

Kinetic Study of the Photocatalytic Reaction of Paracetamol and Determination of the Reaction Order

Fatima I. Jasim , Layla.A.Al.Juber

Department of Chemistry, College of Science, Tikrit University, Tikrit

Corresponding author Email: fatima.ibrahem@st.tu.edu.iq

Abstract :

This research aims to investigate the kinetics of the photodegradation of paracetamol using a nanophotocatalyst composed of silver oxide hybridized with polyaniline. The variation in absorbance at a wavelength of 243 nm was monitored using a UV-Vis spectrophotometer to determine the reaction behavior and establish its order. The results revealed that the reaction follows a pseudo-first-order kinetic model, as evidenced by the linear relationship between $(\ln A_t/A_0)$ and time (t), with a correlation coefficient of $R^2 = 0.98$. This indicates good agreement between the experimental data and the first-order kinetic model. These findings highlight the importance of kinetic studies in evaluating the efficiency of nanocatalysts employed for the removal of pharmaceutical pollutants from water.

Keywords: Paracetamol Photodegradation, Hybrid Nanocatalyst, Xenon Light Irradiation, Pseudo-First-Order Kinetics .

دراسة حركية التفاعل الضوئي التحفيزي للباراسيتامول وتحديد رتبة التفاعل

فاطمة إبراهيم جاسم ، ليلى عبد الرحمن الجبر

جامعة تكريت / كلية العلوم - قسم الكيمياء

مستخلص:

يهدف هذا البحث إلى دراسة حركية التحلل الضوئي للباراسيتامول باستخدام محفز نانوي ضوئي مكون من أكسيد الفضة المهجن مع البولي أنيلين. تم تتبع تغير الامتصاصية عند طول موجي مقداره 243 نانومتر باستخدام جهاز مطيافية UV-Vis لتحديد سلوك التفاعل وتعيين رتبته. أظهرت النتائج أن التفاعل يتبع نموذج حركية الرتبة الأولى (Pseudo-First Order)، وذلك من خلال العلاقة الخطية بين $(\ln A_t/A_0)$ والزمن (t)، مع معامل ارتباط بلغ $R^2 = 0.98$ ، مما يشير إلى توافق جيد بين البيانات التجريبية ونموذج الرتبة الأولى. وتؤكد هذه النتائج أهمية الدراسات الحركية في تقييم كفاءة المحفزات النانوية المستخدمة في إزالة الملوثات الدوائية من المياه.

الكلمات المفتاحية: التحلل الضوئي للباراسيتامول، محفز نانوي هجين، اشعاع ضوء الزينون، حركية الرتبة الأولى-الزائفة.

1-Introduction

The study of reaction kinetics is a fundamental aspect in understanding the mechanism of the photodegradation of organic pollutants, as it enables the determination of reaction rates and the factors influencing them[1]. Paracetamol is one of the most widely detected pharmaceutical compounds in aquatic environments due to its excessive consumption and the difficulty of its removal by conventional treatment methods[2]. The use of nanomaterials as photocatalysts, such as silver oxide hybridized with polyaniline, has been shown to accelerate degradation processes and enhance their efficiency owing to their superior surface and electronic properties[3]. This study aims to analyze the experimental data of paracetamol photodegradation under xenon light and to determine the reaction order based on the change in absorbance over time, thereby providing a deeper understanding of the reaction's kinetic mechanism.

Nanocatalysts have gained significant attention in recent years due to their high surface-to-volume ratio, en-

hanced charge separation, and superior catalytic activity compared to bulk materials[4]. Among these materials, silver oxide (Ag_2O) exhibits excellent photocatalytic performance owing to its narrow band gap and strong visible-light absorption[5]. Polyaniline (PANI), a conductive polymer, has also been widely used to improve photocatalytic activity by enhancing electron transfer and reducing recombination rates[6]. When Ag_2O is hybridized with PANI, the resulting nanocomposite provides a synergistic effect, improving stability, charge mobility, and pollutant adsorption capacity, thereby enhancing its photocatalytic efficiency. Paracetamol has been classified as an emerging contaminant due to its persistence in wastewater, hospital effluents, and natural water bodies[7]. High concentrations of paracetamol pose ecological risks, including toxicity to aquatic organisms and potential long-term environmental impacts[8]. Its incomplete removal by traditional treatment methods necessitates the development of efficient photocatalytic routes for degradation. Xenon lamps are commonly used in photocatalysis

