Removal of Organic Pollutants from Wastewater Using Different Oxidation Strategies

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ABSTRACT

Many countries use nontraditional methods to treat wastewater, especially those with water lacks. Among these methods, heterogeneous photocatalysis is more commonly widely used since it converts organic molecules into carbon dioxide and water. In this study, the photocatalytic degradation process of total organic carbon was investigated by TIO_2/UV technique (TUT). This treatment is carried out in a batch recycle reactor using a UV light and catalyst TIO_2. The optimum operating parameters were investigated regarding the best organic removal including, total organic carbon concentration, flow rate, pH, irradiation time, and photocatalysis dosage. The result showed that the TUT is affected by reducing total organic carbon (TOC) from synthetic wastewater (SW) by 61% at 50 ml/min of flow rate, 250 mg of catalyst concentration TIO_2, and a concentration of TOC of 25 mg/l. Then the result of TUT was compared with a process of combining TIO_2/UV and an oxidizing agent (Hydrogen peroxide H_2O_2). It was found that 73% of organic removal was obtained which is best than TUT when using an H_2O_2 dosage of 100 mg/l. Experimentally, Ozone was also added to the process of TUT and the result showed that the removal percentage increased to 80%.

Keywords: catalysis, wastewater, oxidation, UV, organic matter removal.

INTRODUCTION

A natural resource that is vital to human survival is water. However, the lack of this priceless resource has emerged as a significant issue for the majority of nations worldwide. This is typically caused by effluent from human activities, primarily industry and agriculture, contaminating its sources (Preisner, 2020). due to the presence of organic matter and biological and, raw water is invalid for human consumption (Ali et al., 2012). There are many different technologies applied in wastewater decontamination, primarily including electrodialysis (Zazouli et al., 2017), membrane filtration (Zularisam et al., 2006), precipitation (Azimi et al., 2017), adsorption (Yagub et al., 2014), electrochemical reduction (Mousset et al., 2020), and electro deionization (Arar, 2014). These processes usually consume large amounts of energy and may be more complicated by transferring pollutants between different fluids, various

wastes, and by-products generated to treat wastewater (Ren et al., 2021). also, these techniques might not be very successful. Due to the costly equipment required for these processes (Mohammed et al., 2022). An efficient substitute for the treatment of wastewater has been created called the advanced oxidation process (AOPs), This process is highly efficient and can be used to treat a wide range of pollutants, including persistent organic pollutants (POPs). furthermore, the advanced oxidation process AOPs are cost-effective and can be used in large-scale applications (Zhang and Sun, 2021). AOPs are additionally non-destructive and do not create any harmful by-products. Although hydrogen peroxide frequently supplies (Teh and Mohamed, 2011) the active hydroxyl radicals, utilizing it increases the process's operating costs. Highly active hydroxyl radicals (Ledezam Estrada, et al., 2012), which are produced by a number of sources, are involved in the oxidation process (Ledezam Estrada,

et al., 2012). The combination of photocatalyst with the ozone method has been successfully used for the degradation of organic substances in an aqueous solution, such as formic acids (Wang, et al., 2002), dibutyl phthalate (Kercet et. al, 2003), and mono chloroacetic acid and pyridine (Li et al., 2005) . This paper aimed at three different parts: the first part is the study of the removal of total organic carbon (TOC) from (SW) using combined of TIO$_2$/UV technique (TUT) under various operating settings, including TOC concentration, flow rate, irradiation time, and TIO$_2$ dosage. The second part investigates the impact of TiO$_2$ and H$_2$O$_2$ together on organic deterioration. The third part is the impact of TiO$_2$ and O$_3$ together on organic deterioration. Also, study the kinetics of organic decomposition using (Pseudo-first-order model).

MATERIALS AND METHODS

Materials

Materials that are used in this study is titanium dioxide nanopowder as a catalyst, with particle sizes of 10±30 nm, a specific surface area of 50±100 m^2/g, and a weight ratio of 70 anatase to 30 rutile. The stock solution is prepared for each experiment including (potassium hydrogen carbonate, sodium hydrogen carbonate, Bacterial peptone, Glucose anhydrous, and Beef extract broth) as shown in Table 1. A typical biodegradable and nontoxic wastewater has been utilized as a substrate to measure its effect of treatment methods (Wilson et al., 1997; Doskaliyev et al., 2018). Under various operational conditions, TUT was used in a photo reactor to analyze synthetic wastewater with different concentrations of total organic carbon. Distilled water was used to dilute the stock solution in order to obtain various concentrations.

