



# Photocatalytic Degradation of Sulfamethoxazole from a Synthetic Pharmaceutical Wastewater Using Titanium Dioxide (TiO<sub>2</sub>) Powder as a Suspended Heterogeneous Catalyst

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## Abstract

Some medications in aquatic media pose a serious environmental risk. Sulfamethoxazole (SMX) is a member of the sulfonamide group. Photocatalysis offers a promising technique to degrade organic pollutants into environmentally friendly substances. This study examined the effect of operating conditions (pH, time, and temperature) of the ultraviolet (UV)/TiO<sub>2</sub> photocatalytic process on the degradation of SMX in an aqueous solution. Decreasing the pH value positively affects SMX degradation, and better removal values were obtained at a pH equal to 4. The optimum operating conditions for complete degradation in a solution containing 500 mg/L of SMX, TiO<sub>2</sub> 0.5 mg/L irradiation time of 420 min, and pH 4. Under these conditions, Chemical Oxygen Demand (COD) removal was 62.6% at a temperature of 25 °C. The effect of temperature was studied at three temperatures (25, 40, and 60 °C) with pH 4. The elevation of temperature increased the COD removal rate to 99.62% at 60 °C. Finally, the results of the reaction kinetics study showed that a first-order kinetics model described organic contamination removal data over time, and the obtained activation energy was 42.195 kJ/mol.

## 1. Introduction

The existence of pharmaceutical substances in wastewater might cause harmful effects on living organisms and posing environmental concerns [1]. Pharmaceutical compounds shaped new micropollutants entering the aquatic ecosystem [2]. Globally there are two thousand active pharmaceutical substances prescribed for humans and animals. The concentration is within the range ng/L to mg/L in water bodies [3]. Trace concentrations of pharmaceuticals can cause physiological effects on humans and animals because it designed for attacking pathogenic bacteria [4]. Among different pharmaceutical compounds, antibiotics have been significant because they can develop antibiotic resistance in pathogenic bacteria [5]. Antibiotics are the most utilized medicine in the hospital to treat different diseases, so they are expected to have high concentrations in effluents [6]. Antibiotics

are chemotherapeutic medicine that inhibits or kill various microorganisms like bacteria, fungi, viruses, microalgae, or protozoa. Antibiotics are divided into different groups depending on chemical structure, and their mechanism of action including beta-lactams, aminoglycosides, diaminopyrimidines, glycopeptides, macrolides, quinolones, sulfonamides, tetracyclines, and others [3]. The bodies of humans and animals metabolize antibiotics. The body gets rid of 20 to 90% of these substances through urine and excretion [7]. Antibiotics can endure natural decomposition and consider toxic, bio-accumulative, and mobile substances. Antibiotics are created to affect living organisms even at low doses [3].

One of the oldest antibiotics widely utilized is sulfonamides [8]. Sulfonamides have been detected in water treatment plants' effluents, groundwater, surface water, and drinking water [9]. Sulfamethoxazole a member of the sulfonamide group, and it is prescribed to treat different infection diseases in humans [10]. Sulfamethoxazole is detected as less biodegradability among other antibiotics microcosm studies [11]. The concentration ranges of sulfamethoxazole in fresh water for human consumption from 100 pg/L to a few ng/L. Whereas in wastewater treatment plants, effluents range from 10 to 1500 ng/L and groundwater from 0.2 to 1100 ng/L [12]. Antibiotics have been assigned as the leading polluter of the aquatic environment among the pharmaceuticals. Sulfamethoxazole poses a high-risk ranking of antibiotics relative to others because of their discharge, persistence, toxic properties, and higher consumption [9].

The advanced oxidation process has received significant interest for the removal of medical substances disposed in wastewater [2]. The advanced oxidation process using heterogeneous catalysts is preferred because of its low toxicity and cost, chemical stability, and high reactivity [13]. Heterogeneous photocatalysis is gaining much interest after the Fenton process because of its simplicity and sustainability. The utilization of solar energy as a light source is considered green and sustainable technology for wastewater treatment [3]. Highly reactive radicals like hydroxyl radicals are produced in the heterogeneous photocatalysis process; these radicals attack a wide range of organic compounds and transform into more biodegradable and less toxic substances [14]. Different solid metal oxides are used in heterogeneous photocatalysis, such as  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{CeO}_2$ ,  $\text{CdS}$ ,  $\text{MoO}_3$ ,  $\text{SrTiO}_3$ ,  $\text{MoV}_4$ ,  $\text{WO}_3$ , which improves the photocatalytic efficiency and reduce the radiation required in the process [15,16]. The mechanism of the photocatalytic process includes the activation catalyst by sunlight or artificial light [5]. Titanium dioxide has been a broad catalyst used in heterogeneous photocatalysis due to less toxicity, low cost, and high reactivity and chemical stability.  $\text{TiO}_2$  has semiconductor properties when it absorbs enough energy, electrons transform from valance band to the conduction band, and quick recombination of electrons and electron holes [13]. The advantages mentioned above using  $\text{TiO}_2$  as a catalyst have pushed the scientists to conduct searches in photocatalysis fields for treatment of wastewater which contaminants with pharmaceutical compounds.

