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Performance of natural sunlight on paracetamol removal from synthetic pharmaceutical wastewater using heterogeneous TiO_2 photocatalyst

Chee Mei Lee[a], Nurul Aiin Binti Ab Aziz[a], Puganeshwary Palaniandy[a,*], Salem S. Abu Amr[b]

[a]*School of Civil Engineering, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia, Tel. +6016-5636951; email: leecheemei_951@yahoo.com (C.M. Lee), Tel. +6019-2745010; email: aiinaziz91@gmail.com (N.A.B.A. Aziz), Tel. +604-5995883; email: cepuganeshwary@usm.my (P. Palaniandy)*
[b]*Environmental Engineering Technology, Malaysian Institute of Chemical and Bioengineering Technology, Universiti Kuala Lumpur (UniKL, MICET), Melaka, Malaysia, Tel. +606-551 2155; email: salem@unikl.edu.my*

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ABSTRACT

Paracetamol has been remarked as one of the most heavily used and prescribed drugs nowadays. The presence of paracetamol in the sewage effluent with the average concentration of 0.01 mg/L has been reported in this paper. This study investigated the removal of paracetamol from synthetic pharmaceutical wastewater using titanium dioxide (TiO_2) photocatalysis treatment method under natural solar irradiation. Compound parabolic collecting reactor was used as a treatment medium. The effect of each variable (pH, concentration of TiO_2 and initial concentration of paracetamol) on the photocatalytic degradation efficiency of paracetamol was investigated by using the single-variable-at-a-time method. Central composite design based on the response surface methodology was used to optimize TiO_2 and paracetamol concentrations. Experimental results and analysis of variance analysis showed that the model was significant with the high coefficient of determination (R^2) of 0.9883. The optimum conditions of 1.0 g/L of TiO_2 concentration and 0.06 g/L of paracetamol initial concentration were predicted for the maximum removal efficiency of 88%. Finally, the performance of UV lamp and natural sunlight in the photocatalytic degradation of paracetamol was compared and discussed in detail. The in situ experimental results in this study have proven the reliability of the solar operation on the photocatalysis treatment process.

Keywords: Heterogeneous photocatalyst; Synthetic wastewater; Paracetamol; Titanium dioxide; Solar energy; Compound parabolic collecting reactor

1. Introduction

One of the most rising issues in the global concern is the occurrence of the pharmaceutical compounds in the aquatic environment. Various types of pharmaceuticals have been detected in the water compartments such as surface water, groundwater, effluents of sewage treatment plant, seawater and even in drinking water [1–4].

There are two main problems which contribute to the increment of pharmaceutical compounds in the natural water sources. The first problem is the malfunction of the conventional wastewater treatment system in removing the retained pharmaceutical compounds. Most of the pharmaceutical compounds are found to be polar, predominantly water soluble in nature, chemically stable in water, not photodegradable, hydrolysis resistant, neither volatile nor biodegradable [5–8]. Besides, they are lipophilic, biologically active and persistent, to maintain their therapeutic activity until the specific physiological function (on both human and animals) has been performed [9–12]. The aforementioned properties enable them to release from the sedimentation and biological treatment processes in the sewage treatment plants [13].

* Corresponding author.

The other problem is the lack of baseline data regarding the occurrence of pharmaceutical compounds in the aquatic environment. Pharmaceutical pollution has not been given a significant attention despite pharmaceutical is increasingly and extensively applied for different purposes throughout the world. Ignorance of this matter is due to the fact that pharmaceutical products are not regulated as environmental pollutants and not listed as pollutants in the World Health Organization (WHO) guidelines for drinking water quality [14]. This, in turn, prohibits the evaluation of public exposure and the subsequent effects [15–17].

Among the pharmaceutical compounds, paracetamol (acetaminophen) receives the major concern due to its high global consumption rate and wide-spread nature in the aquatic environment [18,19]. Throughout the years, the treatment processes of photolysis, sorption, hydrolysis, biodegradation, ozonation and H_2O_2 photolysis have been applied for the elimination of paracetamol [20–23]. Results showed that these methods may remove the parent compound of paracetamol, but none of them are able to attain the complete mineralization of intermediates which are generated during the treatment process [24,25]. In recent years, plenty of the biorecalcitrant pollutants including some of the pharmaceutical compounds have been successfully eliminated by using heterogeneous-photocatalytic treatment method. This treatment method is one of the most promising advanced oxidation processes, which is able to destruct the organic pollutants and achieve the complete mineralization without any residual left at the end of the treatment process [26–29].