Experimental setup

In this study, three different configurations were performed as shown in Figures 1a and 1b, a set-up of two schematics for an experiment. In configurations (I) and (II), an annular photo reactor is used for batch recycling with TUT while H$_2$O$_2$ is added in configuration (II) named TiO$_2$-UV, H$_2$O$_2$ technology (TUHT). (A clear glass tube with a UV wavelength of 254 nm, 42 v, 6 W, measuring 1.6 cm in diameter and 2.12 cm in length (TUV 6 W 4P-treated wastewater included in 500 ml). The irradiation volume was 57 ml, in contrast. The peristaltic pump was used to control the flow rate (Drive model BT300M, Drive size 234×154×143 mm), and max flow (250 ml/min). A pH meter (INOLAB 72 WTW CO., Weilheim, Germany) was used to measure the solution's pH. In configuration III, the ozone generator is used with the same schematic as configuration I and II.

Process analysis

Samples were taken out of each experiment at intervals of two hours for analysis. then, it was filtered using Chromophile Xtra (0.2 MN) to determine the total organic carbon (TOC) content of the sample. The TOC-LCSH standalone method

Table 1. Stock wastewater's composition

Constituents	Concentration, g/l*
Beef extract broth	0.3
Bacterial peptone	0.42
Glucose (C$_6$H$_{12}$O$_6$)	0.165
Sodiumhydrogen carbonate (CHNAO$_3$)	0.04
Potassium hydrogen carbonate (CHKO$_3$)	0.04

Note: * The concentration of total carbon was 0.9 g/l.
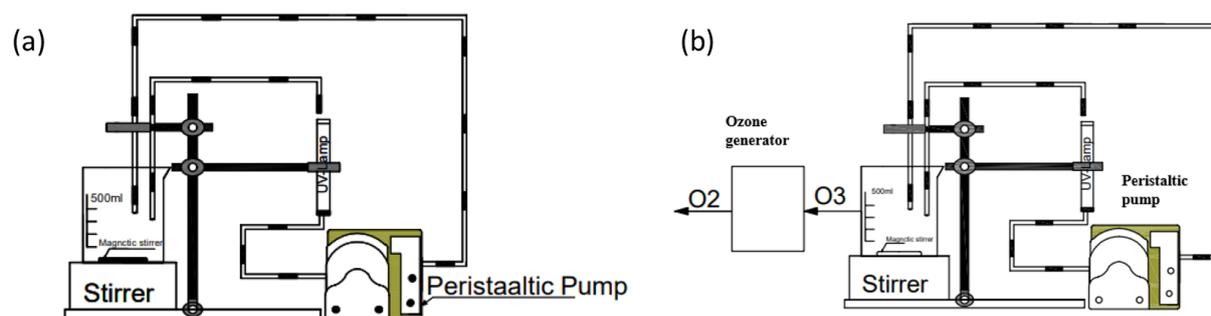
Figure 1. Diagram depiction of the experimental unit: (a) TUT, (b) TUOT

Table 2. Experimental conditions

Parameter	Range
Flow rate (ml/min)	50±250
TOC (mg/l)	25±500
TiO$_2$ (mg)	50±500
Total volume treated (ml)	500
UV lamp (w/nm):	6/245
Temperature (C): room temperature	21–25
Time (hours)	2

Table 3. The TOC analysis details

Carrier gas	Nitrogen (99.999%)
Technique of digestion	High-temperature combustion
The heat required for combustion	680 °C
Catalyst	Regular
Sample volume (ml)	50 μl
Rinse volume (ml)	2000 μl
Repeats for the TOC	3

was used to measure TOC concentrations. Table 2 shows the experimental conditions used in this work and Table 3 provides further information on the TOC analysis.

Removal finding

Equation (1) was used to calculate the percentage of TOC removal.

$$\% \text{ Removal} = \left(1 - \frac{C_t}{C_i}\right) \times 100 \qquad (1)$$

where: C_i is the total organic carbon concentration at the start of the treatment procedure; C_t is the total organic carbon concentration at a certain point in time.