because their emission spectrum closely mimics natural sunlight, covering both UV and visible regions[9]. This broad spectrum effectively activates visible-light-responsive photocatalysts such as $\text{Ag}_2\text{O}/\text{PANI}$, enhancing degradation efficiency under simulated sunlight conditions. Photocatalytic degradation frequently follows pseudo-first-order kinetics, especially at low pollutant concentrations, according to the Langmuir–Hinshelwood mechanism[10]. Evaluating the kinetic behavior of paracetamol degradation is essential for assessing catalyst performance and understanding the reaction pathway.

1- Apparatus and Materials

2-1 Apparatus used:

- UV–Vis spectrophotometer.
- Xenon light source with a power of 300 W.
- Digital pH meter.
- Magnetic stirrer to maintain homogeneity during irradiation.

2-2 Chemical Substances and Solutions:

2-2-1 Synthesis of Silver Oxide Nanoparticles (Ag_2O NPs)

a- A silver nitrate solution was prepared by dissolving 0.445 g of AgNO_3 in 35 mL of deionized water under dark conditions and stirring magnetically for 2 hours.

b- A 0.15 M sodium hydroxide solution was then prepared by dissolving 0.45 g of NaOH in 75 mL of deionized water. The NaOH solution was added dropwise to the AgNO_3 solution using a burette until the total volume was completed, leading to the formation of a brown precipitate indicating the formation of nano–silver oxide.

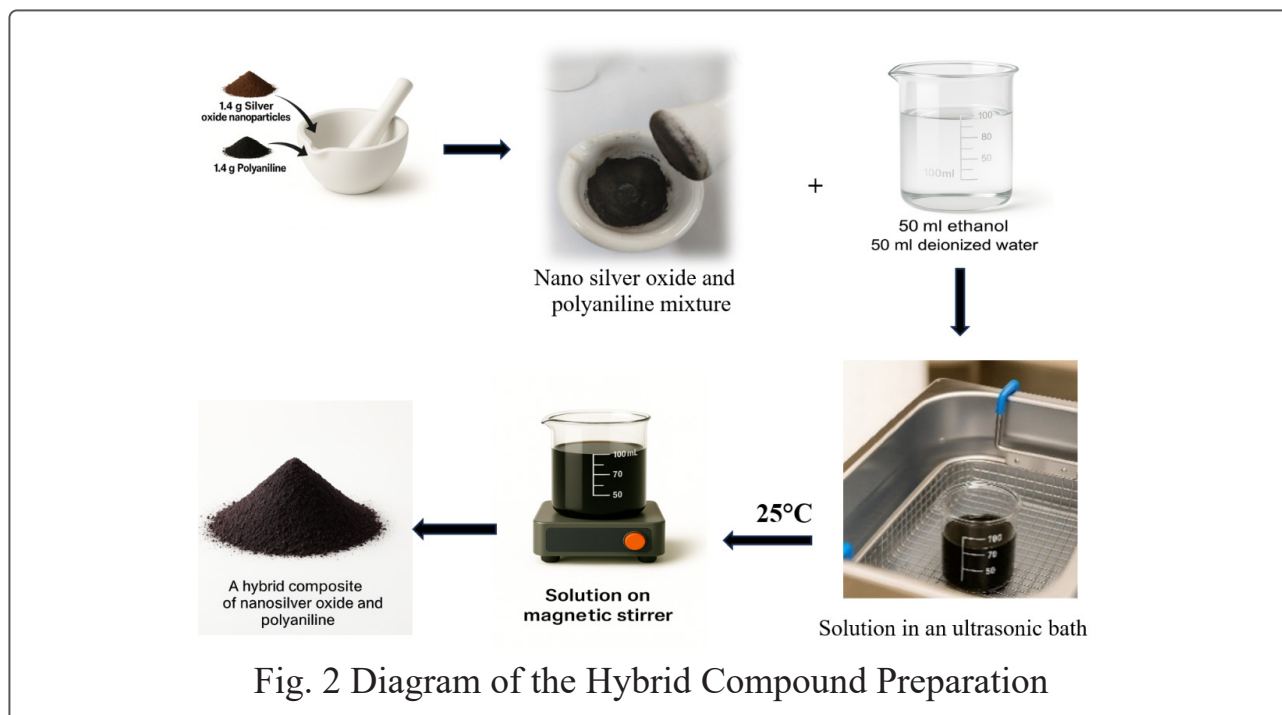
c- The obtained precipitate was stirred for an additional 30 minutes, washed several times with deionized water until a neutral pH was reached, and then dried in an oven at 60 °C.