To date, heterogeneous-photocatalytic treatment process often associated with the application of commercial UV lamp or solar simulator as the UV source [9,12,30–33]. Zhang et al. [9] have conducted the photocatalytic degradation of paracetamol under a 250 W metal halide lamp. About 95% of paracetamol was decomposed under the treatment conditions of 1 g/L of titanium dioxide (TiO_2) concentration, 100 μmol/L of paracetamol initial concentration as well as 100 min of UV irradiation. In addition, Aguilar et al. [12] applied the long-wave UV–Vis lamps (λ_{max} = 365 nm, Cole-Parmer E-09815-55) to initiate the photocatalytic degradation process of paracetamol. 100% of paracetamol removal efficiency was achieved under the treatment conditions of 2 g/L of TiO_2 concentration, 120 mg/L of paracetamol initial concentration as well as 300 min of UV irradiation. Lately, Rytwo et al. [33] carried out the photocatalysis experimental work by using a continuous-flow device which was equipped with four 8-W RMR-1849/253.7 nm lamps. Based on their study, 2 ppm of paracetamol was completely removed within 1 h of UV irradiation in the presence of TiO_2. So far, there are only two studies conducting the TiO_2 photocatalysis treatment process of paracetamol under the natural sunlight irradiation [34,35]. Yet, both of these studies focused more on the preparation of immobilized TiO_2 and its performance (in terms of photocatalytic activity, stability and reusability). Notably, there is a lacking part regarding the performance of natural sunlight in the photocatalysis degradation process although it has been introduced as a promising alternative UV source [11,29,36]. Besides, Spasiano et al. [37] had mentioned that the lack of "in situ" experiments on the long-term reliability of solar operation is one of the barriers, which needs to be overcome in the near future.

In the present study, characterization towards the effluent from a selected hospital sewage treatment plant located at the north-east of Peninsular Malaysia was first done, taking into account the macro-pollutants and micro-pollutants. Next, experiments were conducted to investigate the effects of the variables (pH, concentration of TiO_2 and initial concentration of paracetamol) on the photocatalytic degradation of paracetamol under the natural sunlight irradiation. In the last stage of the study, optimization process was conducted using the central composite design (CCD) based on the response surface methodology (RSM), followed by the comparison of performance between the UV lamp (previous studies [9,12,30,35,38,39]) and natural sunlight (present study) in the photocatalytic degradation of paracetamol.

2. Materials and methods

2.1. Wastewater sampling and characterization

Wastewater sampling was conducted to determine the baseline data regarding the concentration of paracetamol in the sewage effluent and to prove the ineffectiveness of the conventional treatment plant in removing the micro-pollutants. Samples were collected from the outlet point of the selected hospital sewage treatment plant. This sewage treatment plant is designed to cater 5,000 population equivalent. The existing treatments in the treatment plant are aeration and sedimentation. Grab samples were collected at 8 am and 6 pm, for two consecutive days. The sampling, preservation and analysis of wastewater samples were conducted according to the standard methods for the examination of water and wastewater provided by APHA et al. [40].

2.2. Equipment (photoreactor)

Photoreactor is a specific device which plays an important role in the solar photocatalytic treatment process. Photoreactor can efficiently bring solar photons and chemical reagents into contact with the photocatalyst such as TiO_2. It also generates a continuous circulation of flow to create a good homogeneous concentration and suspension of TiO_2 throughout the volume. Unlike the classic chemical reactors, photoreactors are more concerned on the physical geometry to collect the solar radiation effectively for the optimal photocatalytic treatment process. In this regard, compound parabolic collecting reactor (CPCR) is often recognized as a better option among the available photoreactors (such as parabolic trough reactor and thin-film fixed-bed reactor). This is mainly due to its geometric design of the platform which is able to concentrate both direct and diffuse solar radiation to the reactor tube as illustrated in Fig. 1 [41]. This subsequently maximizes the usage of solar radiation for the photocatalytic activity.

Fig. 2 shows the schematic diagram of the CPCR applied in this study. This CPCR was modified from the original CPCR at the Plataforma Solar de Almeria in Spain (PSA), manufactured by Industrial Solar Technology Corporation, Denver, Colorado (USA) [26]. Basically, the CPCR was modified in terms of the number of compartments and the arrangement of the main components. The original and modified CPCR composed of eight and four similar connected compartments, respectively. Unlike the original CPCR, all the main components (such as the water tank, water pump, flow rate

controller, reactor tube, reflector, etc.) were equipped within the modified CPCR. It is noticeable in Fig. 2 that the CPCR composed of two major parts: the stand and the platform, where the platform was equipped with an angle adjuster for the gradient adjustment. In addition, each of the compartments in the CPCRs platform consisted of reflector and reactor tube. The reflector made from polished aluminium was high in UV–solar reflectivity to concentrate the UV radiation to the reactor tube. As for the reactor tube, it was made from polyvinylidene fluoride with the thickness of approximately 2 mm. This material was capable of withstanding harsh thermal, chemical and ultraviolet conditions, as well as transparent to UV for the excitation of TiO_2. During the photocatalysis treatment process, CPCR was placed at the open space and the platform was adjusted to 37° to maximize the illumination of sunlight.

