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Adsorption and photodegradation as processes enabling the removal of antiviral drug ritonavir from the aquatic environment

Humam Ahmed[1], Benish Siddiqui[2], Ewa Felis[1*]

[1] Faculty of Energy and Environmental Engineering, Environmental Biotechnology Department, Silesian University of Technology, ul. Akademicka 2A, 44-100, Gliwice, Poland
[2] Department of Chemistry, University of Karachi, KU Circular Rd, Karachi City, Sindh, Pakistan
* Corresponding author's e-mail: ewa.felis@polsl.pl

ABSTRACT

The presence of antiviral drugs in the aquatic environment raises serious concerns due to the potential risk associated with their biological activity and potential metabolites, which themselves may have negative interactions with living organisms. This study systematically explores the removal of the antiviral drug ritonavir (RTR) using a photochemically induced advanced oxidation process. In this work, solar light-driven photolysis, homogeneous photocatalysis induced by sunlight in the presence of H_2O_2, and photocatalysis in the presence of TiO_2 were tested. Under solar light irradiance (500 W/m²), the removal of ritonavir is limited to 15% in Milli-Q (MQ) water and 38% in tap water (TW), with corresponding rate constants (k) of 0.0009 min^{-1} and 0.0026 min^{-1}, respectively. The influence of H_2O_2 was further examined and showed that exposure to artificial light (500 W/m²) resulted in the concentration of RTR in MQ water dropping below the limit of detection (LOD) at doses of 125.0, 250.0, and 500.0 µL, achieving complete degradation at 100%. The highest pseudo degradation rate was observed at a 500 µL H_2O_2 dose (k = 0.1439), with an R^2 value of 0.9844. Additionally, the photocatalytic activity of pure TiO_2 (10.0 mg/L) on ritonavir in MQ water was investigated under dark conditions and solar light. The results demonstrated immediate and complete adsorption of RTR, reaching 100% on the TiO_2 surface, with an adsorption capacity of 3.9952 mg/g. It is assumed that photochemical degradation of the antiviral drug was minimal in TiO_2, but the adsorption process on the photocatalyst surface dominated. Hence, the kinetic parameters of this process were calculated. Under solar light, the TiO_2 surface retained 72% of the RTR, with a maximum adsorption capacity (qmax) of 3.7580 mg/g, suggesting cyclical sorption and desorption processes occurred until an equilibrium state was established. These findings highlight the efficacy of this method in addressing the issue of antiviral drug residues in an aqueous environment but also indicate that the heterogeneous photocatalysis process may not always be feasible, especially in cases where there is a high affinity of a given substance for sorption on the photocatalyst surface. However, the drug itself is susceptible to decomposition when the source of hydroxyl radicals is H_2O_2.

Keywords: aquatic environment micropollutions, antiviral drug, ritonavir, photodegradation, TiO_2, UV/H_2O_2.

INTRODUCTION

In 2019, with the onset of the COVID-19 pandemic, there was a significant increase in the global consumption of antivirals, corticosteroids, and antibiotics (Galani et al., 2021). Among these pharmaceuticals, Ritonavir (RTR), an antiviral, is notable for its high dosage requirements, low metabolic rate, and limited removal efficiency in wastewater treatment plants (Wang et al., 2023). During the pandemic, the average daily intake of RTR reached as much as 200 mg per person (Kumari and Kumar, 2021). Approximately 60% of the orally administered RTR is excreted unmetabolized, entering domestic sewage and contaminating surface water systems due to the inadequacies of conventional wastewater treatments (Jia et al., 2024). RTR concentrations in urban wastewater have been reported at levels as high as 373 ng/L, while river concentrations have

reached 52.2 ng/L, both exceeding historical records (Kuroda et al., 2021). Consequently, it is imperative to investigate the behaviour of RTR in aquatic environments to provide a solid theoretical basis for ensuring water ecological security and addressing the environmental threats caused by pharmaceutical compounds especially RTR (Ahmed and Felis, 2023).