2-2-2 Preparation of Ag₂O/PANI Hybrid Nanocomposite

a- A mixture of 1.4 g of nano-silver oxide and an equal amount of polyaniline was ground thoroughly using a ceramic mortar. The resulting powder was then transferred into a beaker containing 50 mL of ethanol and 50 mL of deionized water.

b- The mixture was sonicated in an ultrasonic bath for 4 hours, to break up agglomerates and improve particle homogenization. It was then continuously stirred on a magnetic stirrer for 24 hours. After settling, the product was washed several times with deionized water and dried in an oven at 60 °C.



2-2-3 preparation of paracetamol solution

A stock solution of paracetamol (100 ppm) was prepared by dissolving 0.01 g of pure paracetamol powder in 100 mL of deionized water. A 15ppm paracetamol solution was then obtained by diluting 7.5 mL of the stock solution to a final volume of 50 mL with deionized water.

2- Photocatalytic Degradation of Paracetamol using the Hybrid nanocomposite

The efficiency of the hybrid nanocomposite Ag_2O -PANI in photocatalyzing the degradation of paracetamol was tested under a 300 W xenon light source, aiming to determine the reaction order[11]. A 15ppm paracetamol solution was prepared by diluting an appropriate volume of the 100ppm stock solution with deionized water to ensure an accurate concentration for the experiment[12]. Then, 0.12 g of the Ag_2O -PANI nanocomposite was added to the paracetamol solution, and the resulting suspension was magnetically stirred in the dark for 60 minutes to establish adsorption-desorption equilib-

rium between paracetamol molecules and the catalyst surface[13]. After that, the suspension was exposed to continuous xenon light irradiation to initiate the photocatalytic reaction.

Samples were withdrawn at different time intervals (0–90 minutes) with 5 mL being withdrawn every 10 minutes, and the absorbance was measured at 243 nm to monitor the photocatalytic degradation of paracetamol[14].

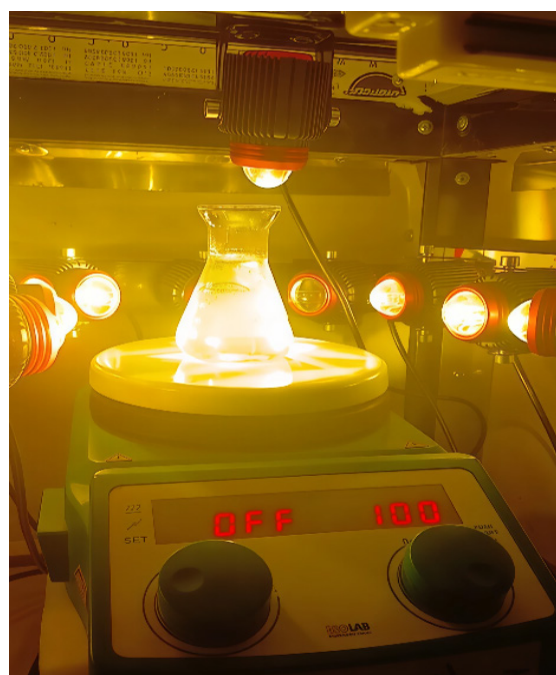


Fig. 3 Xenon irradiation of the paracetamol solution with the hybrid catalyst

3- Result and Discussion:

