Enhancement of Photochemical Reaction for Phenol Degradation via TiO_2 Nanomaterials under H_2O_2 and $FeCl_3$: Mechanism and Kinetic Modeling

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Abstract

The surface and groundwater are being contaminated by the fast development of industries, which disturbing the environment for a living organism. The introduction of an economical and eco-friendly treatment approach for fully degrading such harmful contaminants is highly encouraged. The main objective of this research is to illustrate the influence of two different types of accelerators namely hydrogen peroxide (H_2O_2) and ferric chloride ($FeCl_3$) for the enhancement of photocatalytic degradation of phenol in aqueous suspension in the presence of commercial TiO_2 nanomaterials (Degussa P-25, TiO_2). The several photocatalytic degradation processes using dark, direct photolysis (only light), TiO_2, H_2O_2 or $FeCl_3$/light, and H_2O_2 or $FeCl_3$/TiO_2/light in a batch photoreactor were performed. Different doses of H_2O_2 (0.25-1.0 mL) and $FeCl_3$ (0.5-2.0 mL) were used for maximum phenol degradation. The degradation results revealed that 0.5 mL of H_2O_2/light/TiO_2 and 1.0 mL of FeI_3/light/TiO_2 showed highest phenol degradation of 95.13 and 92.27 %, respectively. The photocatalytic degradation of phenol followed pseudo first order and Type 1 pseudo second order kinetics with the highest values of R^2 (more than 0.995). This enhancement of phenol degradation in the presence of H_2O_2 and $FeCl_3$ was strongly attributed to the formation of free hydroxyl radicals over the TiO_2 surface.

Keywords: Photocatalytic Degradation, TiO_2, Green Oxidants, Kinetic Modelling

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Introduction

Phenol is belonged to an aromatic organic compound being produced by 3.7 million tonnes in Asia out of 8.9 million tonnes of total annual production. Phenolic compounds are being released in the form of a waste stream into the aquatic environment by various industrial sectors such as pharmaceuticals, petroleum, paint, textile, pesticides, petrochemicals and coal conversion [1]. Phenol is considered as a significant contaminant and harmful to living organisms even in small concentrations owing to their carcinogenicity as well as toxic characteristics [2, 3]. Therefore, it is highly desirable to treat phenol-containing industrial wastewater before incoming to the water bodies [4] According to Environmental Protection Agency (EPA), wastewater should contain less than 1 ppm of phenol content [1, 5]. The higher concentration of phenol into the water body can produce several problems such as erosion of tissues, degradation of protein, pancreas, kidney, liver problems and disturb central nervous system [1, 6]. It has been reported that approximately 3 million tonnes of phenolic contaminants are detected annually in the environmental system [7]. The Department of Environment (DOE) in Malaysia has reported that about 1000-6700 ppm of phenolic contaminants are being entered in the environment of Malaysia from various chemical industries including petroleum refinery, oil palm, textile petrochemicals, pulp and paper [3, 8]. Several techniques have been implemented for the treatment of phenolic wastewater such as electrochemical oxidation [9], membrane filtration [1, 10], adsorption [11], advance oxidation [12], biological degradation [10, 13] and photocatalytic degradation [6]. The above-mentioned processes are not suitable to remove the phenolic compounds from wastewater due to some critical operating problem such as convert organic pollutants into other phase and need to be reproduced, which increase the operation cost [3]. The photocatalytic degradation is known to be a more appropriate process to remove the phenol from wastewater via employing suitable semiconductors. TiO_2 is a well-known semiconductor, which is normally utilized in wastewater treatment owing to less cost, non-toxic and degradation performance [14-16]. Nevertheless, establishing an efficient photocatalysis system to achieve excellent photodegradation activity with the lowest recombination rates is still a task in the field of photocatalysis [17-19].

