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Photodegradation of paracetamol using TiO_2 in a rectangular bubble column reactor

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HIGHLIGHTS

- A rectangular bubble column was used for the photodegradation of paracetamol in synthesis wastewater.
- Maximum COD removal (78%) was achieved by introducing air bubbles at a flow rate of 1 L/min.
- pH affected pollutant adsorption, with the optimum pH for photocatalysis found to be 7.

Keywords:
Paracetamol degradation
Photocatalyst
Bubble column

ABSTRACT

Surface water, wastewater, and drinking water have all been found to contain paracetamol and its toxic breakdown products. Effective ways to degrade these products must be discovered to lessen their harmful effects on aquatic microorganisms and human health. The study focuses on finding effective methods to degrade harmful products, specifically paracetamol, to mitigate their negative impact on aquatic microorganisms and human health. To achieve this, the research investigates a photocatalytic process enhanced by introducing air bubbles, aiming to improve the degradation of paracetamol. The experiments were carried out in a batch reactor and a semi-batch rectangular bubble column, which measured 1500 mm in height, 30 mm in depth, and 200 mm in width, all under UV light. Titanium oxide (TiO_2) served as the catalyst. The study examined the impact of various operating conditions, pH levels (ranging from 3 to 10), airflow rates (0 to 2 L/min), and irradiation times (0 to 240 minutes) on the removal of paracetamol the results show that changes in pH values affected the photodegradation of paracetamol, and using pH 7 gives higher COD removal percentage values. Indeed, using air bubbles improves the COD removal percentage to 78%. The degradation of paracetamol was investigated using HPLC analysis, and the maximum removal of paracetamol was 91.2% using optimum operating conditions of pH=7, flow rate 1 L/min, after 240 min. The kinetic study is consistent with the pseudo-first-order reaction model.

1. Introduction

Pharmaceuticals can be considered one of the types of organic pollutants present in wastewater and surface water in all world countries [1-3]. A large variety of these organic pollutants, including analgesics, blood lipid regulators, anti-inflammatories, antimicrobials, and others, are present at very low rates of approximately one microgram per liter, not only in wastewater and surface water but even in drinking water and soil [4-12]. These low levels have been linked to several negative consequences, including acute and chronic harm, tissue accumulation, reproductive damage, suppression of cell growth, and behavioral abnormalities [2,13]. Several emissions from production facilities, consumer use and disposal, and medical waste regularly introduce these developing contaminants into the aquatic ecosystem [14].

Paracetamol is a general analgesic and antipyretic medicine increasingly widely used worldwide [15-16]. According to a prior study, nearly 58-68% of paracetamol and its metabolites are eliminated from the body following therapeutic usage [17]. At the same time, other researchers have stated that the proportion of paracetamol eliminated from the body is between 85 and 95% [18, 19]. However, most pollutant paracetamol sources are from production waste [20].

Currently, chemical oxidation techniques such as electrochemical are used to detoxify paracetamol effluent [21], ozonation [22], H_2O_2/UVoxidation [20,22], TiO_2 photocatalysis [15,23], and solar photoelectron-Fenton oxidation [24]. Although various chemical treatments are available for treating these pollutants, the severe reaction conditions, additional pollutant production, and high operational costs have frequently rendered them unappealing [24-25]. General pharmaceutical component

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biodegradation is being investigated as an ecologically beneficial and low-cost approach, potentially eradicating medicines by decomposing them into harmless end products such as CO_2 and H_2O_2 [25, 26].

Due to its low cost, limited intermediate product generation, and absence of further waste, the photocatalytic process has become more prevalent in water treatment. Photocatalysts are a fast-growing technology for removing refractory and harmful organic contaminants from water, such as colors, insecticides, and medicines [27-29]. The efficiency of these ecologically friendly photochemical wastewater treatment systems is related to the in situ creation of highly oxidizing hydroxyl radicals (OH−) [30], which oxidize a broad spectrum of organic contaminants that may be present in water and wastewaters [31-33]. The photocatalytic process begins when the photocatalyst titanium dioxide TiO_2 is exposed to ultraviolet (UV). When the energy of incoming photons surpasses the band gap of the material, electrons (e-) at the surface of the photocatalyst become "excited" and shift into the conduction band refer to Figure 1. This transition forms a positive hole (h+ VB) in the valence band, as illustrated in Equations (1-3).

$$TiO_2 + hv \rightarrow h^+_{VB} + e^-_{CB} \quad (1)$$

$$e^- + O_2 \rightarrow \cdot O^-_2 \quad (2)$$

$$h^+_{VB} + H_2O \rightarrow \cdot OH + H^+ \quad (3)$$

Some researchers have used different methods of treating paracetamol, and some of them used the electrocoagulation process as a method of paracetamol removal from synthetic and real industry wastewater [34], the results of the TOC and COD tests were 63.2 and 60.8%, respectively for synthetic wastewater, and 66 and 62.5%, respectively for real wastewater. Some used the Fenton process for paracetamol removal, and the results of COD, TOC, and BOD were 92.7, 92.7, 95.5, and 99.1, respectively [35]. In 2012, Pei Xiong et al. [36], investigated the degradation of acetaminophen (paracetamol) by the UVA/LED/TiO_2 process. The findings indicated that the selected UVA/LED resulted in a minimal degradation of Ace, whereas when TiO_2 was included, there was a significant reduction in the concentration of Ace. Paracetamol oxidation is studied utilizing ozonation and H_2O_2 photolysis, where it was found that both systems can convert part of the first carbon into carbon dioxide with a degree of decomposition up to 30 and 40% by ozonation and H_2O_2 photolysis, respectively [22]. The photocatalytic destruction of the growing pollutant paracetamol in an aqueous solution was applied with the presence of four commercial TiO_2 powders, namely sub-micrometric anatase and rutile, and nanometric brookite and P25, the rutile powder had modest activity. However, the anatase and brookite powders exceeded P25 in total paracetamol conversion to carboxylic acids, which end products of its breakdown [37]. Stoyanova et al. [38], study synthesizes and analyzes pure and La-doped TiO_2, evaluating their photocatalytic and antibacterial activities. Nanopowders were prepared using a non-hydrolytic sol-gel method, with La content of 0.4, 1, and 5 mol%, and characterized by XRD, IR, and UV–Vis analysis. Results showed that La doping reduced particle size, maintained anatase as the dominant phase, and enhanced photocatalytic degradation of paracetamol under UV light. Mohammed et al. [39], study focused on the synthesis of TiO_2 nanoparticles and the formation of nanocomposites by varying the loading of graphitic carbon nitride (GCN). Characterization results confirmed successful modification, while photocatalytic tests indicated that loading of 2 wt.% GCN achieved the highest degradation rate of 0.0364 min^{-1} under specific conditions. The synergistic effect between TiO_2 and GCN significantly enhanced photocatalytic activity, positioning these nanocomposites as promising candidates for treating pharmaceutical wastewater.