Kinetic rate model

The correlation between the experimental results and the response deterioration may be measured using typical kinetic rate expressions. Pseudo-first-order reactions are used in the majority of degradation processes. (Hameed and Mousa, 2019) expressed used in equation (2) :

$$R = \frac{dC}{dt} = -kC \qquad (2)$$

where: K is the rate constant for the pseudo-first-order, min^{-1}.

By integrating equation (2):

$$\frac{C_t}{C_i} = e^{-kt} \qquad (3)$$

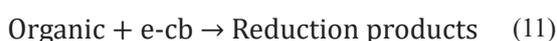The following relationship can be found by taking the natural logarithm of equation (3):

$$\ln\frac{C_t}{C_o} = -kt \qquad (4)$$

In equation (4), the plot ln (C_t) as a function of time for a first-order reaction is linear.

RESULTS AND DISCUSSION

Process configuration by TUT

In the first part of this study, the process configuration that is shown in Figure 1a is occupied by photocatalytic and TiO$_2$. The reaction occupied by TiO$_2$ photocatalysts is activated by light radiation, specifically photons, as reported by (Baran et al., 2008). Excitation of electrons occurs when the energy of solar radiation surpasses the bandgap of TiO$_2$, leading to the transition of electrons from the valence band (VB) to the conduction band (CB). The aforementioned process generates electron-hole pairs, whereby the valence band (VB) holes exhibit notable oxidation reaction activity within the range of 1.0 to 3.5 volts, while the conduction band (CB) electrons demonstrate favorable reducibility within the range of 0.5 to 1.5 volts. Upon exposure to light, TiO$_2$ generates positive holes and electrons in its valence band (hv + vb) and conduction band (e-cb), as reported by (Poulopoulos et al. 2004). The formation of hydroxyl radicals (Equation 3) or direct reaction with organic molecules can result in the oxidation of organic molecules as posited by Ahmad et al. (2016). Reduction products can be generated by a sequence of reactions (Equations 5-11) in which electrons engage with organic compounds. The involvement of oxygen in these reactions is significant, as it undergoes a reaction with the electrons generated by the photochemical process. Organic compounds have the potential to undergo oxidative degradation via their interactions with hydroxyl and peroxide radicals, valence band holes, and reductive cleavage through electron reactions. This process leads to the formation of diverse byproducts and ultimately mineral end-products.

$$hv + TiO_2 \rightarrow hv+vb + e\text{-}cb \quad (5)$$

$$OH\text{-}surface + hv+vb \rightarrow OH\bullet \quad (6)$$

$$H_2O \; absorbed + hv+vb \rightarrow H+ + OH\bullet \quad (7)$$

$$e\text{-}cb + O_2 \; absorbed \rightarrow O^{-2} \quad (8)$$

$$Organic + hv+vb \rightarrow Oxidation \; products \quad (9)$$

$$Organic + OH\bullet \rightarrow Degradation \; products \quad (10)$$

$$Organic + e\text{-}cb \rightarrow Reduction \; products \quad (11)$$

Effect of initial TOC concentrations

Figure 2a shows the change of concentration over time for various initial total organic carbon (TOC) concentrations that were studied (20±500) mg/l at pH 7, 250 mg of TIO_2, 50 ml/min of flow, and UV light. It is obvious that the removal of TOC is reduced generally by the rise in concentration. The explanation for this reality, there are more molecules available in the solution at low concentrations which makes it easier for UV light to reach the catalyst surface and increases the photocatalytic removal rate. However, at greater concentrations, the initial organic carbon content had a negative impact on the photocatalytic treatment because there were fewer reactive species present as present previously by (Sharma et al., 2010).

Effect of flow rate

Different flow rates are used in this study at an initial concentration of 20 mg/l, and TiO_2 of 250 mg as shown in Figure 2b. The result shows that the TOC removal was increased when the flow rate decreased due to the prolonged duration of the residence period. A high flow rate condition, results in an increased opportunity for the TOC to participate with the radicals present at the interface of the solution and the catalytic surface. However, the removal efficiency was found to be restricted at high flow rates. Elevating the flow rate resulted in a reduction of the residence time and an increase in the thickness of the water layer. This, in turn, impeded photon penetration to the liquid/solid interface (Kane et al., 2022).