2.3. Photocatalytic procedure

In this study, synthetic pharmaceutical wastewater was applied in the TiO_2 photocatalysis treatment process. All chemicals used for the preparation of synthetic wastewater were of analytical grade: the commercial Panadol (containing 500 mg of paracetamol per tablet) and TiO_2 powder (uncoated anatase form with particle size of 0.15 μm, supplied by R & M Chemicals Essex, UK). For each run, 15 L of TiO_2 suspension (a mixture of deionized water, paracetamol and TiO_2) was freshly prepared. The pH of the suspension was adjusted by using 3 M of NaOH and H_2SO_4 solution. By utilizing MS Horizontal Centrifugal Pump, the TiO_2 suspension was continuously circulated between the water tank and reactor tube

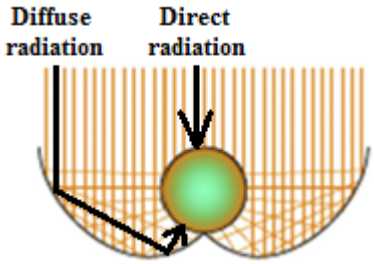

Fig. 1. Behaviour of solar radiation on a reflector of CPCR [37].

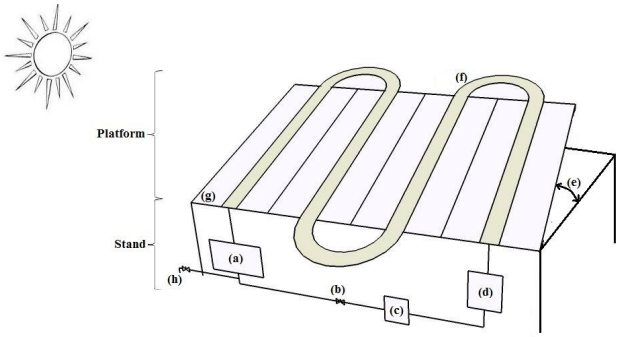

Fig. 2. Schematic diagram of CPCR. (a) Water tank; (b) control valve; (c) water pump; (d) flow rate controller; (e) angle adjuster; (f) reactor tube; (g) reflector and (h) sampling point.

of the CPCR at a constant flow rate of 40 L/min, to prevent the deposition of particles in the hydraulic circuit. Based on the trial experimental runs (results on this part were not discussed), the suitable sunlight exposure period was 6 h (from 10 am to 4 pm, with the peak UV intensity ranging from 500 to 4,000 μW/cm^2), in order to achieve the maximum degradation of paracetamol. The treated solution was channeled into a sedimentation tank to allow the suspended TiO_2 particles to settle down. The supernatant in the sedimentation tank was collected on the next day. Both of the untreated and treated samples were analyzed by using high-performance liquid chromatography (HPLC, Agilent Technologies, Series 1200) which associated with a UV-diode array detector to quantify the initial and final concentrations of paracetamol. The photocatalytic degradation efficiency was evaluated based on the removal percentage of paracetamol as shown in Eq. (1):

$$\text{Removal efficiency (\%)} = (C_o - C_e)/C_o \times 100\% \quad (1)$$

where C_o and C_e are the initial and final concentrations of paracetamol (g/L), respectively.

2.4. Preliminary study

During the preliminary study, the effects of the selected variables (pH, concentration of TiO_2 and initial concentration of paracetamol) on the photocatalytic degradation of paracetamol were studied independently through the single-variable-at-a-time method. The ranges for these selected variables are shown in Table 1.