It is generally believed that loss of free hydroxyl radicals, as well as photogenerated electrons hole-pairs, are major factors in triggering the photodegradation mechanism [3]. For this achievement, recombination rates of photogenerated electrons and holes pairs could be further minimized through adding suitable oxidants as electrons acceptors for the formation of free hydroxyl radicals as well as superoxide radicals. The accelerators have powerful capabilities to decompose different harmful contaminants by generating these extra free hydroxyl radicals and superoxide radicals [20]. In the past research works, numerous oxidants such as H_2O_2, $FeCl_3$, persulphate ions, iron salt, peroxomonosulfate and peroxodisulfate as electrons acceptors have been employed and showed a power decomposition activity for the organic substances [21]. Their primary mechanism is to produce free radicals to prevent a strong recombination rate between the photogenerated electrons and hole pairs to degrade the pollutant into harmless by-products. Among these oxidizing agents, H_2O_2 and $FeCl_3$ are the most widely used accelerator agents to enhance the activity of employed photocatalysts. Semiconductors are more suitable powders in the presence of light for the degradation of phenol pollutants. Thus, the photocatalytic degradation mechanism delivers alternative motivating direction to the environmental treatment of phenolic wastewater.

The entire research aims are to treat the phenolic-based aqueous solution via the photocatalytic degradation process using TiO_2 as photocatalyst. The effects of H_2O_2 and $FeCl_3$ along with TiO_2 over degradation capabilities were investigated. To attain this goal, the photocatalytic destruction of phenol was performed via employing various processes. Furthermore, pseudo first order (PFO) and pseudo second order (PSO) kinetic models were employed onto the phenol degradation results at different phenol concentrations. The formation mechanism of hydroxyl radicals was also proposed.

Materials and Methods

Materials and Regents

The following chemicals have been used for phenol degradation studies. Commercial titanium dioxide nanopowders purchased from Sigma-Aldrich, Malaysia, have a surface area of 49.16 m^2/g, a particle size of 21 nm, anatase of 80 % and rutile of 20 % (TiO_2, 99.50 %). All other chemicals such as hydrogen peroxide (H_2O_2, 95 %), ferric chloride ($FeCl_3$, 95 %), sodium hydroxide (NaOH, 95 %) and nitric acid (HNO_3, 95 %) were purchased from Merck company. Phenol (C_6H_6O, > 99 %) was also purchased from Sigma Aldridge, Malaysia.

Photocatalytic Degradation of Phenol

The photocatalytic performance was evaluated against degradation of phenol using TiO_2, H_2O_2 and/or $FeCl_3$. The stock solution of phenol was diluted by the addition of a suitable quantity of denoised water to prepare the desire concentration of phenol aqueous solution. 1.0 g/L of TiO_2 was dispersed into 300 mL of phenol with an initial concentration of 50 mg/L and kept at room temperature to obtain adsorption-desorption equilibrium in dark condition for 45 min. H_2O_2 (30 wt. %) and $FeCl_3$ (3 wt. %) were used in the range from 0.25-1.0 mL and 0.5-2.0 mL, respectively. 0.1 M HNO_3 and NaOH were used for pH adjustment. Before turned on the light, the phenol solution was mixed with photocatalyst under the dark conditions to complete the adsorption-desorption condition for 60 min. High-pressure halogen lamp with 500 watts was used for a light source on continuous stirring at room temperature. The aliquot samples of phenol were taken out from the solution through a plastic syringe attached with 0.45 μm filter and absorbance values were recorded for each sample using a *UV-vis* spectrophotometer. All the measurements were taken in triplicates and average values were reported. The rate of phenol degradation was examined using the following formula:

$$Phenol\ removal\ efficiency = \frac{C_o - C}{C_o} \times 100 \qquad (1)$$

In the above formula, C_o is the initial concentration of phenol ions. C is the equilibrium concentration of phenol ions. t is the reaction time in min [3].

Results and Discussion

Influence of H_2O_2 Over Phenol Degradation

The possible effect of H_2O_2 onto the removal of phenol molecules was scrutinized. Several degradation experiments were performed in the presence of TiO_2 and light at various H_2O_2 amounts (0.25, 0.5 and 1.0 mL). Moreover, the phenol degradation experiments with photolysis (only light), under dark condition (without TiO_2), only TiO_2 and H_2O_2/light were also performed. Calculate removal efficiency of phenol by using the highest wavelength (269 nm). The highest removal efficiencies of phenol using H_2O_2 in the presence of TiO_2 are presented in Figure 1. The results showed that approximately 10-15 % and 4-9 % removal performance was accomplished under photolysis and darkness conditions while 39.56 % was removed under H_2O_2 with the light process. About 80.85 % degradation efficiency was obtained via TiO_2, which was gradually increased by increasing the H_2O_2 dose from 0.25-0.5 mL up to 95.13 % after that degradation rate was found to be decreased at 1.0 mL, which could be due to the blockage of surface-active sites of TiO_2. Although more free hydroxyl radicals were formed, this increase in phenol degradation was primarily due to the rapid decrease in the recombination of photogenerated electron holes onto the surface of the employed semiconductor [22]. The strong effect of hydrogen peroxide on the decomposition of selected contaminants can be explained by the photoreduction of oxygen onto the semiconductor surface as well as the oxidation of species of hydroxyl radicals by photolysis of hydrogen peroxide [2]. In the entire study, the optimum dose of H_2O_2 in the presence of TiO_2 is suggested to be 0.5 mL for maximum phenol degradation.