Effect of catalytic dosage

Figure 3a shows the effect of a catalytic dosage ranging between (50±500) mg in 500 ml on total organic carbon (TOC) removal. The experimental results depicted that a 24% removal rate in TOC was achieved when using 50 mg TiO_2/500 ml. The increase of catalysis dosage to 250 mg TIO_2/500 ml resulted in a 61% removal of total organic carbon (TOC), which exhibited negligible variation when the titanium dioxide dosage was increased to 500 mg TIO_2/500 ml. According to Chakrabarti et al. (2004), beyond a certain time, the process is not accelerated by an increase in the amount of catalyst as the treated solution becomes impenetrable to UV irradiation. It is obvious that TUT played a critical role in attaining significant total organic carbon (TOC) removals. As a result, the dosage of 250 mg TIO_2 per 500 milliliters was subsequently employed.

Effect of irradiation time

The effect of reaction time on the photocatalytic degradation efficiency of TIO_2 on TOC removal was investigated, as depicted in Figure 3b. It was noticed that the overall TOC removal was increased from 7% to 61% as the oxidation time increased from 30 to 120 minutes. However, the removal rate remained constant as the oxidation time was further extended. According to that, the most favorable parameters for achieving the highest levels of total organic carbon (TOC) removal efficiencies were found to be 120 min of irradiation time, 20 mg/l of initial TOC concentration, 250 mg/500 ml of TIO_2 and 50 ml/min of a flow rate.
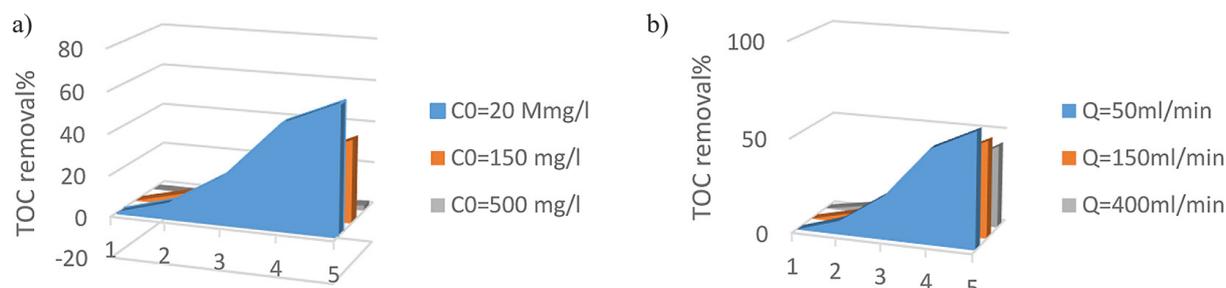

Figure 2. Removal efficiencies of TOC (a) at different concentrations for TIO_2 = 250 mg, Q = 50 ml/min. (b) at different flow rates for TIO_2 = 250 mg, TOC = 20 mg/l

a)

b)
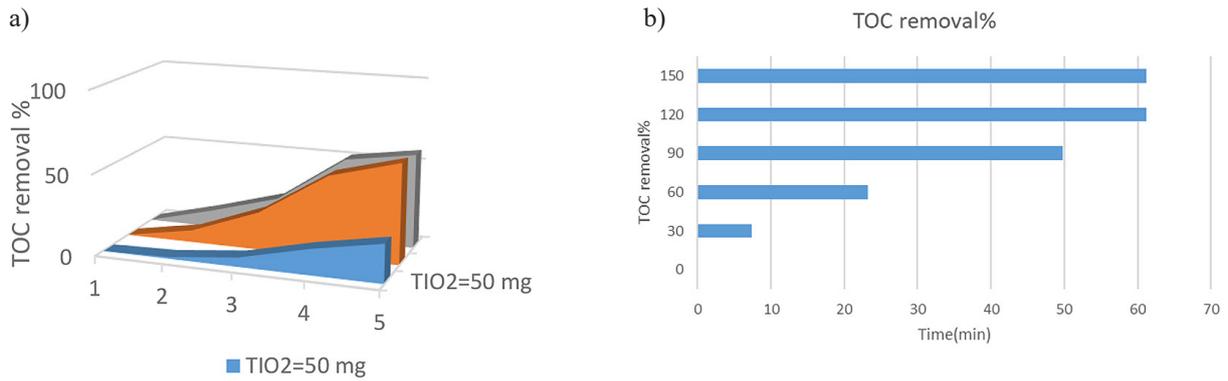
Figure 3. Removal efficiencies of TOC: (a) at various catalysis dosages for TOC = 20 mg/l, UV, Q = 50 l/min, (b) effect of oxidation time on the removal efficiencies of TOC