This work aimed to deal with the removal of SMX antibiotic ( $\text{C}_{10}\text{H}_{11}\text{N}_3\text{O}_3\text{S}$ ) from synthetic pharmaceutical wastewater by using  $\text{TiO}_2$  powder as a suspended photocatalyst. The effects of pH, reaction time and temperature on the removal of SMX and their oxidized derivatives by COD were examined and the kinetics of the total organic removal studied.

## 2. Experimental Procedure

The chemicals used in these experiments were SMX (100%), sodium hydroxide (97%), and sulfuric acid (98%).  $\text{TiO}_2$  (with  $4.23 \text{ g/cm}^3$  apparent density and 25 nm average particle diameter) was used as a suspended heterogeneous catalyst. All the chemicals used in this work were purchased from Sigma-Aldrich. The experimental setup was composed of a tubular Perspex reactor (length of 30 cm, inner diameter of 1.8 cm). This photoreactor was placed in a perforated wood box emitted by the two UV lamps of 16W (254 nm wavelength). The contaminated solution was recirculated to the reactor from a reservoir container whose temperature was controlled by a bath placed on a magnetically stirred heater (LABINCO, model L-81). The reaction temperatures were 25, 40 and 60 °C. The reservoir tank (1 L) was loaded with a SMX solution of 500 mg/L (as COD), and it was recirculated through the system with a rate of 1.2 L/min. Afterward,  $\text{TiO}_2$  powder was added to the solution, and the resulting suspension (0.5 g  $\text{TiO}_2$ /L) was recirculated for one hour in the darkness to ensure that the adsorption equilibrium was achieved. Then, the light was turned on, and the photodegradation started. The reaction time was up to 420 minutes and the samples were taken periodically.

The SMX and the formed organic intermediates concentration as COD was measured by using a COD reactor (Lovibond® Water Testing, MD 200 COD, tube tests, Germany). The sample was withdrawn, and 2 mL of it was added to a tube containing a standard amount of oxidizing mixture of potassium dichromate and would be oxidized at 150°C for two hours. The vial was left at room temperature until it cooled down and measured with a MD200 photometer (Lovibond® Water Testing, Thermoreactor RD 125, Germany). The organic removal efficiency (as COD) has been measured using Eq. (1).

$$COD\ removal, \% = \frac{COD_o - COD_t}{COD_o} \times 100 \quad (1)$$

Where  $COD_o$  was the initial organic concentration, and  $COD_t$  was the concentration of the organics at time (t).

The pH of the experiments was carried out at 4 and 7. The initial pH values were adjusted by adding 0.5 M sulfuric acid or 0.1 M NaOH solution.