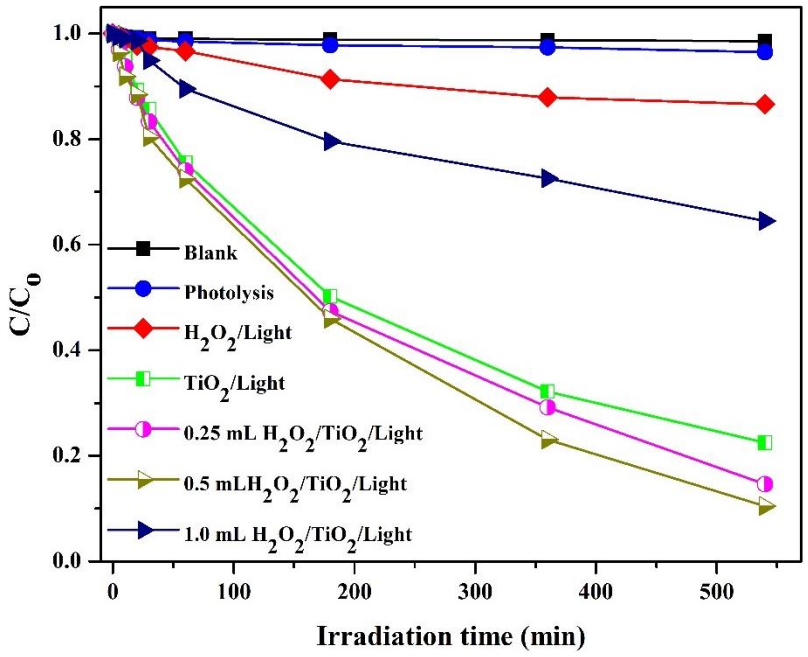

Figure 1. Effect of several photocatalytic degradation processes by using H_2O_2 for maximum phenol removal.

Effect of $FeCl_3$ Over Phenol Degradation

The possible effect of $FeCl_3$ onto the removal of phenol molecules was also scrutinized by performing several experimental processes with TiO_2 and various amounts of $FeCl_3$ (0.5, 1.0 and 2.0 mL), showing a significant reduction of phenol. Figure 2 shows the phenol degradation performance of $FeCl_3$ in the presence of TiO_2. During the photocatalytic degradation of phenol by the addition of $FeCl_3$ with TiO_2, the formation of Fe^{+2} was verified. The presence of Fe^{+3} or Fe^{+2} ions into the phenol solution strongly influenced the hydroxyl radicals generation resulting in the increase of phenol degradation. The degradation results illustrated that removal of phenol was rapidly improved with rising the dose of $FeCl_3$ from 0.5-1.0 mL while the removal rate was observed to decline with rising further dose of $FeCl_3$ (2.0 mL). The phenol degradation reached 92.27 % by using 1.0 mL of $FeCl_3$ in the presence of TiO_2. However, a higher dose of $FeCl_3$ have a tendency to retard the effect of degradation by means of a short-circuiting mechanism, which was also investigated in other studies [20, 23]. The degradation rate may also be decreased due to the blockage of surface-active sites of TiO_2 due to aggregation of ferric ions. Thus, it can be stated that the addition of $FeCl_3$ has significant influence over the removal of phenol via employing TiO_2. The $FeCl_3$ in the presence of TiO_2 for the removal phenol showed a well separation of photogenerated electrons hole-pairs. The optimum dose of $FeCl_3$ was suggested to be 1.0 mL for maximum phenol removal.