Among the various advanced oxidation processes (AOPs), the photodegradation of RTR using UV/ solar assisted H_2O_2 homogeneous photocatalysis and heterogeneous photocatalysis stands out for its effectiveness in removing selected pharmaceutical pollutants and other emerging contaminants (Galaburda et al., 2024; Sabouni and Gomaa, 2019; Thi et al., 2021). This approach leverages the synergistic effects of combining a catalyst with light irradiation (Heberer, 2002).

Photocatalysis is a process that offers numerous advantages across various applications, particularly in environmental remediation and energy conversion (Velempini et al., 2021). One of its primary benefits is the stability of the photocatalyst, which enables it to sustain its effectiveness over extended periods (Zhang et al., 2024). Additionally, the recoverability of the photocatalyst allows for easy separation and reuse across multiple reaction cycles, thereby reducing waste (Ye et al., 2022). This approach does not rely on additional chemicals, which not only efficiently run the reaction process but also minimizes the potential for harmful byproducts. Furthermore, solar light driven photocatalysis is characterized by low energy consumption, considering it as an eco-friendly alternative to traditional chemical processes (Li et al., 2020; Mancuso and Iervolino, 2022). The cost-effectiveness of photocatalysis stems from its ability to utilize abundant light sources, such as sunlight, to drive chemical reactions, making it an appealing option for sustainable practices in both industrial and research environments (Morshedy et al., 2024).

While UV or solar light coupled with H_2O_2, also plays a potential role for removing pharmaceutical pollutant from water environment (Gligorovski et al., 2015). This method involves using UV or solar light to activate H_2O_2, leading to the generation of hydroxyl radicals – highly reactive species capable of decomposing a wide range of pharmaceutical contaminants (Zhou et al., 2015). As a result, this technology presents a highly effective solution for enhancing water quality and protecting public health, targeting pollutants that are often resistant to degradation in conventional wastewater treatment systems.

The aim of the study was to determine the susceptibility to degradation of the selected antiviral drug, ritonavir, in solar light-induced processes, i.e. solar light driven photolysis, solar light driven homogeneous photocatalysis in the presence of hydrogen peroxide and heterogeneous photocatalysis in the presence of TiO_2 as a photocatalyst. The research emphasizes the impact of H_2O_2 dosage, light intensity, catalysts dose and the degradation rate of RTR. The results aim to deepen our understanding of the UV/ H_2O_2 process and optimize its parameters, thereby enabling the scaling up of these techniques for industrial applications.

MATERIALS ANS METHODS

Reagents

RTR was purchased in highest available purity (≥ 98%) CAS number (155213-67-5) from Cayman Chemical, (Poland). Acetonitrile Chromoscan® for HPLC analysis was purchased from POCH S.A. (Poland). Hydrogen peroxide (30% v/v; H_2O_2) was purchased from Avantor, (Poland). TiO_2 P-25, acetic acid and sodium acetate for Acetate buffer (pH 5.0) were purchased from Sigma-Aldrich.

Preparation of standard solution of Ritonavir

A standard solution of ritonavir (RTR; 4.0 mg/L) was prepared by dissolving 4.0 mg into 1000 ml of the Milli-Q water. The solution was sonicated for 2 hours at 30 °C with 800 rpm (revolution per minutes) and transferred to the volumetric flask and was stirred overnight to dissolve the compound. The compound was partially dissolved in water. This solution is labelled as stock solution, and it was refrigerated about 1 week. About 2.0 mg/L working standard solution was prepared by dilution of 200 mL standard solutions in MQ and TW respectively to appropriate concentrations immediately before the use.

EXPERIMENTAL SETUP

Laboratory scale analysis

Laboratory scale experiment of decay of RTR was performed using artificial sunlight system,