Although many researchers have studied pharmaceutical waste removal using the photocatalyst process, the need to improve this process is still under investigation. Hence, unlike other research, this work aims to improve the efficiency of the process and reduce its time by using air bubbles in a rectangular bubble column. Accordingly, the work aims to study the effectiveness of air bubbles in the degradation of paracetamol in a UV-photo catalyst, where it was done under flow rates (0-2) L/min and different variables of the pH (3-10) by conducting COD and HPLC analysis.

2. Materials and methods

2.1 Materials

Table 1 shows the materials utilized in this study, which are all of analytical quality.

Table 1: Materials and source

Chemical	Manufacturing	Purity
Hydrochloric acid (HCl)	Austria	99%
Sodium hydroxide (NaOH)	India	98%
Titanium Oxide Nanoparticles/ Nanopowder (TiO_2 99.5% purity) (diameter 10-30 nm) Anatase	USA	More than 99.5%
Paracetamol	Samaraa SDI/Iraq	

2.2 Experimental apparatus

The photocatalytic experiments were carried out in two stages, the first in a batch system equipped with a beaker and stirrer and the second in a semi-batch system equipped with an air compressor and UV light, as shown in Figure 1. The semi-batch system includes a rectangular glass column with dimensions of 200 mm in width, 30 mm in depth, and 1500 mm in height, featuring a thickness of 6 mm. Air bubbles are injected at the base of the column via a gas distributor positioned at the center of the bottom plate. This distributor comprises 21 needles, each with a square cross-section measuring 5 mm and an inner diameter of 1 mm. A gas compressor is utilized to compress the air, while a flow meter controls the flow rate. The glass bubble column was irradiated with an ultraviolet lamp (UVC 100-280 nm, ev 4.43-12.4). This lamp was 60 cm long and mounted on a stand 15 cm from the glass column. The glass column was insulated, and ultraviolet radiation was radiated with aluminum foil to avoid interference [40]. The photocatalysis process was carried out at room temperature. The experiments were repeated three times, and the average results were adopted with standard deviation as (mean ±2sd.dev)

A solution for wastewater was created by incorporating 300 mg of powdered paracetamol into a beaker filled with 1 liter of distilled water. The mixture was stirred for 5 minutes. Next, 0.5 mg of TiO_2 homogenate was added to the solution, which was then left to sit for 4 hours. To adjust the pH of the solution to 3, 7, and 10, hydrochloric acid (0.1 M) was added for the acidic medium, while sodium hydroxide (0.1 M) was used for the basic mediums. The pH-adjusted solution was transferred to a bubble column, where air was pumped through at 1 and 2 L/min rates. The solution was exposed to ultraviolet radiation for 60, 120, 180, and 240 minutes. The removal method's effectiveness was assessed by measuring the chemical oxygen demand (COD) at each irradiation duration.

High-performance liquid chromatography (HPLC) was used to detect the intermediates and the end products of the paracetamol degradation. The analysis was carried out using the high-performance liquid chromatography technique (HPLC), and the operating conditions were as follows: mobile phase ashitonatimutyl, mobile phase velocity (10 ml/min), detector (UV), and wavelength (245 nm). Where the analysis was done for the standard (active) paracetamol drug, and the retention time (2.3 min) was accurate. For the analysis of the unknown sample (after 240 minutes of photocatalysis), the peak appears at the same time (2.3 min) as indicated by the analysis of the unknown sample. The TiO_2 was characterized using an FTIR spectrophotometer [Type, IRAffinity-1-SHMADZo Origin: Germany] with ATR technology.