Process configuration by TUHT

The effect of the addition of hydrogen peroxide to TUT as oxidant on TOC removal, Optimized catalyst concentration, and optimized initial TOC concentration was studied by varying amounts of H_2O_2 (50, 100, 150) mg/l shown in Figure 4 which shows the variation in the photo-degradation rate of TOC for a different amount of H_2O_2.
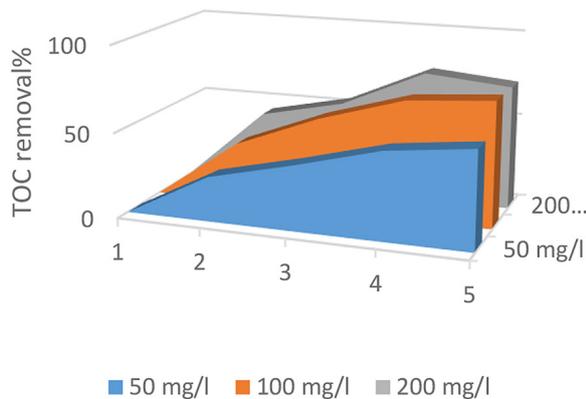
Figure 4. at different H_2O_2 dosage for TOC = 25 mg/l, UV, Q = 50 l/min, and TIO_2 = 250 mg

The highest rate of degradation was found for H_2O_2 (100) mg/l. but over-dosing of H_2O_2 (more than 100) may lead to concurrent reactions that might consume H_2O_2 or lead to H_2O_2 self-decomposing into oxygen and water, reducing the production of OH radicals and decreasing the effectiveness of TOC removal (Kruithof et al., 2007).

Process configuration by TUOT

For the treatment of organic compounds that are barely degradable, a combination of photocatalysts and ozone is a feasible option since the organic compounds are anticipated to degrade more quickly and accomplish complete mineralization to water and carbon dioxide. Adsorbed ozone can clearly operate as a very powerful electrophilic agent to form OH radicals through O^3. reaction pathways (Equation 12) by trapping photoproduced electrons in the heterogeneous photocatalytic process with ozone (Sanchez et al., 1998). Ozone input dosage of 200 mg/h with 250 mg of TIO_2 to obtain the removal efficiencies of TOC 80%.
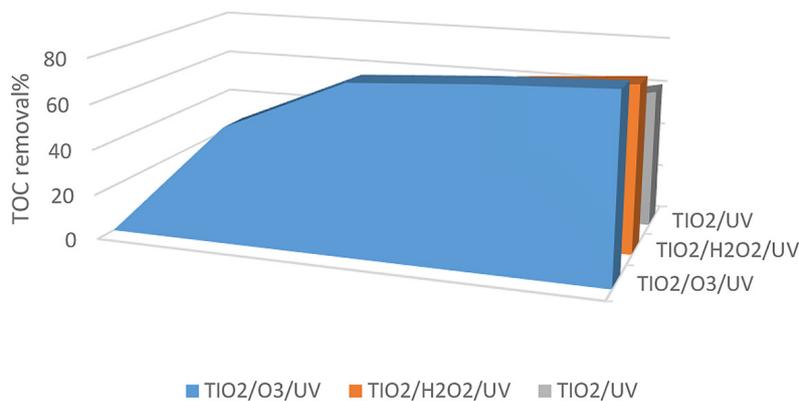
Figure 5. Removal efficiencies of TOC at different process TUT, TUHT, TUOT

$$O_3 + e^- \rightarrow O_{3\sigma}^- \tag{12}$$

$$O_{3\sigma}^- + H^+ \rightarrow HO_3 \tag{13}$$

$$HO_{3\sigma} \rightarrow O_2 + OH_\sigma \tag{14}$$
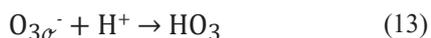
Kinetic results

Equation (4) was applied to all of the experimental results to find the rate of reaction (removal of TOC by TUT). In pseudo-first order; a plot of (-ln Ct/Ci) vs. time is shown in Figure 6. The slope of the line in this plot is equal to the pseudo-first-order rate constant k (min^{-1}) and the intercept is equal to ln (Ci). The calculated value of k for the different operating conditions listed in Table 4.