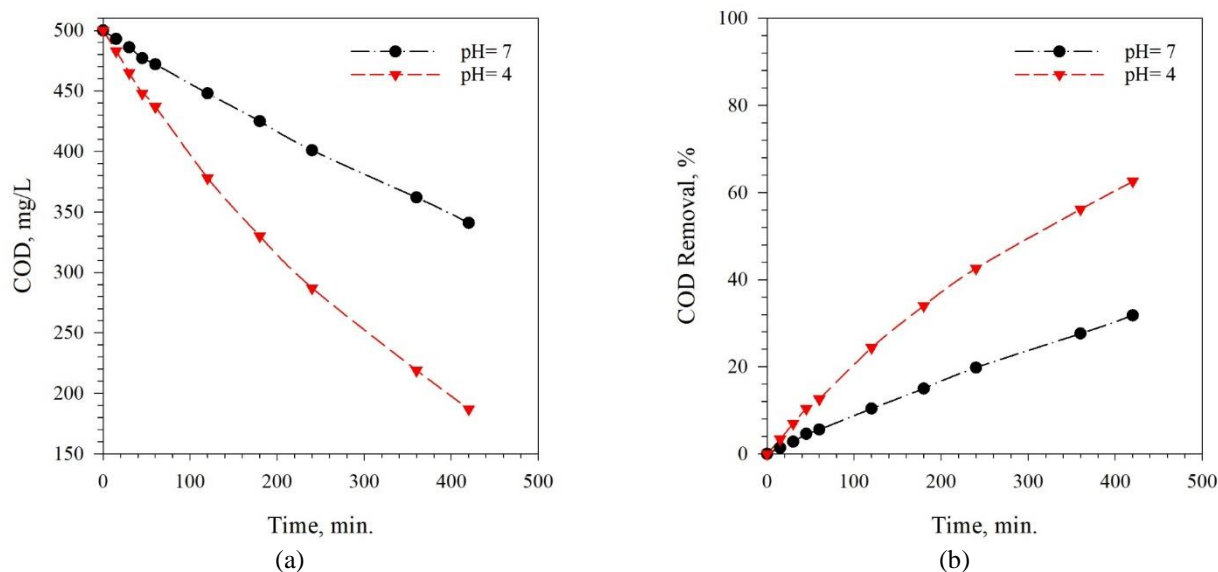
### 3. Results and Discussion

#### Effect of pH

pH is considered an essential factor because of it influences the surface charge properties of the semiconductor. The effect of the initial pH on the degradation of SMX experiments were conducted at pH 4 and 7. The experimental conditions were initial COD concentration 500 mg/L,  $TiO_2$  0.5 g/L, and irradiation time up to 420 min. Figure (1 a & b) shows the effect of pH on the degradation in terms of COD concentration and COD removal, respectively. COD concentration at pH 7 after 420 min was 341 mg/L. Whereas COD concentration at pH 4 after 420 min was 187 mg/L as shown in Figure (1 a). The degradation of organic pollutants was more in acidic solution. pH effect on the photocatalytic process is extraordinarily complex task because of its multiple roles such as electrostatic interactions between the semiconductor surface, substrate, solvent molecules and charged radicals shaped during the reaction process. The ionization state of the surface of the photocatalyst can be protonated under acidic as shown in Eq. (2) [17].



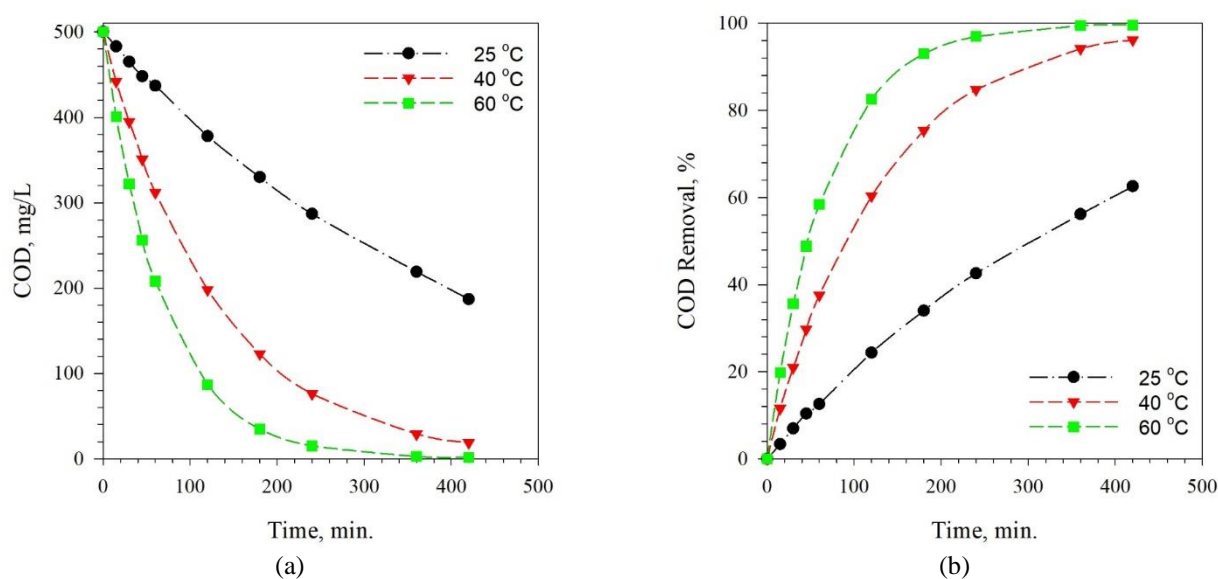
The experimental findings have shown that the degradation of SMX was strongly affected by the reaction pH. The best efficiency for the degradation of the organics at pH 4 might be attributed to adsorption affinity. With acidic condition, SMX is positively charged which is the same as  $TiO_2$  surface resulting in repulsion between them [17]. Figure (1 b) shows the removal increased to 62.2 % at pH 4 while the removal at pH 7 was 31.8% at room temperature. This suggests that photocatalytic oxidation under UV/ $TiO_2$  is the best candidate to treat water or wastewater contaminated with SMX compounds under pH 4.