2.5. Batch study

A multivariable experimental design was done by CCD based on RSM in the Design-Expert software (Version 6.0.6, Stat Ease, Inc., MN, USA) to determine the interaction effects of the selected variables on the photocatalytic degradation of paracetamol [42]. Among the selected variables, only TiO_2 and paracetamol concentrations (1–2 g/L and 0.02–0.08 g/L, respectively) were applied for the multivariable experimental design. pH adjustment for the sample was not carried out in this stage of study because the natural pH of the suspension was favourable for the treatment process (as explained in the preliminary study). Besides, De la Cruz et al. [43] had mentioned that the acidification and neutralization of a large amount of wastewater were not practical, thus should be avoided in the real large-scale wastewater treatment application. In this study, 13 experimental runs were involved and the experimental results were analyzed systematically by using the ANOVA analysis. In the optimization process, numerical optimization was used to determine the maximum removal of paracetamol

Table 1
Selected variables with their respective range of study

Variable	Range	Interval
pH	5 and 11	–
TiO_2 concentration, g/L	0.5–3.0	0.5
Initial concentration of paracetamol, g/L	0.02–0.20	0.02

with the minimum usage of TiO_2 and the maximum initial concentration of paracetamol. The experimental result was compared with the predicted value to determine their correlation as well as the reliability of the model.

3. Results and discussion

3.1. Sampling and characterization of hospital sewage

Table 2 shows the characteristics of effluent from the hospital sewage treatment plant. As presented in Table 2, it is noticeable that the conventional parameters of the effluent such as COD, pH and temperature were under the acceptable conditions of sewage discharge of Standard B, in the Second schedule of Environment Quality (Sewage) Regulations, 2009 (as stated in DOE [44]).

Next, paracetamol with the average concentration of 0.01 mg/L has been detected in the effluent samples. This detected paracetamol concentration (mg/L) was found to be higher as compared with the previously detected concentrations (μg/L) in other countries [45]. As mentioned by Gómez et al. [46], the high concentration of paracetamol is not surprising as this pharmaceutical is extensively applied in the hospital. Besides, different production and usage patterns of pharmaceuticals in different countries may contribute to the different distribution tendencies in wastewater [15]. Overall, the results in Table 2 have proven that the conventional sewage treatment plant was effective to degrade the conventional parameters to the acceptable conditions. Yet, it was unable to remove the micro-pollutants such as paracetamol [47,48].

3.2. Preliminary study

3.2.1. Effect of pH

As mentioned by Dalrymple et al. [49], pH is able to affect the surface charge of the compound. Therefore, it exerts a significant impact on the adsorption of substrate onto the surface of catalyst, thereby the degradation efficiency. Fig. 3 illustrates the surface charges of paracetamol and TiO_2 at different pH levels. As shown in Fig. 3, TiO_2 has a point of zero charge at pH 6.3, where it is positively charged at pH < 6.3 and becomes negatively charged at pH > 6.3; whereby paracetamol possesses a pK_a value of 9.5, where it is neutrally charged at pH < 9.5 and negatively charged at pH > 9.5 [19,23,35].

In this study, the effect of pH was studied based on the different surface charges of paracetamol since the substrate exhibited the similar adsorption behaviour on the surface of catalyst when it was under the same surface charge. For the neutrally charged zone, the natural pH of the suspension (pH = 5.0 ± 0.1) was selected; whereby pH 11 was chosen for the negatively charged zone.

Fig. 4 illustrates the effect of pH on the photocatalytic degradation of paracetamol. As shown in Fig. 4, the degradation of paracetamol was more favourable at the neutrally charged zone. This can be explained that at pH < 9.5, no electrostatic interaction occurred between the neutrally charged paracetamol and negatively charged TiO_2. Meanwhile, the amount of hydroxyl ions on the surface of TiO_2 increased with the pH of the suspension up to pH 9.5, subsequently contributing to a higher formation rate of hydroxyl radical for the degradation of paracetamol [19,30]. At the higher pH of > 9.5, both the surfaces of paracetamol and TiO_2 were negatively charged, causing the development of electrostatic repulsive force that significantly reduced the degradation of paracetamol [9,35,50]. Besides, the formation of superoxide radical anion may also be suppressed due to the oxygen reduction by the electron was being inhibited [30]. Overall, the experimental results showed that the neutrally charged surface of paracetamol can yield a better degradation efficiency of paracetamol.

3.2.2. Effect of TiO_2 concentration

Fig. 5 shows the effect of TiO_2 concentration on the photocatalytic degradation of paracetamol. It is noticeable

Table 2
Characteristics of effluent from the hospital sewage treatment plant

Conventional parameter	Average concentration	Standard[a]	
		A	B
COD, mg/L	94	50	100
pH	6.9	6–9	5.5–9
Temperature, °C	33	40	40
TSS, mg/L	114	–	
Turbidity, NTU	33	–	
Pharmaceutical			
Paracetamol, mg/L	0.01	–	

[a]Standard – Environmental Quality (Sewage) Regulations, 2009.