Table 5 shows that the rate of TOC removal k increases as the initial concentrations of TOC decrease 0.0083, 0.0042, and 0.0020 min^{-1} for TOC initial 20, 150, and 500 mg/l respectively. The K values using different TIO$_2$ dosages were 0.0024, 0.0083, and 0.0076 min^{-1} For 50/500, 250/500, and 500/500 mg/l respectively. The rate constant increases at a TIO$_2$ concentration of 250 mg/500 ml. Also, the k values increase as the flow rate decrease 0.0083, 0.0063, and 0.0049 min^{-1} for flow rate 50, 150, and 250 ml/min.

For K values increase when using TUOT to 0.013 min^{-1} which is higher than the k value of 0.0083 min^{-1} using TUT for the removal of 20 mg/l TOC concentration. Also, k values are high when using TUHT to 0.011 min^{-1}.
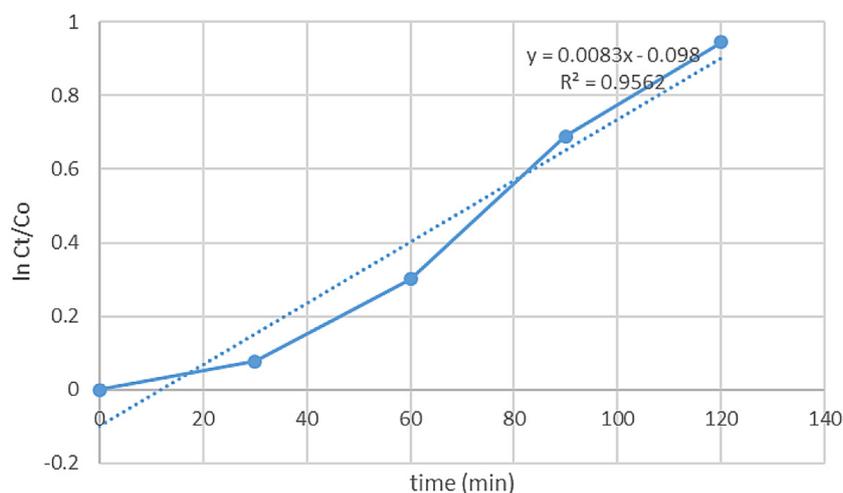

Figure 6. First-order rate constant of TOC removal by TUT at 20 mg/l concentration, 250 g TIO$_2$

Table 4. First-order rate constant k (min^{-1}) under various conditions of operation

| Exp.	Toc conc., mg/l	TIO$_2$, mg/l	Flow rate, ml/min	K, min^{-1}	R2
1	20	250/500	50	0.0083	0.956
2	150	250/500	50	0.0042	0.9704
3	500	250/500	50	0.002	0.6636
4	20	50/500	50	0.0024	0.9107
5	20	250/500	50	0.0083	0.956
6	20	500/500	50	0.0076	0.9316
7	20	250/500	50	0.0083	0.956
8	20	250/500	150	0.0063	0.9556
9	20	250/500	250	0.0049	0.9427

Table 5. First-order rate constant k (min^{-1}) under various conditions of process

Process	Toc conc., mg/l	TIO$_2$, mg/L	Flow rate, ml/min	H$_2$O$_2$, mg/l	O$_3$, mg/h	K, min^{-1}	R
TUT	20	250/500	50	0	0	0.0083	0.956
TUHT	20	250/500	50	100	0	0.011	0.975
TUOT	20	250/500	50	0	200	0.013	0.880