**Figure 1.** (a) Organic concentration as COD, (b) COD removal, versus time at different pH values and 25°C.

### Effect of Reaction Temperature

The reaction temperature of photocatalysts was another significant factor. Figure (2 a & b) shows the COD concentration and COD removal at temperature 25, 40, 60 °C, respectively. Experiments were carried out at acidic conditions pH 4 because of the best removal was 62.6%. Figure (2 a) shows the COD concentration reached 1.9 mg/L after 420 min while at room temperature the COD concentration was 187 mg/L and at 40 °C the COD concentration was 19 mg/ L. Therefore, after calculation of the removal efficiency (Eq. 1) and as shown in Figure (2 b), the organic pollutants removal at pH 4 was 99.62 % at 60°C. Increasing the reaction temperature contributes significantly to increasing the energy of the interacting molecules and increasing the number of collisions between them, which contributes significantly to increase the rate of the reaction [18]. The obtained results were consistent with the previous study [19] that found the elevation of temperature will increase the photodegradation within a certain range. The removal findings were promising compared to antibiotics' removal by adsorption [20-26].



**Figure 2.** (a) Organic concentration as COD, (b) COD removal vs. time at various temperatures at pH equals 4.

### Kinetics Analysis

The study of reaction kinetics aims to provide useful information for the reactor design, scale up, and to test the desired reactor. A kinetic model of SMX and formed organic intermediates degradation by the photocatalysis process had been proposed that had been tested [27]. The flow model was used for fitting the experimental data of organic degradation (as COD) was shown in Eq. (3).

$$V_{photo}(-r_{COD}) = -V_T \frac{dCOD}{dt} \quad (3)$$

Where:  $V_{photo}$  is the volume of the photoreactor (0.0763 L),  $r_{COD}$  is the reaction rate of organic (degradation or removal rate of COD),  $V_T$  is the total volume of the system (1.08 L).

Assuming the oxidation reaction via photocatalytic process follows an apparently first-order kinetic model [18] as in Eq. (4).

$$-r_{COD} = k COD \quad (4)$$

Where:  $k$  is the apparent reaction rate coefficient.

Inserting Eq. (4) into Eq. (3) and after using the integration approach to obtain the suggested model (Eq. 5).

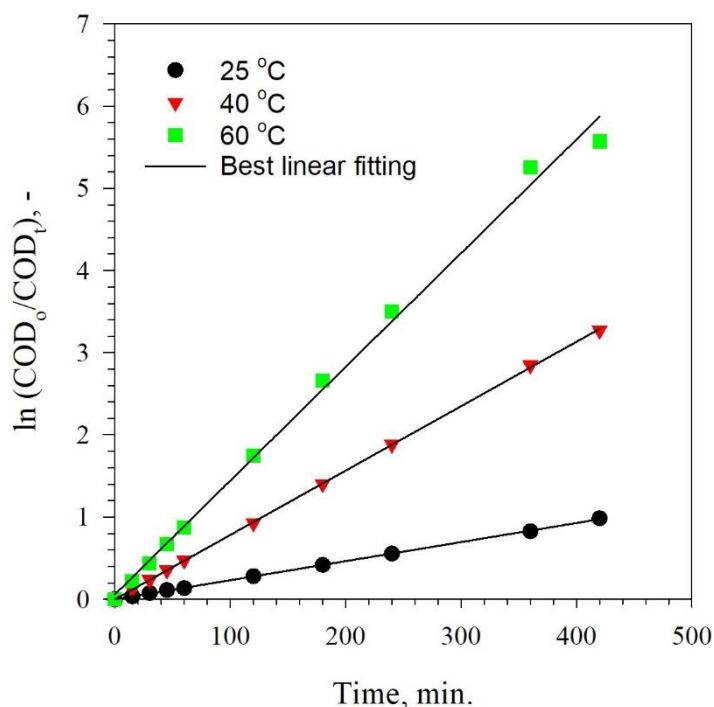
$$COD_t = COD_o \exp\left(-\frac{V_{photo}}{V_T} kt\right) \quad (5)$$

Rearrangement and linearization of Eq. (5), gives Eq. (6).

$$\ln\left(\frac{COD_o}{COD_t}\right) = \left(\frac{V_R}{V_T}\right) kt \quad (6)$$

The kinetic data that obtained experimentally was used to find the values of  $k$  from Eq. (6), at different temperatures (25 to 60 °C), as shown in Figure (3). Table (1) summarized values of Eq. (6) slope, correlation coefficient ( $R^2$ ), and the calculated  $k$  at different temperatures.