i.e. system of Solar box 1500e, which can also act as an aging chamber using solar radiation (Co. fo.me.gra, Italy). The light source was a 1500 W polychromatic Xenon lamp. The specification of Solar box system is described in previously published work (Ahmed and Felis, 2024). This study examined the performance of the selected drug in two aquatic matrices, which can be understood as components of the broadly understood aquatic environment, that is, MQ and TW. The studies were conducted by periodically exposing solutions containing the tested antiviral drug (so-called "light studies") and so-called "dark studies" were conducted under the same conditions, but without switching on the source of electromagnetic radiation (i.e. xenon lamp). The studies without switching on the source of radiation were conducted to assess the effect of adsorption on the final effect of the process, because in the case of studies with a photocatalyst, some substances show a strong affinity for sorption on the surface of the photocatalyst and then this process is the dominant process, not the process of photodecomposition. For photolysis, approximately 200 mL of an aqueous RTR solution has been placed in a glass beaker and stirred with a magnetic stirrer inside the solar light stimulator for 120 minutes. For photocatalysis as well as photodegradation assisted with H_2O_2, the studies were carried out with a selected concentration of H_2O_2; 150 µL, 250 µL, and 500 µL and with a specific dose of pure TiO_2 i.e., 10.0 mg/L. All the experiments were done in duplicate.

Analytical analysis

The quantification of RTR was conducted using high-performance liquid chromatography (HPLC) with a variable ultraviolet (UV/ VIS) detector (UltiMate 3000 system; Dionex Corporation, Sunnyvale, CA, USA), that was used for micropollutant analysis and described in our previous works (Ahmed and Felis, 2024). The samples have been purified using 0.22 µm MCEMF-Millipore® filter membranes from Merck, Germany. Thermo Scientific Inc. (Polygen, PL) provided a C18 Hypersil™ Gold column (250 × 4.6 mm; pore size: 5 µm) for chromatographic separation. The mobile phase consists of acetate buffer (pH 5.0) and acetonitrile in a 30:70 (v/v) ratio, resulting in an RTR retention time of 8.0 ± 0.5 minutes within the required limits. The investigated antiviral drug, i.e. RTR, had a limit of quantification (LOQ) of 0.2 mg/L, which corresponded to the first lowest calibration point on linear regression curves ($R^2 > 0.98$). The analysis was performed at a wavelength of 248 nm, and the data were processed using Dionex Chromeleon™ 6.8 software.

Sorption studies

To investigate the adsorption isotherms of the selected pharmaceutical pollutant on TiO_2 surface, an aqueous stock solution of RTR was prepared at a concentration of 500 mg/L. The stock solutions were diluted with Milli-Q and tap water respectively to obtain the concentration of 200 mg/L of the investigated pollutant. All experiments were performed in beakers covered with aluminum foil to protect them from sunlight. The samples were stirred continuously during the experiment using magnetic stirrer. Next, the samples were filtered using MCEMF-Millipore® Membrane Filters with 0.22 µm pore size (Merck, Germany). The concentrations of the RTR in the liquid phase were quantified using HPLC-UV. The tests were performed in duplicates.

KINETICS STUDIES

To study photolysis and photocatalytic degradation of drugs using pure TiO_2, the pseudo-first-order kinetics technique is applied to all experimental data. This approach is based on the concentration of the reactant in a chemical reaction. The linear form of the pseudo-first-order equation is presented below and used to calculate these values in our other publications (Ahmed and Felis, 2024):

$$\frac{C_{RTR}}{C_{0,RTR}} = exp^{-kt.t} \quad (1)$$

where: C_{RTR} and $C_{o,RTR}$ are the amount adsorbed at equilibrium and at time t, respectively (mg/g), and kt is a rate constant (min^{-1}), derived from the graph C/C₀ vs time (min). The reaction's half-life can be estimated by the equation below:

$$\frac{1}{2}t = \frac{ln\,2}{kt} \quad (2)$$

The half-life of a chemical reaction refers to the duration it takes to remove 50% of a selected pollutant through photolytic or photocatalytic processes (½t, min). It is a crucial parameter for understanding the efficiency of these reactions

in environmental applications. For the analysis and calculation of pseudo-first-order kinetics, all necessary computations are calculated using the SAP Interactive Excel application. This method enables accurate tracking and assessment of pollutant degradation over time, providing information about treatment effectiveness and reaction dynamics. Given that the primary factor influencing the degradation of solar light over time is cumulative energy, we can substitute cumulative energy (QUV) for time (t) in the pseudo-first-order reaction, leading to the following equation:

$$ln\left(\frac{C_t}{C_0}\right) = -k_{UV} Q_{UV} \quad (3)$$

where: k_{UV} (L kJ^{-1}) is the pseudo-first-order rate constant of selected drug photocatalysis considering the value of cumulative energy, wherein the cumulative energy (Q_{UV}) (kJ L^{-1}) is calculated as:

$$Q_{UV,n+1} = Q_{UV,n} + \overline{UV}_{G,n+1} \cdot \frac{A_i}{V_t} \cdot \frac{\Delta t_n}{1000}; \quad \Delta t_n = t_{n+1} - t_n \quad (4)$$