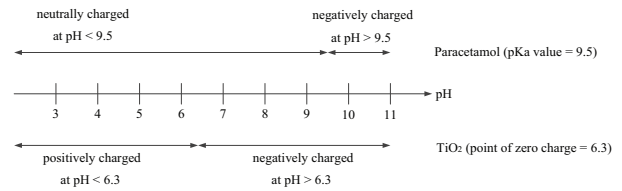

Fig. 3. Surface charges of paracetamol and TiO_2 at different pH levels.

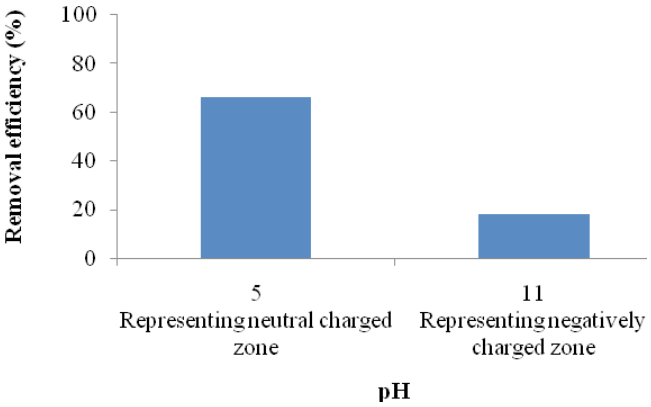

Fig. 4. Effect of pH on the photocatalytic degradation of paracetamol (initial concentration of paracetamol = 0.1 g/L, concentration of TiO_2 = 1.5 g/L, sunlight exposure period = 6 h).

in Fig. 5 that the degradation efficiency of paracetamol increased with the TiO_2 concentration from 0.5 to 1.5 g/L. This may due to the higher availability of catalyst active sites that has promoted the formation of hydroxyl radicals which take part in the degradation process [9]. The paracetamol degradation efficiency reached a plateau at the TiO_2 concentration of 1.5 g/L. Beyond the optimum TiO_2 concentration of 1.5 g/L, a decreasing tendency of degradation efficiency was observed. According to Dalrymple et al. [49], Yang et al. [30] and Borges et al. [19], this decrement is attributed to the superfluous of catalyst that may induce three main unfavourable conditions:

- Agglomeration and sedimentation of TiO_2 particles; this will cause the decrement of available catalyst surface which is able to absorb the photons for the generation of reactive oxygen species (ROSs).
- High turbidity of TiO_2 suspension; this will cause the increment of opacity and reduction of light transmissivity of the TiO_2 suspension.
- Deactivation of the originally activated TiO_2; at a higher photocatalyst loading, the ground-state catalyst may deactivate the originally activated TiO_2 by collision.

3.2.3. Effect of initial concentration of paracetamol

Fig. 6 displays the effect of paracetamol initial concentration on the photocatalytic degradation efficiency. As shown in Fig. 6, the initial concentration of paracetamol under 0.04 g/L was able to attain the 100% removal efficiency. This is because, at a lower initial concentration of paracetamol, TiO_2 may provide a higher amount of active sites to receive a larger amount of photons as well as in contact with the substrates [51]. At a higher initial concentration of paracetamol (>0.04 g/L), a decrement tendency on the paracetamol removal efficiency was observed due to some unfavourable conditions. First, a higher initial concentration of paracetamol may occupy the active surfaces of a large number of TiO_2 particles, where the generation of ROSs will be suppressed. Besides, a higher initial concentration of paracetamol will absorb more photons and cause the shortage of available photons for the activation of TiO_2 particles [30].

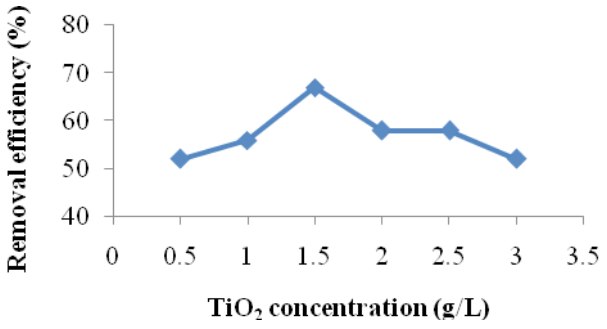

Fig. 5. Effect of TiO_2 concentration on the photocatalytic degradation of paracetamol (initial concentration of paracetamol = 0.1 g/L, pH = natural pH of suspension [pH = 5.0 ± 0.1], sunlight exposure period = 6 h).