The ratio (A_t/A_0) was calculated for each time point, and the following

plots were constructed to determine the reaction order[15][16]

- First-order: $\ln \frac{A_0}{A_t} = k \times t$
- Second-order: $\frac{1}{A_t} = k \times t + \frac{1}{A_0}$
- Zero-order: $A_t = A_0 - k \times t$

Where (A_0) represents the initial

absorbance before irradiation, and (A_t) represents the absorbance at a specific time (t).

The results showed good linearity with a high correlation coefficient (R^2), confirming that the reaction follows pseudo-first-order kinetics[17].

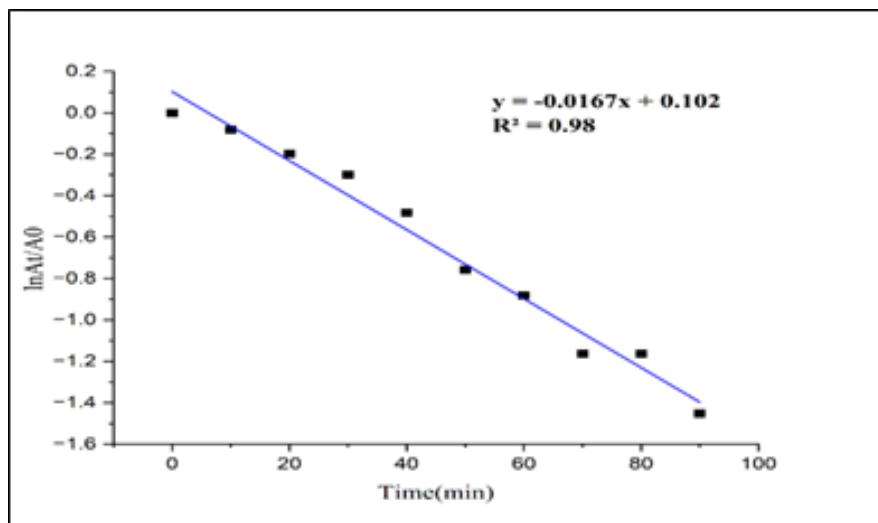


Fig. 4 The relationship between $\ln(A_t/A_0)$ and time (t) at different time intervals.

Another method was also used to calculate the reaction rate constant by plotting $\ln (A_0 - A_\infty)/(A_0 - A_t)$ versus time (t). The plot yielded a straight line whose slope represents the rate constant (k), which was found to be 0.0295 min^{-1} , with a correlation coefficient of $R^2 = 0.8782$. However, the results from the first method confirmed that the reac-

tion follows first-order kinetics, based on the higher correlation coefficient, indicating pseudo-first-order behavior[18].

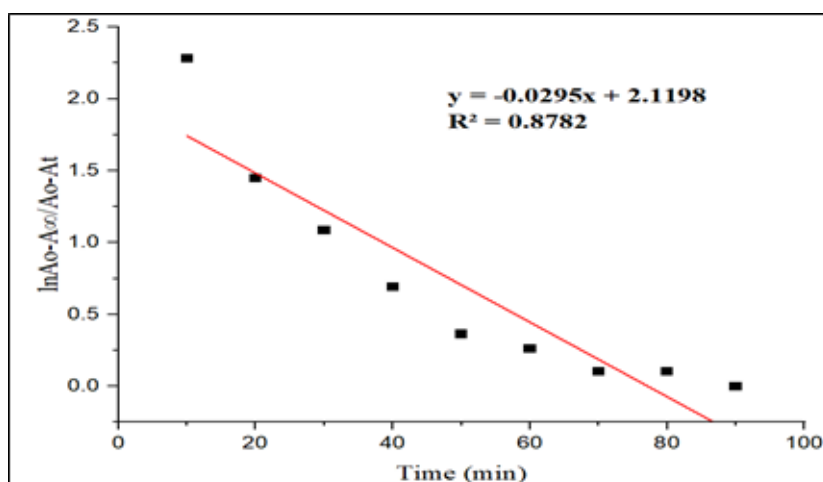


Fig. 5 The relationship between $\ln (A_0 - A_t) / (A_0 - A_t)$ and time (t).