The best fitting results indicated that the calculated values of  $k$  increase with temperature. As lowest value was  $0.03256 \text{ min.}^{-1}$  at a temperature of 25 °C, while the value of the reaction coefficient was  $0.19958 \text{ min.}^{-1}$  at the highest degree used (60 °C).



**Figure (3).** Kinetics of the organic concentration (as COD) and the best fitting according to Eq. (6) at different temperatures at pH equal to 4.

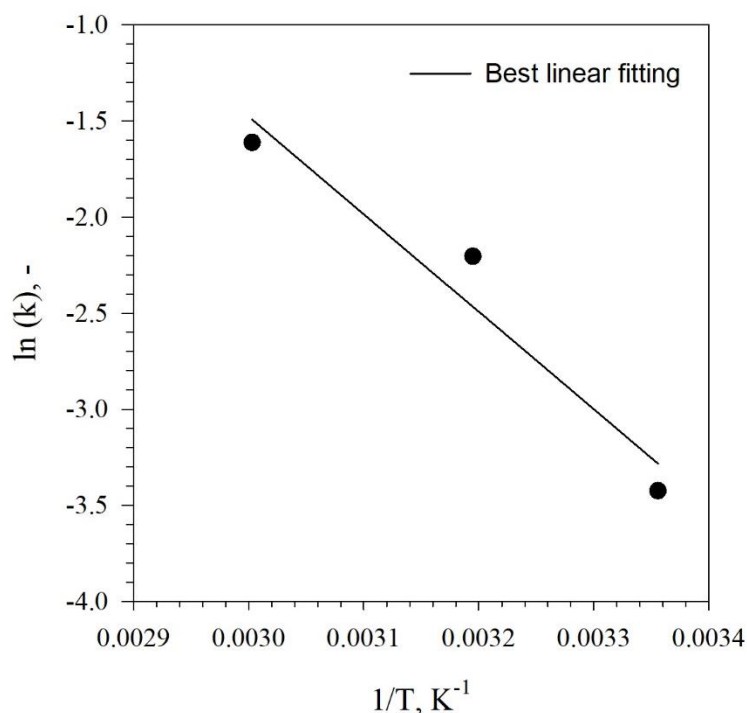
**Table (1).** Kinetics model slopes,  $R^2$ , and the calculated  $k$  at different temperatures at pH equal to 4.

Temp., °C	Eq. (6) slope = $\left(\frac{V_R}{V_T}\right)k$ , min. <sup>-1</sup>	$R^2$ , -	$k$ , min. <sup>-1</sup>
25	0.0023	0.9998	0.03256
40	0.0078	0.9989	0.11041
60	0.0141	0.9977	0.19958

The linear form of the Arrhenius equation (Eq. 7) was fitted and plotted in Figure (4) with the obtained data to consider the effect of the absolute reaction temperature ( $T$ ) in Kelvin on the reaction rate coefficient ( $k$ ) and to calculate the activation energy ( $E$ ) and frequency factor ( $k_o$ ) of the oxidation reaction of organic pollutants by a photocatalytic reaction.

$$\ln(k) = \ln(k_o) - \frac{E}{RT} \quad (7)$$

Where:  $R$  is the universal gas constant (8.314 J/mol. K).



**Figure (4).** Arrhenius plot (Eq. 7) for the photocatalytic oxidation reaction of SMX and the formed intermediates at pH equal to 4.

The calculated value of the frequency factor was equal to  $935653 \text{ min}^{-1}$  and the activation energy of the oxidation of SMX and the formed organic intermediates via photocatalyst reaction using  $\text{TiO}_2$  was  $42.195 \text{ kJ/mol}$ .

#### 4. Conclusions

This study reveals the optimum conditions for photocatalytic process on the degradation of SMX in an aqueous solution. The degradation of organic pollutants was more in acidic solution, at pH 4 the removal was 62.6% after 420 min at a temperature  $25 \text{ }^\circ\text{C}$ . Moreover, when studied the effects of temperature at three various degrees 25, 40,  $60 \text{ }^\circ\text{C}$ , the removal was increased to 99.6% at  $60 \text{ }^\circ\text{C}$ . Therefore, the best conditions for removal  $500 \text{ mg/L}$  of SMX, by using  $\text{TiO}_2$   $0.5 \text{ mg/L}$  as a catalyst with ultraviolet irradiation time 420 min, at pH 4 and temperature  $60^\circ\text{C}$ . The results of the reaction kinetics data fitted with a first-order kinetics model and the activation energy of the oxidation of SMX via photocatalytic reaction was  $42.195 \text{ kJ/mol}$ .

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