Table 6. Comparison between TIO$_2$, TUT, TUHT, TUOT for different times

Type	Time (min)					LSD$_{0.05}$ p-value
	0	30	60	90	120	
TIO$_2$	0 d	1.34% c	3.90% b	4.53% ab	6.64% a	3.743 0.0049 HS
TUT	0 e	7.42% d	23.18% c	49.83% b	61.15% a	4.357 0.0051 HS
TUHT	0 d	35% c	54.50% b	69.30% a	73.20% a	4.632 0.0017 HS
TUOT	0 d	51.50% c	74.56% b	77.90% ab	80% a	3.666 0.023 S
LSD$_{0.05}$ p-value	NS	4.249 0.0032 S	3.489 0.0026 S	5.341 0.0013 HS	3.440 0.0143 S	

Note: NS – non-significant difference at 0.05 level S: significant difference at 0.05 level, HS – high significant difference at 0.01 level . Different letters are significant difference between groups.
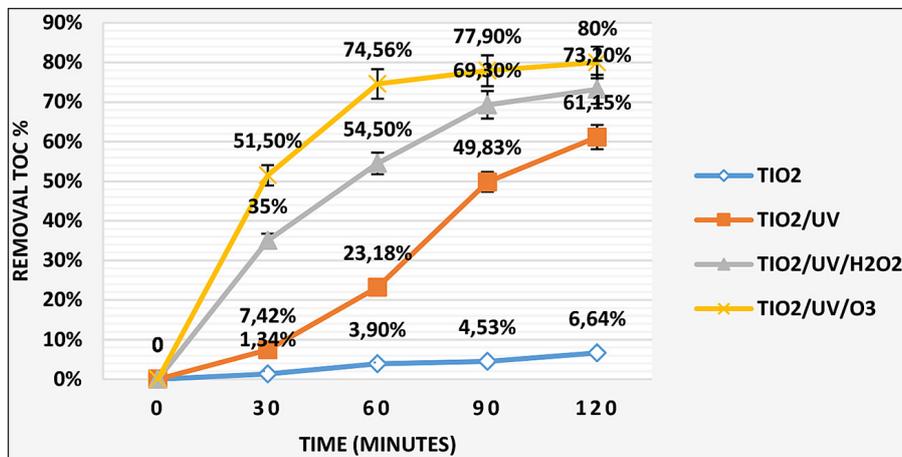
Figure 7. Comparison between TIO$_2$, TUT, TUHT, and TUOT for different times

Statistical analysis

The statistical program SPSS (Statistical Package for Social Science) version 26 is used to analyze the dataset used throughout this study. the analysis of variance (ANOVA) is used to compare between the groups. lest square difference (LSD) test was used to check the multiple comparisons between groups with a significant level of 5% (p-value < 0.05) and 1% (p-value < 0.01) (Table 6). The result of the statistical analysis is shown in Figure 7.

CONCLUSIONS

The photocatalytic method was used to clean synthetic wastewater that was primarily made up of organic carbon in this study. Total organic carbon removal was measured using different combinations of titanium dioxide, UV, hydrogen peroxide, and ozone. It was concluded, TUT method is a good method for TOC where 61% of TOC removal is achieved under 25 mg/l of TOC initial, 250/500 mg/l of TIO$_2$. Also, the result concluded that adding 100 mg/l H$_2$O$_2$ to the TUT system called the TUHT process was 73% successful for TOC removal. As a result, the addition of a zone significantly increased the TOC removal to (80%). It was concluded that the removal of total organic carbon is decreased as its initial concentration increase, reaching 61% at 20 mg/l TOC concentration at 2 hours. but was not exceeded 3% at 500 mg/l. Also, effect of flow rate and catalytic TIO$_2$ dosage on the TUT methods were systematically evaluated, and the most favorable conditions were found to be at the flow rate of 50 l/min, and TIO$_2$ dosage of 250 mg/500 ml. Increasing the concentration of H$_2$O$_2$ from 50 to 100 mg/l increased TOC removal from 56% to 73%. The kinetic study concluded that the TOC removal increases when using TUOT to 0.013 min^{-1} of K values which is higher than the 0.0083

min^{-1} k value when using TUT for the removal of 20 mg/l TOC concentration. Also, it was increased to 0.011 min^{-1} k when using TUHT. As a final observation, this work concluded that TUOT is a good technology for organic removal.

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