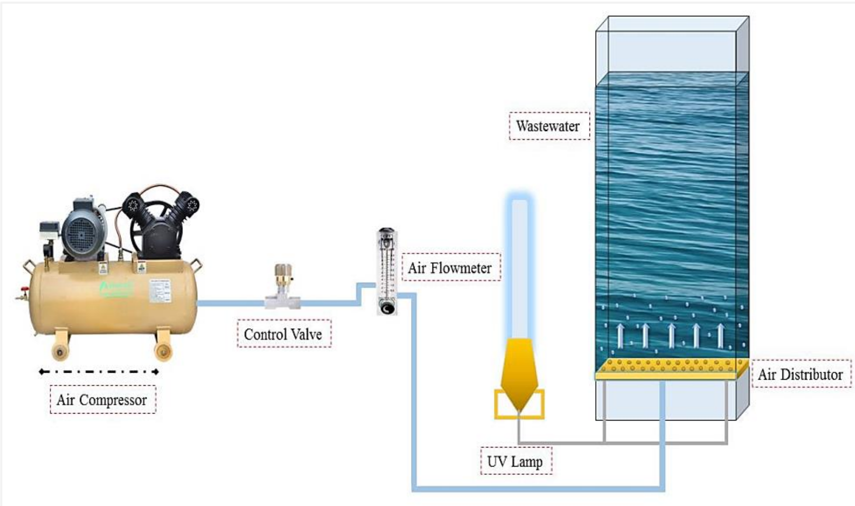


Figure 1: The schematic apparatus

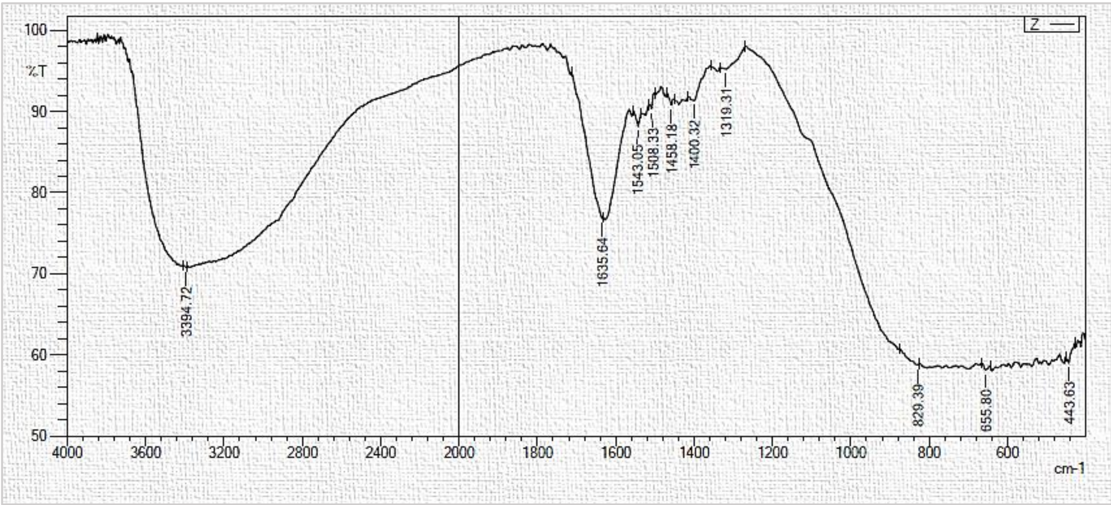
3. Results and discussion

3.1 The FTIR characterization

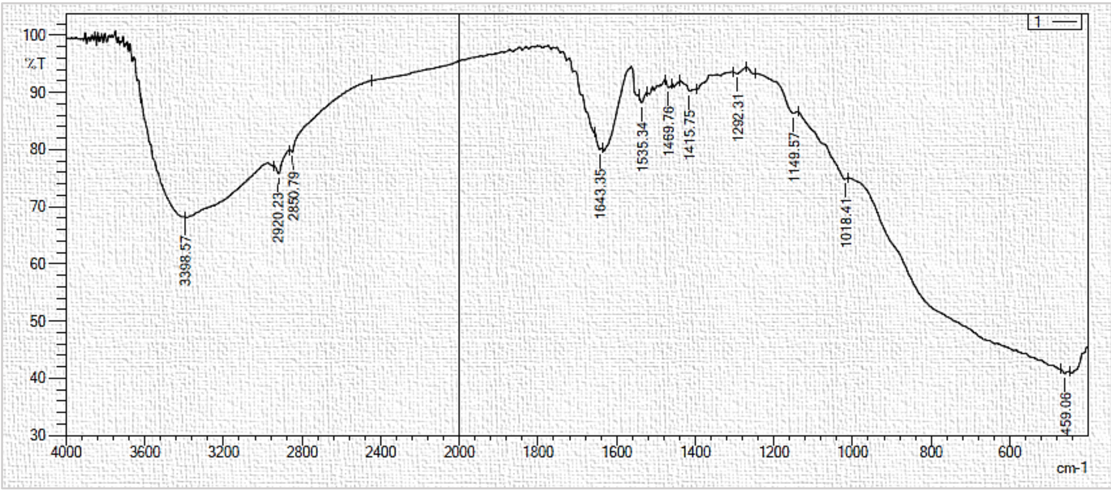
FTIR (Fourier-transform infrared spectroscopy) identifies the functional groups and chemical structures of TiO_2 particles. Figures 2a and 3b display tests on TiO_2 powder before and after the process, showing the powder's filtering post-reaction. The FTIR spectra were collected over a range of 4000 to 400 cm^{-1}. The FTIR analysis demonstrates the adsorption process of paracetamol on the TiO_2 powder after 240 minutes of decomposition. The FTIR spectrum of a sample of PAM as shown in Figure 2a reveals several bands indicative of an aromatic ring presence. This suggests that a mixture of trans-alkene molecules has modified part of the aromatic system, yielding significant out-of-plane bending signals for C=C–H in the 1319.31 to 1400.32 cm^{-1} range. Additionally, multiple C=C stretch bands are observed between 1508.33 and 1543.05 cm^{-1}, further confirming the presence of an alkene mixture. A C–H stretch band associated with aromatics or alkenes is identified at 3394.72 cm^{-1}.

After four hours of irradiation, Fourier Transform Infrared (FTIR) analysis (illustrated in Figure 2b) reveals a significant increase in carboxylic acids within the sample extract. This is evidenced by the prominent C=O stretching band observed at 1535.34 cm^{-1}, a hallmark of this particular functional group. Additionally, a broad -OH stretching band is detected, spanning a range from 2850.79 to 2920.23 cm^{-1}, further confirming the presence of these acids. A chemical transformation occurs throughout the irradiation as carboxylic acids and alkenes use reactions that substitute the amide groups on the aromatic ring. After these four hours, the aromatic amide is converted into a complex mixture primarily comprising p-aminophenol and p-nitrophenol. Meanwhile, only minimal alkane and alkene carboxylate salts are observed, indicating a selective transformation process during irradiation.

In conclusion, the IR investigations show that paracetamol is oxidized via photocatalysis and transforms into various organic molecules.



(a)



(b)

Figure 2: FTIR test of TiO_2, a) before test, b) after test (240 min)

3.2 The photocatalytic reaction process

3.2.1 Effect of pH

The pH value is a key operational parameter that might influence photocatalytic processes. The impact of pH on the paracetamol photodegradation was assessed at pH (3,7, and 10) with an initial paracetamol concentration of 300 mg/L. The results are shown in figures (3-5) under different flow rates in terms of COD removal percentage. The figures show that in the batch process (Q=0 l/s), the maximum removal efficiency of COD was at pH value 7, with a removal rate of approximately 55%. The removal percentage decreased after 240 min at pH values of 3 and 10, reaching 32 and 12%, respectively.

In the semi-batch system, the same trend of pH effect on COD removal, in which the highest removal percentage was at the neutral pH=7, where it was 78 and 60 % at 1L/min and 2L/min respectively. Indeed, the removal percentage decreased at the acidic pH =3 to reach 54 and 29 % at 1L/min and 2L/min respectively. Likewise, at an alkaline solution pH=9, the removal rates were 26 and 18 % at 1L/min and 2L/min respectively.