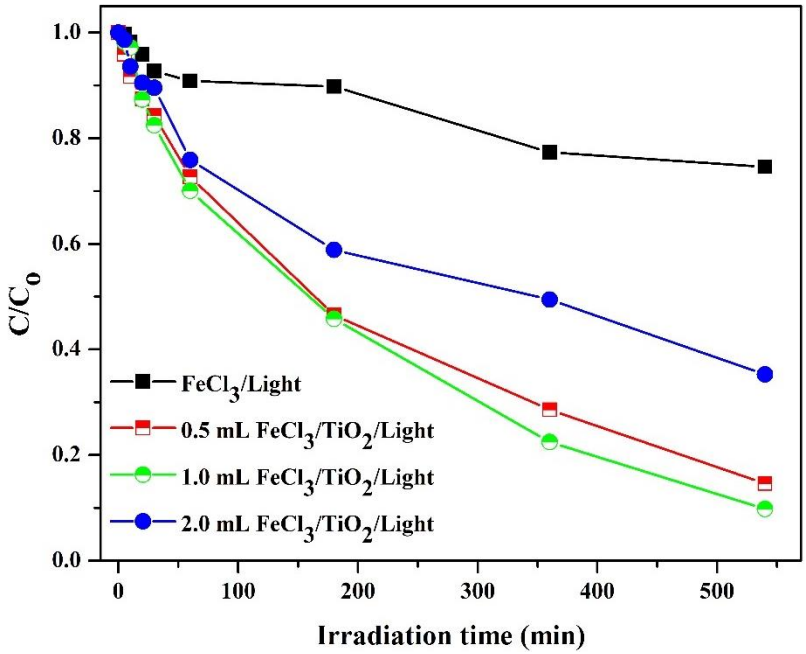

Figure 2. Effect of different photocatalytic degradation processes using $FeCl_3$ for maximum phenol removal

Kinetic Modelling

The kinetic modelling is one of the most significant studies to illustrate the removal mechanism of various contaminants. The kinetic modelling studies are generally employed to explain the kinetic behavior for the photocatalytic degradation process based upon the degradation rate. The kinetics analysis has a strong capability to illustrate the adsorption properties of selected substrates over the photocatalyst surface. In the present research, two common types of kinetics namely PFO and PSO models were performed at different phenol concentrations from 5-150 mg/L. PFO reaction rate equation can be expressed in the following form [24]:

$$Rate = -\frac{dc}{dt} = K_1 C \qquad (2)$$

$$\ln \frac{C}{C_o} = -K_1 t \qquad (3)$$

Where, K_1, C *and* C_o represent PFO rate constant, phenol concentration at any time (t) and initial phenol concentration, respectively. The graph between lnC/C_o versus *time* was planned to attain the kinetics valuation. Similarly, Type-1, Type-2 and Type-3 PSO reaction rate equations can be expressed in the following form [24]:

$$Rate = -\frac{dc}{dt} = K_2 C^2 \qquad (4)$$

$$\frac{1}{C} = K_2 t + b \qquad (5)$$

$$\frac{1}{C_t} = \frac{1}{C_o t} + K_2 \qquad (6)$$

$$C_t = \frac{1}{K_2} + C_o t \qquad (7)$$

Where, K_2 and C^2 represent PSO rate constants and phenol concentration at any time (t), respectively. The graphs were plotted between $1/C$ versus t, C_t versus $1/t$ *and* C_t versus t by using Type-1, Type-2 and Type-3 PSO models, respectively. Fig. 3 illustrates the PFO and PSO kinetics behavior for phenol degradation via TiO_2 while all the values of kinetic constraints are listed in Table 1. Based upon kinetics estimation, it could be predicted that the PFO linear regression coefficient (R^2) of phenol degradation was higher (0.991-0.998) as compare to Type-1, Type-2 and Type-3 PSO kinetic models. The Type 1 PSO kinetic model has R^2 (0.914-0.996), which is much higher than other types of PSO kinetics. This suggested that PFO and Type 1 PSO kinetic equations are more capable to represent the phenol degradation mechanism over the TiO_2 surface as compared to Type 2 and Type 3 PSO kinetic equations. In this study, phenol degradation is suggested to be a chemical process involving valance or attractive foresees via sharing or exchange of photoelectrons [3]. The photocatalytic degradation of phenol was suggested to be a chemical process involving valance or attractive foresees via sharing or exchange of photoelectrons between photocatalyst and phenol solution. This may be due to the much higher competition for sorption surface active sites relatively at high phenol concentration [3]. These degradation constants results

described that degradation of phenol mainly takes place over the surface of photocatalyst via H^+ or hydroxyl radicals.