3.3. Batch study

3.3.1. ANOVA analysis

Table 3 tabulates the experimental data in CCD for the photocatalytic degradation of paracetamol. A quadratic equation (as shown in Eq. (2)) of the model for paracetamol removal efficiency was formed as a function of the independent variables to identify the highest removal efficiency of paracetamol:

$$Y = 96.14 + 2.50*A - 15.17*B - 1.98*A^2 - 9.98*B^2 + 3.25*A*B \quad (2)$$

where Y, A and B symbolize the response value (%), the concentration of TiO_2 (g/L) and the initial concentration of paracetamol (g/L), respectively.

Fig. 7 illustrates the plot of predicted (Y_{cal}) vs. actual values (Y_{exp}). The straight line represents the predicted values

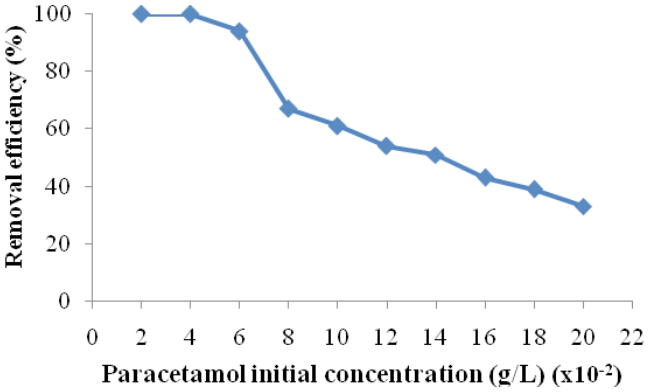

Fig. 6. Effect of paracetamol initial concentration on the photocatalytic degradation of paracetamol (TiO_2 concentration = 1.5 g/L, pH = natural pH of suspension [pH = 5.0 ± 0.1], sunlight exposure period = 6 h).

Table 3
Experimental data in CCD for the photocatalytic degradation of paracetamol (sunlight exposure period = 6 h and pH = natural pH of suspension, pH = 5.0 ± 0.1)

A Concentration of TiO_2 (g/L)	B Concentration of paracetamol (g/L)	Y_{exp} (%)	Y_{cal} (%)
2.00	0.05	95	96.66
1.00	0.08	62	63.26
1.50	0.02	100	101.32
1.50	0.05	95	96.14
1.50	0.05	95	96.14
1.50	0.08	72	70.99
2.00	0.02	100	98.59
1.00	0.02	100	100.09
2.00	0.08	75	74.76
1.50	0.05	98	96.14
1.00	0.05	93	91.66
1.50	0.05	98	96.14
1.50	0.05	95	96.14

which are calculated through the approximating functions employed for the model, whereas the points are referred to the actual values which are obtained from the experimental study. As illustrated in Fig. 7, a good correlation between the actual and predicted values can be observed since the points were located near to the straight line. Besides, this good correlation can also be proven through the coefficient of determination (R^2), which is a measure of the degree of fit. The R^2 value of 0.9883 for the paracetamol removal efficiency was close to 1, indicating that the model fitted well with the actual experimental data.

According to the ANOVA analysis, the probability value (P value) was smaller than 0.05, indicating that the specific model term was significant. Table 4 presents the P values for the different variables. Based on Table 4, the variables A, B, B^2 and AB significantly affected the response factor. The model term of "Lack of Fit" was found to be insignificant. However, the insignificance of this model term was good as it indicated that the model was fit.

3D surface response and contour plots as shown in Fig. 8 were used to identify the interactive relationship between the independent variables and the response. It is noticeable in Fig. 8 that the highest removal efficiency of paracetamol occurred at a lower initial concentration of paracetamol, regardless the concentration of TiO_2. There was no significant difference in terms of removal efficiency at the initial concentration of paracetamol from 0.02 to 0.04 g/L. As the initial concentration of paracetamol increased from 0.04 to 0.08 g/L, the removal efficiency of paracetamol reduced dramatically. On the other hand, the removal efficiency of paracetamol increased slightly with the increase of TiO_2 concentration, regardless of the initial concentration of paracetamol. This was followed by a slight drop in the removal percentage of paracetamol when the concentration of TiO_2 was beyond 1.75 g/L. As displayed in Fig. 8, the highest removal percentage of paracetamol was about 100% under the treatment conditions of 0.04 g/L of initial concentration of paracetamol and 1.70 g/L of TiO_2 concentration. In short, the increment and decrement patterns of paracetamol removal efficiency in this experimental study have proven that the concentrations of TiO_2 and paracetamol were greatly affecting the response. Next, optimization was conducted to determine the highest removal efficiency of paracetamol with the minimum usage of TiO_2.