For comparison between different kinetic models, the second-order model was tested by plotting $1/A_t$ versus time (t). Figure 6 shows a straight line whose slope represents the reaction rate constant (k), which was found to be $0.442 \text{ L} \cdot \text{mol}^{-1} \cdot \text{min}^{-1}$, with a correlation coefficient of $R^2 = 0.911$. This R^2

value is lower than that obtained for the first-order model ($R^2 = 0.98$), indicating that the second-order model does not adequately describe the reaction behavior. Therefore, it can be concluded that the reaction follows first-order kinetics.

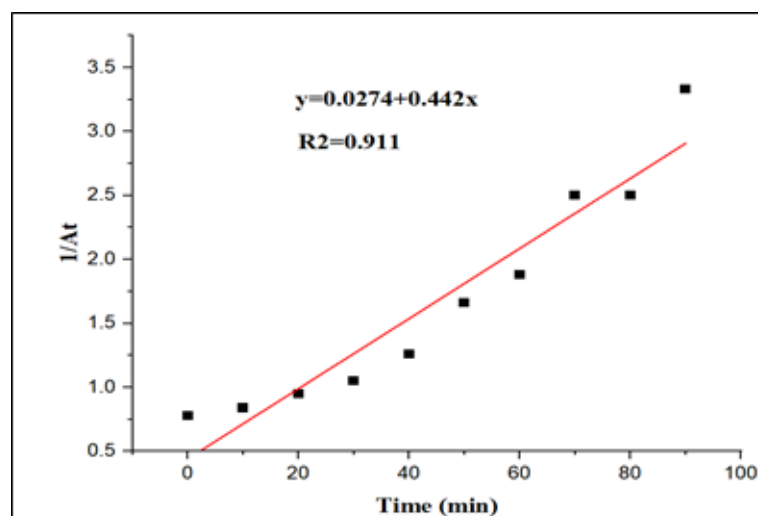


Fig.6 The relationship between $1/A_t$ and time (t).

Table 1 Photodegradation Data of Paracetamol in the Presence of Ag₂O-PANI Hybrid Nanocatalyst

Time (min)	Absorbance (At)	At/A ₀	ln(At/A ₀)
0	1.28	0	0
10	1.18	0.921	-0.081
20	1.05	0.820	-0.198
30	0.95	0.742	-0.298
40	0.79	0.617	-0.482
50	0.6	0.468	-0.757
60	0.53	0.414	-0.881
70	0.4	0.312	-1.163
80	0.4	0.312	-1.163
90	0.3	0.234	-1.451

In addition, the optical band gaps (E_g) of the synthesized materials were estimated using Tauc plots. Pure polyaniline (PANI) exhibited a band gap of approximately 1.00 eV due to its highly conjugated structure[19]. Silver oxide nanoparticles (Ag₂O) showed a band gap of around 1.56 eV, which is consistent with their direct semiconductor nature[20]. For the Ag₂O/PANI hybrid nanocomposite, the band gap decreased to approximately 1.40 eV.

4- Conclusions

a- The degradation of paracetamol in the presence of the hybrid nanocat-

alyst (Ag₂O-PANI) follows pseudo-first-order kinetics.

b- The correlation coefficient (R² ≈ 0.98) confirms the excellent agreement of the experimental data with the kinetic model.

c- The first-order behavior is attributed to the constant concentration of the catalyst relative to the reactant.

d- The results indicate that understanding the reaction kinetics is a crucial step for evaluating the efficiency of photocatalysts and for developing more effective materials for the removal of pharmaceutical pollutants.

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