The pH influence on the catalyst particles' charge, the aggregate size of the catalyst, and the positions of the conductance and valence bands all have different effects on paracetamol removal. In addition, there is the isoelectric point, which plays a significant and influential role in photocatalysis. The isoelectric point or surface charge of the photocatalyst is known to be affected by changes in operating pH due to the nature of the TiO_2 catalyst used. The point of zero charges (PZC) of TiO_2 has been used in numerous studies to examine how pH affects photocatalytic oxidation efficiency. The PZC (point of zero charge) condition for TiO_2 occurs when its surface charge is neutral, with a pH range of approximately 4.5 to 7, depending on the specific catalysts used. In this study, the pH value of the isoelectric point for the TiO_2 employed is approximately 7, as indicated by previous research [41].

Titanium dioxide surface charge is positive in acidic environments (pH < 6.7) from $TiOH_2$+ species and a negative charge in alkaline conditions (pH > 6.7) from TiO_2 species [15,42]. These results are due to several factors, including the influence of cations and anions in the solution, the distribution of paracetamol, and the state of the TiO_2 surface relative to the pH levels, affecting the photodegradation efficiency. Paracetamol is predominantly an anion in alkaline solutions (pH = 9). These anions are highly soluble and, therefore, are not significantly adsorbed onto the TiO_2 surface. Consequently, the electrostatic attraction between the TiO_2 surface (pHPZC = 7) and paracetamol (pKa = 10) becomes a factor, as the negatively charged paracetamol at high pH levels hinders its adsorption. As a result, the degradation of paracetamol is lower in alkaline conditions, which can be shown in COD removal parentage values.

Conversely, in acidic solutions and natural media, paracetamol's water solubility is reduced due to its nonionic form, while the positively charged TiO_2 enhances its adsorption on the surface. This increased adherence leads to a higher degradation rate of paracetamol. However, this finding contrasts with the results of [29], which suggested that pH 9 is the best in paracetamol degradation and is not favored in acidic media. This discrepancy may arise from differences in catalyst type and other experimental conditions.

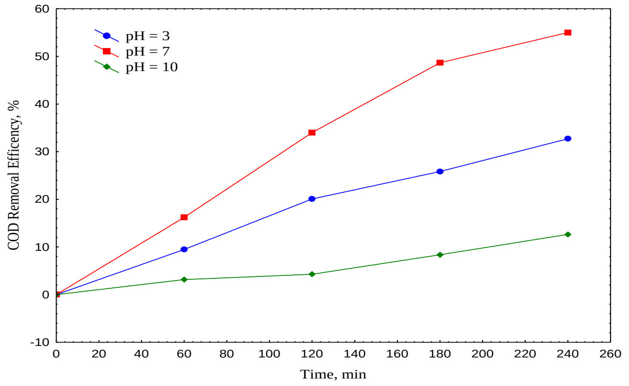


Figure 3: The COD removal efficiency with time at a batch system (Q=0 L/min)

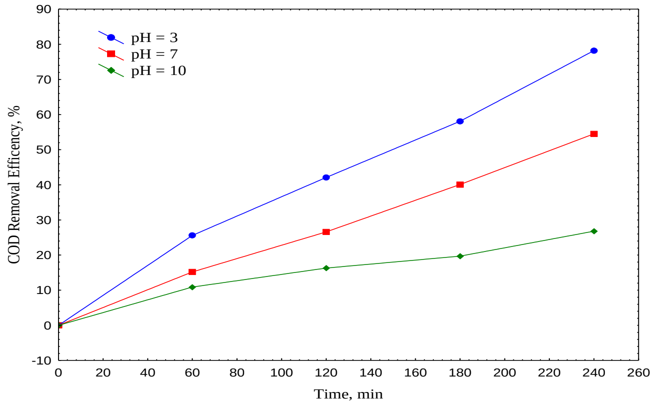


Figure 4: The COD removal efficiency with time at flow rate = 1L/min

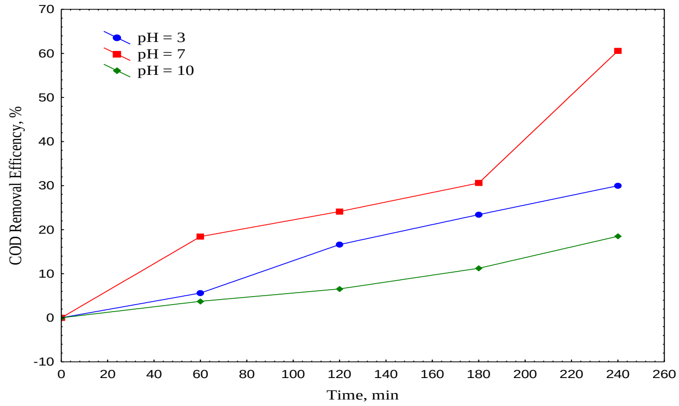


Figure 5: The COD removal efficiency with time at flow rate = 2 L/min

3.2.2 The flow rate effect

The impact of air bubbles on the degradation of paracetamol at flow rates between 0 and 2 L/min was evaluated in terms of COD removal, as illustrated in Figures (6–8). The results demonstrate that the addition of air bubbles significantly improves the efficiency of COD removal. At a pH of 7, the COD removal rate was as much as 25% greater than that of a batch process conducted at the same pH. Comparable enhancements in COD removal efficiency due to air bubbles were noted at pH levels 3 and 10, where the efficiencies were 54 and 26%, respectively. The influence of air bubbles can be attributed to two main factors. The first reason is that introducing air bubbles, combined with turbulent flow, increases the velocity, enhancing the diffusivity of paracetamol molecules towards the TiO_2 active sites, thereby accelerating the degradation rate.

The second cause is that the airflow rate serves as a promoter by delivering oxygen molecules through the air bubbles into the system. These oxygen molecules interact with free electrons generated at the catalyst's active sites due to UV radiation, forming additional hydroxyl radicals as part of the proposed degradation process see Figure 9.

Consequently, the flow rate significantly impacts the degradation of paracetamol. However, when the flow rate is increased to 2 L/min, Chemical Oxygen Demand (COD) removal efficiency decreases. This decline can be attributed to the escalating flow rate, which causes the gas bubbles to coalesce, resulting in larger bubbles. Such larger bubbles disrupt the bubble column's uniformity, leading to a heterogeneous pattern. This heterogeneous behavior reduces the interaction between the nanoparticles and the UV light.