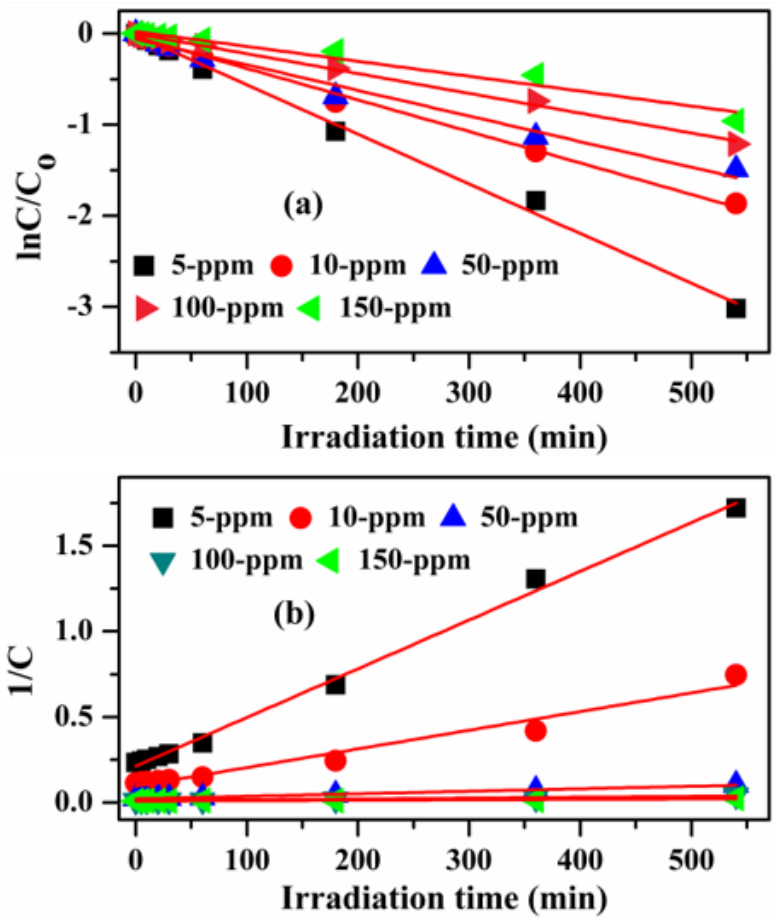

Figure 3. (a) PFO and (b) Type 1 PSO kinetic models for maximum phenol removal using TiO_2

Table 1. Kinetic results for photodegradation of phenol by using TiO_2.

Kinetic models	Variables	Phenol concentrations				
		5 mg/L	10 mg/L	50 mg/L	100 mg/L	150 mg/L
PFO	K_1 (min^{-1})	5.45×10^{-3}	3.46×10^{-3}	2.81×10^{-3}	2.18×10^{-3}	1.64×10^{-3}
	R^2	0.998	0.996	0.992	0.997	0.991
Type 1 PSO	K_2 (min^{-1})	2.84×10^{-3}	1.09×10^{-3}	1.46×10^{-4}	5.02×10^{-5}	2.48×10^{-6}
	b	0.212	0.096	0.022	0.011	0.008
	R^2	0.995	0.963	0.996	0.955	0.914
Type 2 PSO	K_2 (min^{-1})	$1.75 \times 10^{+1}$	$4.42 \times 10^{+1}$	$2.66 \times 10^{+2}$	$5.06 \times 10^{+2}$	$7.87 \times 10^{+2}$
	R^2	0.512	0.452	0.511	0.374	0.376
Type 3 PSO	K_2 (min^{-1})	2.88×10^{-1}	1.34×10^{-1}	2.72×10^{-2}	1.34×10^{-2}	9.71×10^{-2}
	R^2	0.736	0.785	0.762	0.901	0.981

Proposed Formation of Hydroxyl Radicals (OH•)

The formation of hydroxyl radicals is considered as important oxidizing species for the degradation of pollutants in aqueous suspension [20]. In this study, we proposed a degradation reaction system for the formation of hydroxyl radicals with the appearance of two important green oxidants namely H_2O_2, $FeCl_3$, and TiO_2 in the presence of light irradiation source. The visible light could successfully progress the usage performance of employed oxidizing agents and promote the development of hydroxyl radicals that is mainly accountable for the remediation of phenol from aqueous solution. The degradation mechanism showed the powerful attraction between produced molecular oxygen and hydroxyl radicals with photogenerated electrons and holes for determining the phenol removal percentage [25]. The available photogenerated electrons could be allocated from alkaline-based nanotubes to CB for the formation of superoxide radicals by reaction with oxygen molecules. On the other hand, the holes were formed through the photocatalytic degradation process that has a strong activity to oxidize the harmful phenol molecules into harmless degraded species such as carbon dioxide and water as by-products [26]. The phenol degradation using TiO_2 in the presence of oxidizing agents can be described in the following Figure 4.