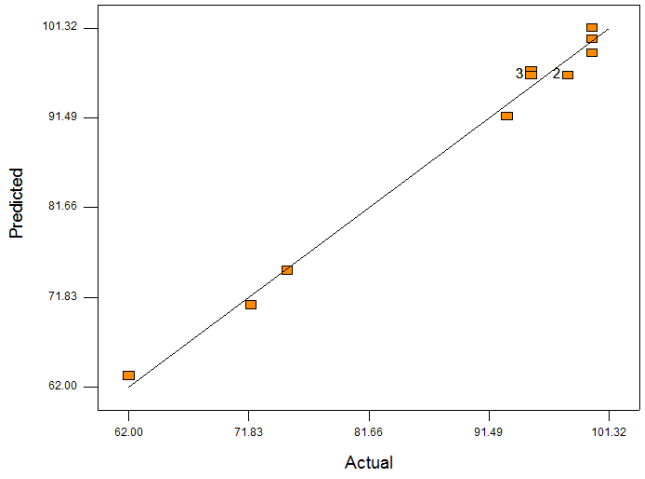

Fig. 7. Plot of predicted vs. actual values for the removal of paracetamol.

Table 4
P values for different variables

Term	Variable	P value
TiO_2 concentration	A	0.0104
Paracetamol concentration	B	<0.0001
Paracetamol concentration × paracetamol concentration	B^2	<0.0001
TiO_2 concentration × paracetamol concentration	AB	0.0078
Lack of fit		0.3760

3.3.2. Optimization of the operating parameters and comparison study

Table 5 presents the variables and their desired goals for optimizing the paracetamol removal efficiency. Based on the criteria in Table 5, the software has suggested the following optimal conditions: 1.0 g/L of TiO_2 concentration and 0.06 g/L of paracetamol initial concentration with the predicted removal efficiency of 88%. The sunlight exposure period was fixed to 6 h and without pH adjustment. Here, 82% of paracetamol removal efficiency was achieved under

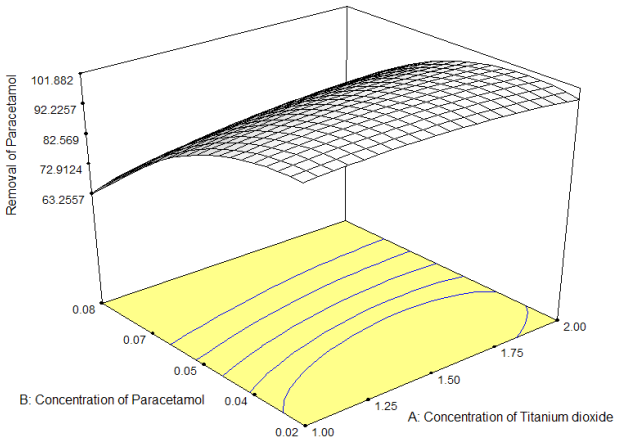

Fig. 8. 3D surface response and contour plots.

Table 5
Variables and their respective desired goal for optimizing the paracetamol removal efficiency

Variable	Goal	Lower limit	Upper limit
Concentration of TiO_2	Minimum	1	2
Concentration of paracetamol	Maximum	0.02	0.08
Removal of paracetamol	Maximum	62	100