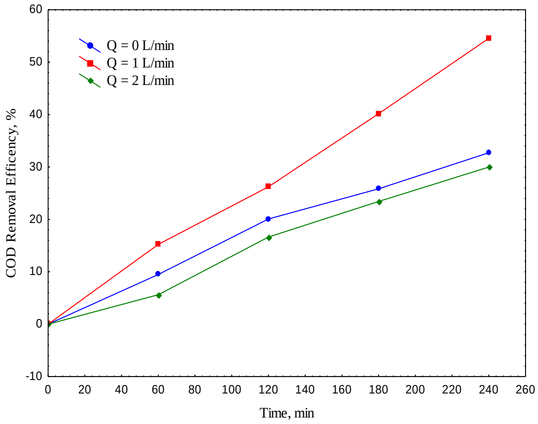


Figure 6: The COD removal efficiency with time at different gas flow rates and pH=3

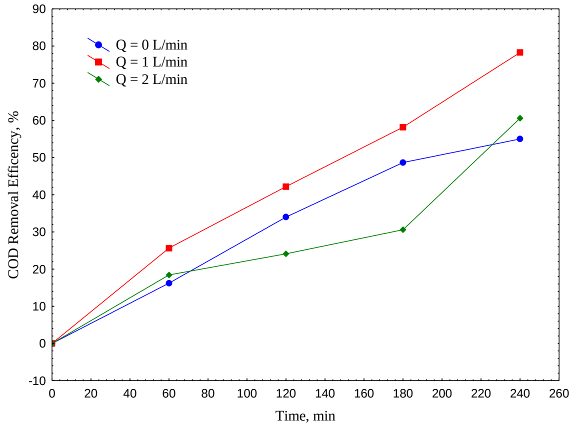


Figure 7: The COD removal efficiency with time at different gas flow rates and pH=7

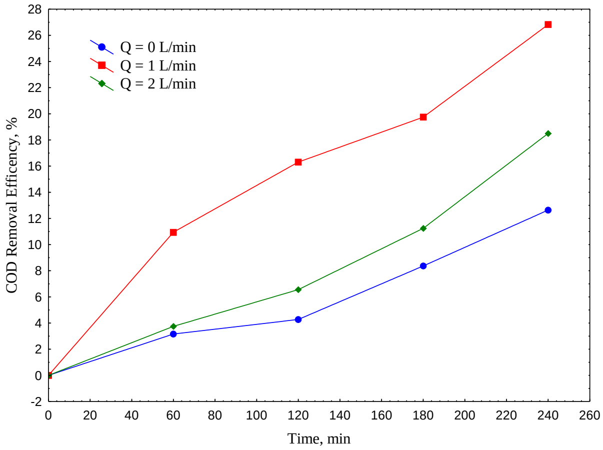


Figure 8: The COD removal efficiency with time at different gas flow rates and pH=10

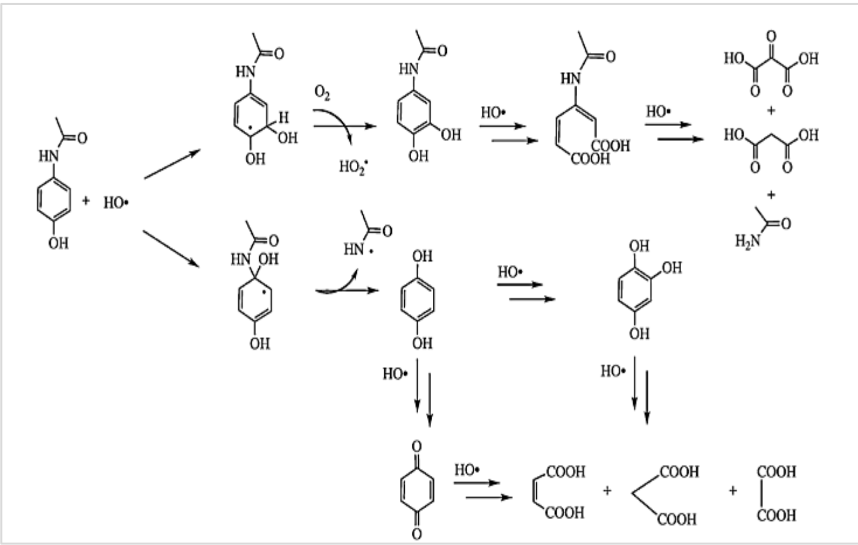


Figure 9: Paracetamol oxidation mechanism [43]

3.2.3 The HPLC analysis

To conduct a quantitative analysis and estimate the concentration of paracetamol in the unknown sample, we prepared various concentrations of the standard substance: 5, 10, 25, 50, and 100 ppm. These concentrations were used to develop a calibration curve by plotting the concentration against the peak area. This process resulted in the following straight-line Equation (4):

$$\lambda = 0.0054\,X + 2.4457 \quad (4)$$

where λ represents the concentration value, and X represents the peak area.

The HPLC analysis on a solution with a paracetamol concentration of 300 ppm revealed optimal conditions for achieving a high COD removal efficiency. The best results were observed at a pH of 7, a flow rate of 1 L/min, and a UV irradiation time of 240 minutes. The chromatogram displayed in Figure 10 illustrates the state of paracetamol following treatment. The paracetamol standard peak appeared at 2.3 minutes, with an area of 4435.3, indicating a concentration of 26.4 ppm. Consequently, under these operating conditions, it can be inferred that a complete degradation of paracetamol, amounting to 91.2%, was achieved. Compared to previous studies, such as those by Dalmazio et al. [43], Yang et al. [15], both reported a degradation rate of 90% in 160 minutes using TiO_2/UV, and our results demonstrate a significant enhancement in degradation efficiency.