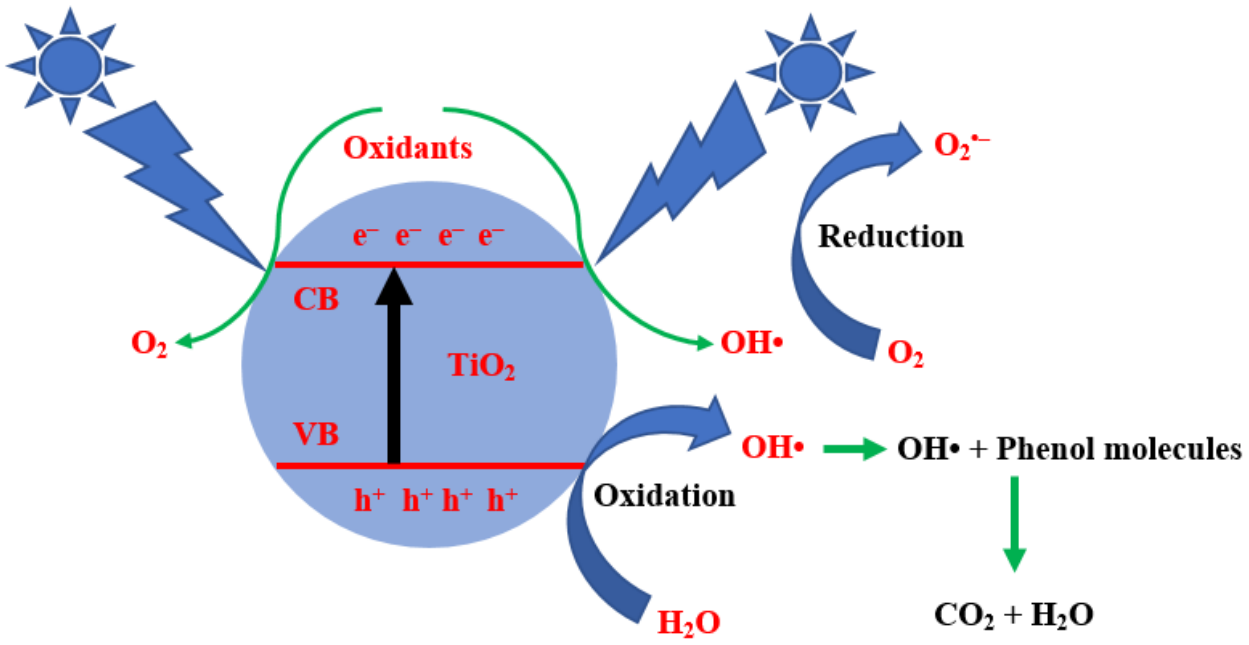

Figure 4. The proposed degradation mechanism of phenol using TiO_2 under oxidizing agents.

Conclusions

The present approach revealed that the effect of H_2O_2 and $FeCl_3$ in the presence of TiO_2 under light irradiation could greatly improve the photocatalytic degradation activity of phenol as compare to direct photolysis and TiO_2 alone. Moreover, a 0.5 mL dose of H_2O_2 and 1.0 mL dose of $FeCl_3$ is more suitable for complete phenol decomposition by readily producing hydroxyl radicals. PFO and Type 1 PSO kinetics are suitable for the phenol degradation results giving the highest values of R^2 (more than 0.995). Hence, the present research revealed that TiO_2 via employing H_2O_2 and $FeCl_3$ has a strong capability to remove phenol from aqueous solution.

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Author Contributions

All authors contributed toward data analysis, drafting and critically revising the paper and agree to be accountable for all aspects of the work.

Disclosure of Conflict of Interest

The authors have no disclosures to declare.

Compliance with Ethical Standards

The work is compliant with ethical standards.

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