Table 6
Summary of heterogeneous photocatalytic studies on paracetamol

(a) Reactor (b) Light source	Remark		Reference
	Treatment conditions	(a) Removal efficiency of paracetamol (b) Removal rate	
(a) Photochemical reactor (b) Metal halide lamp ($\lambda \geq 365$ nm)	• TiO_2 concentration = 1.00 g/L • pH = 6.9, natural pH of the suspension • Irradiation period = 100 min	(a) About 95% of 0.015 g/L of paracetamol (b) 0.00014 g/L/min	[9]
(a) Annular cylindrical reactor (with a quartz sleeve) (b) Black light blue UVA lamp (λ = 365 nm), UVC lamp (λ = 254 nm)	• TiO_2 concentration = 0.4 g/L • Irradiation period = 80 min	(a) More than 95% of 0.3 g/L of paracetamol (b) 0.0036 g/L/min	[30]
(a) Pyrex glass tube reactor (b) Long-wave UV–Vis lamp (λ_{max} = 365 nm)	• TiO_2 concentration = 2.00 g/L • Irradiation period = 120 min	(a) 0.04 g/L of paracetamol (b) 0.00033 g/L/min	[12]
(a) Annular cylindrical reactor (with a quartz tube) (b) UV light (λ_{max} = 365 nm)	• TiO_2 concentration = 2.00 g/L • Irradiation period = 240 min	(a) 0.1 g/L of paracetamol (b) 0.00042 g/L/min	[38]
(a) Batch reactor (with magnetic stirrer, pH meter and thermometer) (b) Blue LED lamps (λ = 440–490 nm)	• $K_3[Fe(CN)_6]$-modified TiO_2 concentration = 1.00 g/L • pH = 6.94 • Irradiation period = 540 min	(a) 91.06% of 0.015 g/L of paracetamol (b) 0.000025 g/L/min	[39]
(a) Cylindrical photoreactor (b) Low-pressure mercury lamp (λ = 200–280 nm)	• TiO_2 concentration = 0.4 g/L • Irradiation period = 150 min	(a) More than 90% of 0.04 g/L of paracetamol (b) 0.00024 g/L/min	[35]
(a) Batch mode plate photoreactor (b) Sunlight	• Immobilized TiO_2 • Irradiation period = 150 min	(a) More than 83% of 0.04 g/L of paracetamol (b) 0.00022 g/L/min	

these suggested optimal conditions. The excellent correlation between the predicted and experimental values provided confidence in the model. In the present study, the achieved removal efficiency of 82% (equivalent to 0.049 g/L) is believed to be sufficient for the actual treatment process. In other words, the degradation of paracetamol in the real situation is likely to occur rapidly since the concentration of paracetamol detected in the sewage effluent (around 0.01 mg/L as discussed in section 3.1) is far lower than that in this study.

Table 6 summarizes the recent heterogeneous photocatalytic studies of paracetamol using UV lamp and natural sunlight irradiation. The performance of these UV sources was evaluated based on the removal rate of paracetamol (g/L/min). As shown in Table 6, the first column tabulates the types of reactors and light sources applied in each study, while the second and third columns present the treatment conditions and removal efficiency of paracetamol, respectively. It is noticeable in Table 6 that some of the previous studies attained higher paracetamol removal rates as compared with the present study which was 0.00014 g/L/min. These better achievements (0.00022–0.00042 g/L/min) might be due to the high and constant UV intensity supplied by the UV lamp, higher concentration of TiO_2 as well as the design and geometry of different photoreactors which, in turn, provide a higher amount of photons for the photocatalytic activity [12,30,35,38].

Nevertheless, the UV radiation from the natural sunlight, which composed of a wider solar spectrum (λ = 290–390 nm) and UV intensity (500–4,000 $\mu W/cm^2$) have also been used with much success for the photocatalytic degradation of paracetamol. For example, Jallouli et al. [35] applied both UV sources in the photocatalytic degradation of paracetamol. In their study, 0.00024 and 0.00022 g/L/min of paracetamol removal rates were attained under the UV lamp and natural sunlight irradiation, respectively. Besides, the present study has achieved the degradation rate (0.00014 g/L/min) as similar as Zhang et al. [9] under the similar treatment conditions (in terms of TiO_2 concentration and without pH adjustment for the solution) but different UV sources irradiation. The excellent performance of natural sunlight can be further proven when the present study achieved a higher paracetamol removal rate as compared with Lin et al. [39] (0.000025 g/L/min), which applied the similar concentration of TiO_2, but under a longer treatment period. Based on these findings, it can be observed that both UV sources were suitable to be applied for the excitation of TiO_2 since no significant difference was observed in terms of their removal rates.

4. Conclusion

In the present study, sewage effluent characterization has proven that the conventional wastewater treatment plant was effective to degrade the conventional parameters to the acceptable conditions, but it unable to remove the paracetamol compounds appeared in the sewage treatment plant. Next, the removal of paracetamol from the synthetic pharmaceutical wastewater by using the solar photocatalyst has been investigated in this study. Based on the experimental results, the pH, concentration of TiO_2 and initial concentration of paracetamol greatly affected the photocatalytic degradation efficiency of paracetamol. Around 82% of paracetamol removal efficiency was attained under the suggested optimum conditions of 1.0 g/L of TiO_2 concentration and 0.06 g/L of initial concentration of paracetamol. Overall, results showed that both UV sources (UV lamp and natural sunlight) were suitable to be applied in the photocatalytic degradation process as their effectiveness in initiating the TiO_2 photocatalysis treatment process were comparable. In conclusion, the photocatalysis treatment process under the natural sunlight irradiation has the potential to be a sustainable and eco-friendly treatment method to remove the pharmaceuticals retained in the various water compartments.

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