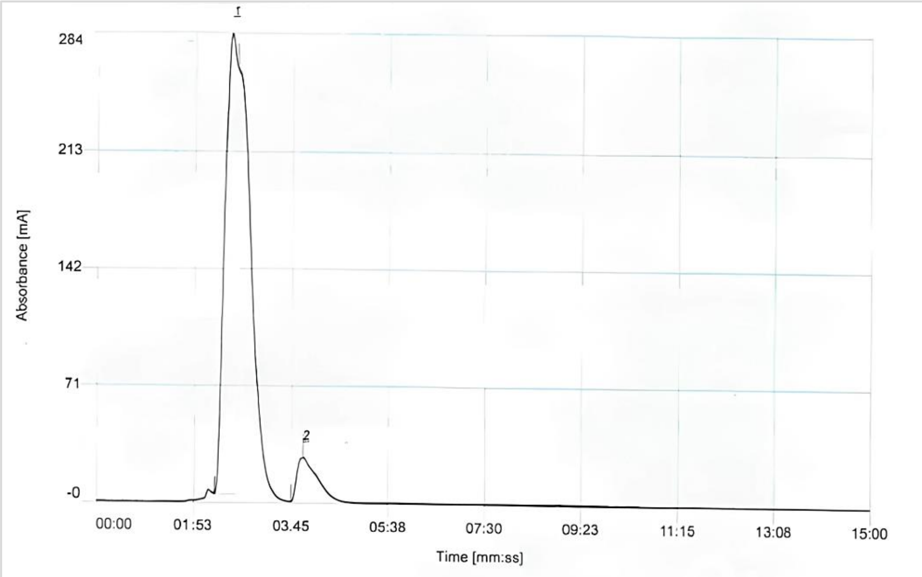


Figure 10: The HPLC analysis (240 min. after photocatalysis)

3.2.4 Kinetic study

The kinetics of the reaction were studied to understand better the photodegradation of paracetamol aided by bubbles. The study was done at pH=7 and a different flow rate=1L/min, which gives the best COD removal percentage. Two models were employed: the first and second Lagergren pseudo-order models. Equations 5 and 6 give the Equations for pseudo-first-order kinetic models [44] and second-order [45].

$$\log (q_e - q_t) = \log (q_e) - \frac{K_1}{2.303} t \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (6)$$

where q_e and qt represent the amounts adsorbed (mg/g) at equilibrium and at time t (min^{-1}), respectively, while k1 and k2 denote the rate constants for pseudo-first-order and pseudo-second-order kinetics ($g\ mg^{-1}\ min$).

The results are tabulated in Table 2. As shown in the Table for the pseudo-first-order model, the rate constant and sorption capacity were increased, respectively. As for the pseudo-second model, the rate increases constantly, but this trend is different for sorption capacity. The pseudo-first-order kinetic model fits well the experimental data due to the values of R^2 (0.9648, 0.996, 0.9757) and also from the values of calculated equilibrium adsorption capacity (q_e, cal), which are close to the values of experimental values of q_e (q_e, exp.) While at the pseudo-second-order, the values are divergent between the calculated and experimental values of q_e.

Table 2: The first and second-order pseud kinetic parameters

Q	q_e,exp	Pseudo first order			
		Equation	**R^2**	**K_1**	**q_e, calc.**
0	380	y = -0.0001x + 2.5771	0.9648	$2.303x10^{-4}$	377.66
1	405	y = -0.0002x + 2.6037	0.996	$4.606x10^{-4}$	401.51
2	421	y = -7E-05x + 2.6191	0.9757	$1.612x10^{-4}$	416
Q	**q_e,exp**	**Pseudo second order**			
0	380	y = 0.0004x + 0.3651	0.5714	$4.382x10^{-7}$	2500
1	405	y = 0.0004x + 0.207	0.8071	$7.729x10^{-7}$	2500
2	421	y = 0.0014x + 0.2773	0.8249	$70.679x10^{-7}$	714.3

4. Conclusion

A photocatalytic process supported by air bubbles and UV light was used to evaluate the degradation of paracetamol through chemical oxygen demand (COD) testing and high-performance liquid chromatography (HPLC) analysis under various operating conditions, including pH, flow rate, and irradiation time. The results indicate that the aqueous solution's pH significantly affects the pollutant's adsorption on the photocatalyst surface, with an optimal pH of 7. This effect is partly due to the pH's impact on pollutant adsorption and the electrostatic repulsion between the TiO_2 surface and paracetamol molecules.

The findings reveal that introducing air bubbles into the solution at a flow rate of 1 L/min resulted in a 78% increase in COD removal efficiency. This improvement can be attributed to two main factors: first, air bubbles enhance the diffusion and mobility of paracetamol molecules toward the catalyst's active sites; second, they promote the generation of active hydroxyl radicals (OH). The highest degradation of paracetamol recorded was 91.2%, measured by HPLC analysis when the pH was set to 7, and the flow rate was 1 L/min after 240 minutes of treatment. The kinetic study aligns well with the pseudo-first-order reaction model. Given solar energy's status as a green and environmentally friendly energy source, intensifying efforts to expand its use within the photocatalytic process is imperative. Additionally, developing pilot plants that utilize actual industrial wastewater under real conditions is crucial for accurately assessing the treatment system's performance.

Author contributions

Conceptualization, **A. Khalel, A. Alwasiti,** and **J. Abdulrzaak**; data curation, **A. Khalel**; investigation, **A. Khalel**; methodology, **A. Khalel**; project administration, **A. Khalel**; supervision, **A. Alwasiti** and **J. Abdulrzaak**; validation, **A. Khalel**, **A. Alwasiti** and **J. Abdulrzaak**; writing—original draft preparation, **A. Khalel**; writing—review and editing, **A. Alwasiti** and **J. Abdulrzaak**. All authors have read and agreed to the published version of the manuscript.

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Data availability statement

The data that support the findings of this study are available on request from the corresponding author.

Conflicts of interest

The authors declare no conflict of interest.

References

[1] M. J. Benotti, R. A. Trenholm, B. J. Vanderford, J. C. Holady, B. D. Stanford, S. A. Snyder, Pharmaceuticals and endocrine disrupting compounds in U.S. drinking water, Environ. Sci. Technol., 43 (2009) 597-603. https://doi.org/10.1021/es801845a

[2] P. J. Philips, S. G. Smith, D. W. Koplin, S. D. Zaugg, H. T. Buxton, E. T. Furlong, K. Esposito, B. Stinson, Pharmaceutical formulation facilities are sources of opioids and other pharmaceuticals to wastewater treatment plant effluents, Environ. Sci. Technol., 44 (2010) 4910-4916. https://doi.org/10.1021/es100356f

[3] R. A. Rodríguez, J. A. Perdigón-Melón, M. Mezcua, M. D. Hernando, P. Letón, E. García-Calvo, A. Agüera, A. R. Fernández-Alba, Removal of pharmaceuticals and kinetics of mineralization by O_3/H_2O_2, in a biotreated municipal wastewater, Water Res., 42 (2008) 3719- 28. https://doi.org/10.1016/j.watres.2008.06.008

