (mg/L)	K (min^{-1})	R^2
Phenol	250	0.0953	0.9838
	500	0.0555	0.9793
	750	0.0088	0.8960
	1000	0.0067	0.8546

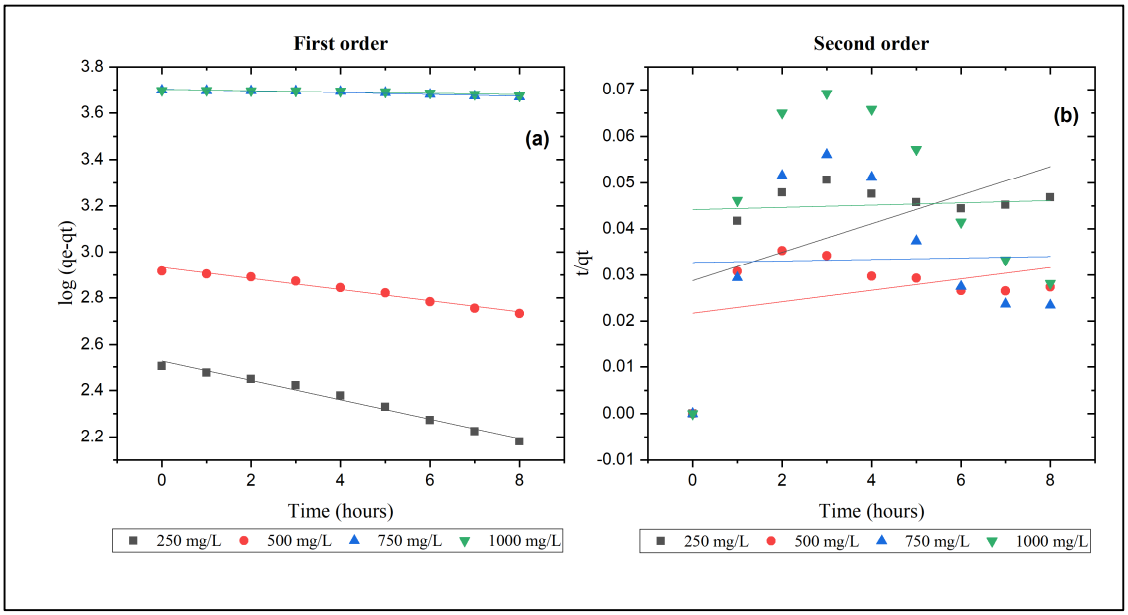

Fig. 4. Phenol degradation corresponds to the (a) first-order and (b) second-order model for 250, mg/L, 500 mg/L, 750 mg/L and 1000 mg/L

4. CONCLUSION

This study adopted three methodologies which were microbial, enzymatic and photocatalytic treatments of phenol for the degradation. Microbial treatment gave 60.07%, enzymatic treatment gives 62.31%, and photocatalytic treatment gives 68.39% phenol degradation in 250 g/L phenolic concentration. All treatments gave approximately the same phenol degradation, but each treatment has some advantages as well as some disadvantages. About 60.07% phenol degradation achieved under 96 h in microbial treatment whereas 62.31% and 68.39% phenol degradation takes place under 8 h in enzymatic and photocatalytic treatment. Based on the time parameter, microbial treatment is a very time-consuming method for phenol degradation while the other methods are less time-consuming.

In enzymatic treatment, additional one-step is required for phenol degradation. That step was enzyme purification. Enzyme purification method was adopted in this study, and that the purified enzyme used as a catalyst. An enzymatic treatment did not show significant phenol degradation even after purified enzyme was introduced in the reaction mixture. In phenol degradation follow another one-step and degrade the phenol which is not much more. Therefore, this enzymatic treatment is not a feasible method for phenol degradation.

A remaining method is a photocatalytic degradation. It requires less time, no need for extra steps. The maximum phenol degradation achieved in this photocatalytic method was 68.39%. The whole photocatalytic degradation was performed under acidic condition, this is one thing which is noticeable. However, there is no need of extra handling of that acidic medium. Overall, from the comparative study of all the three methods reported in this study, the photocatalytic process is efficient for phenol degradation than others.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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