[4] F. Tamtam, F. Mercier, B. L. Bot, J. Eurin, Q. T. Dinh, M. Clement, M. Chevreuil, Occurrence and fate of antibiotics in the Seine River in various hydrological conditions, Sci. Total. Environ., 393 (2008) 84-9. https://doi.org/10.1016/j.scitotenv.2007.12.009

[5] S. Mompelat, B. Le Bot, O. Thomas, Occurrence and fate of pharmaceutical products and by-products, from resource to drinking water, Env. Int. 35 (2009) 803-814. https://doi.org/10.1016/j.envint.2008.10.008

[6] M. Grung, T. Kallqvist, S. Sakshaug, S. Skurtveit, K. V. Thomas, Environmental assessment of Norwegian priority pharmaceuticals based on the EMEA guideline, Ecotox. Environ. Safe., 71 (2008) 328-340. https://doi.org/10.1016/j.ecoenv.2007.10.015

[7] S. Mompelat, B. L. Bot, O. Thomas, Occurrence and fate of pharmaceutical products and byproducts, from resource to drinking water, Environ. Int., 35 (2009) 803-814. https://doi.org/10.1016/j.envint.2008.10.008

[8] K. M. Onesios, J. T. Yu, E. J. Bouwer, Biodegradation and removal of pharmaceuticals and personal care products in treatment systems: a review, Biodegradation, 20 (2009) 441-466. https://doi.org/10.1007/s10532-008-9237-8

[9] A. H. Khalil, A. Alwasiti, J. Abdulrzaak, A. Al-Shalal, The effect of physicochemical properties on paracetamol photodegradation in a cuboid bubble column, Environ. Res. Technol., 6 (2023) 347-358. https://doi.org/10.35208/ert.1337407

[10] K. Kummerer, Antibiotics in the aquatic environment -A review-part I, Chemosphere, 75 (2009) 417-434. https://doi.org/10.1016/j.chemosphere.2008.11.086

[11] C. Postigo, M. J. Alda, D. Barcelo, Drugs of abuse and their metabolites in the Ebro River basin: occurrence in sewage and surface water, sewage treatment plants removal efficiency, and collective drug usage estimation, Environ. Int., 36 (2010) 75-84. https://doi.org/10.1016/j.envint.2009.10.004

[12] H. Li, P. A. Helm, C. D. Metcalfe, Sampling in the Great Lakes for pharmaceuticals, personal care products, and endocrine-disrupting substances using the passive polar organic chemical integrative sampler, Environ. Toxicol. Chem., 29 (2009) 751-762. https://doi.org/10.1002/etc.104

[13] B. I. Escher, R. Baumgartner, M. Koller, K. Treyer, J. Lienert, C. S. McArdell, Environmental toxicology and risk assessment of pharmaceuticals from hospital wastewater, Water Res., 45 (2011) 75-92. https://doi.org/10.1016/j.watres.2010.08.019

[14] K. H. Langford, K. V. Thomas, Determination of pharmaceutical compounds in hospital effluents and their contribution to wastewater treatment works, Environ. Int., 35 (2009) 766-770. https://doi.org/10.1016/j.envint.2009.02.007

[15] L. Yang, L. E. Yu, M. B. Ray, Photocatalytic oxidation of paracetamol: dominant reactants, intermediates, and reaction mechanisms, Environ. Sci. Technol., 43 (2009) 460-465. https://doi.org/10.1021/es8020099

[16] J. An, Q. Zhou, F. Sun, L. Zhang, Ecotoxicological effects of paracetamol on seed germination and wheat seedling development (Triticum aestivum L.), J. Hazard. Mater., 169 (2009) 751-757. https://doi.org/10.1016/j.jhazmat.2009.04.011

[17] N. Muir, J. D. Nichols, M. R. Stillings, J. Sykes, Comparative bioavailability of aspirin and paracetamol following single-dose administration of soluble and plain tablets, Curr. Med. Res. Opin., 13 (1997) 491-500. https://doi.org/10.1185/03007999709113322

[18] J. A. Forrest, J. Clements, L. Prescott, Clinical pharmacokinetics of paracetamol, Clinical pharmacokinetics, 7 (1982) 93-107. https://doi.org/10.2165/00003088-198207020-00001

[19] C. Usher, M. Teeling, K. Bennett, B. McGowan, J. Feely, J., Usage of paracetamol-containing combination analgesics remains high in primary care, Br. J. Clin. Pharmacol, 60 (2005) 648-652. https://doi.org/10.1111/j.1365-2125.2005.02500.x

[20] M. Skoumal, P. Cabot, F. Centellas, C. Arias, R. M. Rodríguez, J. A. Garrido, E. Brillas, Mineralization of paracetamol by ozonation catalyzed with Fe_2+, CU_2+ and UVA light, Appl Catal B: Environ 66 (2006) 228-240. https://doi.org/10.1016/j.apcatb.2006.03.016

[21] E. Brillas, I. Sirés, C. Arias, P. L.Cabot, F. Centellas, Rodríguez RM, Garrido JA .2005 Mineralization of paracetamol in aqueous medium by anodic oxidation with a boron-doped diamond electrode, Chemosphere, 58 (2005) 399-406. https://doi.org/10.1016/j.chemosphere.2004.09.028

[22] R. Andreozzi, V. Caprio, R. Marotta, D. Vogna, Paracetamol oxidation from aqueous solutions using ozonation and H_2O_2/UV system, Water Res., 37 (2003) 993-1004. https://doi.org/10.1016/s0043-1354(02)00460-8

[23] L. M. Yang, L. E. Yu, M. B. Ray, Photocatalytic oxidation of paracetamol: dominant reactants, intermediates, and reaction mechanisms, Environ. Sci. Technol., 43 (2009) 460–465. https://doi.org/10.1021/es8020099

[24] T. Li, J. Liu, R. Bai, D. Ohandja, F. Wong, Biodegradation of organonitriles by adapted activated sludge consortium with acetonitrile-degrading microorganisms, Water Res., 41 (2007) 3465-3473. https://doi.org/10.1016/j.watres.2007.04.033

[25] C. Y. Chen, S. C. Chen, M. Fingas, C. M. Kao, Biodegradation of propionitrile by Klebsiella oxytoca immobilized in alginate and cellulose triacetate gel, J. Hazard Mat., 177 (2010) 856-863. https://doi.org/10.1016/j.jhazmat.2009.12.112

[26] S. A. Hasan, M. I. Ferreira, M. J. Koetsier, M. I. Arif, D. B. Janssen, Complete biodegradation of 4-fluoro cinnamic acid by a consortium comprising Arithrobacter sp. strain G1 and Ralstonia sp. strain H1, Appl. Environ., Microbiol., 77 (2011) 572-579. https://doi.org/10.1128/AEM.00393-10

[27] I. K. Konstantinou, T. A. Albanis, TiO_2-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations–a review, Appl. Catal. B: Environ., 49 (2004) 1-14. https://doi.org/10.1016/j.apcatb.2003.11.010

[28] H. Shemer, Y. K. Kunukcu, K. G. Linden, Degradation of the pharmaceutical metronidazole via UV, Fenton and photo-Fenton processes, Chemosphere., 63 (2006) 269-276. https://doi.org/10.1016/j.chemosphere.2005.07.029

[29] N. Jallouli, K. Elghniji, H. Trabelsi, M. Ksibi, Photocatalytic degradation of paracetamol Antibiotics in the aquatic environment on TiO2 nanoparticles and TiO_2/cellulosic fiber under UV and sunlight irradiation, Arabian J. Chem., 10 (2017) S3640-S3645. https://doi.org/10.1016/j.arabjc.2014.03.014

[30] F. Shahrezaei, Y. Mansouri, A. Zinatizadeh, A. Akhbari, Process modeling and kinetic evaluation of petroleum refinery wastewater treatment in a photocatalytic reactor using TiO_2 nanoparticles, Powder Technol., 221 (2012) 203-212. https://doi.org/10.1016/j.powtec.2012.01.003

[31] Y. Cheng, H. Sun, W. Jin, N. Xu, Photocatalytic degradation of 4-chlorophenol with combustion synthesized TiO_2 under visible light irradiation, J. Chem. Eng., 128 (2007) 127-133. https://doi.org/10.1016/j.cej.2006.09.009

[32] M. A. Al-Nuaim, A. A. Alwasiti, Z. Y. Shnain, The photocatalytic process in the treatment of polluted water, Chemical Papers, 77 (2022) 677-701. https://doi.org/10.1007/s11696-022-02468-7

[33] S. A. Alattar, K. A. Sukkar, M. A. Alsaffar, The role of TiO_2 NPs catalyst and packing material in removal of phenol from wastewater using an ozonized bubble column reactor, Acta Innovations, 46 (2022) 90-101. http://dx.doi.org/10.32933/ActaInnovations.46.7

[34] S. Karthick, S. Wankhede, V. Prasad, K. Haribabu, Experimental and kinetic study on the treatment of synthetic and real pharmaceutical wastewater by electrocoagulation, J. Indian Chem. Soc., 97 (2019) 326-331.

[35] D. Gamze, I. Turkdogan, K. Yetilmezsoy, E. Kocak, Treatment of real paracetamol wastewater by Fenton process. Chem. Ind. and Chem. Eng., 23 (2016) 177- 186. https://doi.org/10.2298/CICEQ150831029D

[36] P. Xiong, J. Hu, Degradation of acetaminophen by UVA/LED/TiO_2 process, Sep. Purif. Technol., 91 (2012) 89-95. https://doi.org/10.1016/j.seppur.2011.11.012

[37] N. Blangetti, F. S. Freyria, M. C. Calviello, N. Ditaranto, S. Guastella, B. Bonelli, Photocatalytic Degradation of Paracetamol under Simulated Sunlight by Four TiO2 Commercial Powders: An Insight into the Performance of Two Sub-Micrometric Anatase and Rutile Powders and a Nanometric Brookite Powder, Catalysts. 13 (2023) 434. https://doi.org/10.3390/catal13020434

[38] A. Stoyanova, H. Hitkova, N. Kaneva, A. Bachvarova-Nedelcheva, R. Iordanova, P. Marinovska, Photocatalytic Degradation of Paracetamol and Antibacterial Activity of La-Modified TiO_2 Obtained by Non-Hydrolytic Sol-Gel Route, Catalysts,14 (2024) 469. https://doi.org/10.3390/catal14080469

[39] E. D. Mohamed, R. R. Ali, N. C. Jusoh, Y. Nagao, K. Aoki, S. Nishimura, Z. I. Ahmad, S. H. Mohd, Enhanced paracetamol photodegradation over synthesized TiO2/g-C3N4 nanocomposites: Effect of g-C_3N_4 loading on the properties and performance, Colloids Surf., A, 694 (2024) 134066. https://doi.org/10.1016/j.colsurfa.2024.134066

[40] M. Al-Nuaim, A. Al-Wasiti, Y. Shnain, A. K. Al-Shalal, The Combined Effect of Bubble and Photo Catalysis Technology in BTEX Removal from Produced Water, Bull. Chem. React. Eng. Catal., 17 (2022) 577-589. https://doi.org/10.9767/bcrec.17.3.15367.577-589

[41] J. P. Holmberg, E. Ahlberg, J. Bergenholtz, M. Hassellöv, Z. Abbas, Surface charge and interfacial potential of titanium dioxide nanoparticles: Experimental and theoretical investigations, J. Colloid Interface Sci., 407 (2013) 168-176. https://doi.org/10.1016/j.jcis.2013.06.015

[42] M. Brunner, A. Schmiedberger, R. Schmid, D. Jager, E. Piegler, H. G. Eichler, M. Muller, Direct assessment of peripheral pharmacokinetics in humans: comparison between cantharides blister fluid sampling, in vivo microdialysis and saliva sampling, Br. J. Clin. Pharmacol. 46 (2002) 425-431. https://doi.org/10.1046/j.1365-2125.1998.00805.x

[43] I. Dalmázio, T. M. Alves, R. Augusti. An appraisal on the degradation of paracetamol by TiO_2/UV system in aqueous medium. Product identification by gas chromatography-mass spectrometry, J. Braz. Chem. Soc., 19 (2008) 81-88. https://doi.org/10.1590/S0103-50532008000100013

[44] S. Lagergren, Zur theorie der sogenannten adsorption geloster stoffe, Kungliga Svenska Vetenskapsakademiens, Handligar 24 (1989) 1-39.

[45] Y. S. Ho, Second-order kinetic model for the sorption of cadmium onto tree fern: a comparison of linear and non-linear methods, Water Res., 40 (2006)119-25. https://doi.org/10.1016/j.watres.2005.10.040