In above equation, $Q_{UV,n+1,}$ and $Q_{UV,n}$ represents the cumulative UV energy per volume unit of the processed drug at times *n* and *n-1*, respectively (kJ L^{-1}), whereas $\overline{UV}_{G,n+1}$ represents the average incident solar UV light estimated in time interval Δt_n (W m^{-2}), where A_i is the irradiated area (m^2); V_t is the overall volume of the RTR (L) and Δt_n is the time period between consecutive samples.

RESULTS AND DISCUSSION

Photodegradation of ritonavir in Milli-Q and Tap water

The degradation activity of the selected drug RTR, which belongs to the class of medications known as protease inhibitors, was thoroughly investigated in two distinct water matrices: MQ water, known for its high purity, and TW water. The findings, represented in Figure 1, reveal that after extensive exposure to solar light (500 W/m²), RTR exhibited inadequate degradation of only 15% within 90 minutes in MQ water. In the TW sample, the degradation rate increased to 38% with a reaction time of 120 minutes. The degradation rate constant of RTR was 0.0009 min^{-1} (MQ water) and 0.0026 min^{-1} (TW), respectively.

These results imply that, under typical environmental conditions, RTR may not experience significant degradation beyond this point. Although the photodegradation of Ritonavir in natural waters may reduce its persistence in the environment, it raises concerns about the potential formation of photoproducts whose ecological or toxicological effects are harmful to the aquatic organisms. The toxic effects of the select drug ritonavir (RTR) – on freshwater organisms are noteworthy. RTR shown toxicity at levels of hundreds of mg/L (Nugnes et al., 2024). To investigate these potential issues, further research will be needed such as a control test to ensure that external factors, such as impurities or matrix effects, do not interfere with the results. Moreover, advanced tools like LC-MS would be utilized to distinguish the parent compound from its photoproducts.

Effect of H_2O_2 on degradation of ritonavir

Based on the data from photolysis of selected drug, the next step of research was an assessment of the possibility on effect of UV/H_2O_2 on the degradation of ritonavir. For this purpose, three doses of H_2O_2 were used as described in experimental setup mentioned above. Figure 2 showed the photolytic degradation of RTR assisted with H_2O_2 in MQ water. It has been noted that after 45 min of the process, under the exposure of 500 W/m^2 artificial light irradiance, the concentration of RTR in MQ water with a selected dose of H_2O_2 were below its <LOD: 100%. According to the results, the kinetic rate constant of RTR obtained by H_2O_2 is higher in 500 µL i.e., (k = 0.1439) with a coefficient of determination (R^2) value of 0.9844 (Table 1), which demonstrates that the regression model matches the experimental data collected

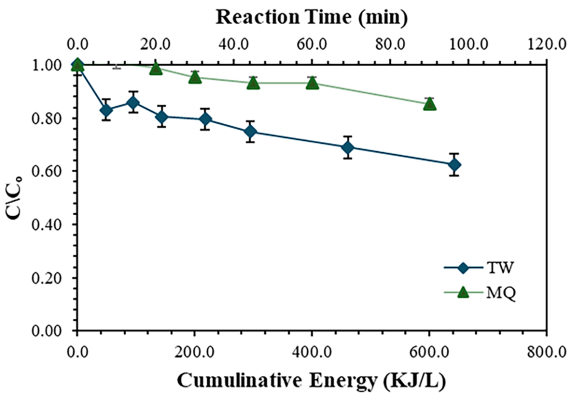

Figure 1. Photodegradation of ritonavir in Milli-Q and tap water

Table 1. Kinetic parameters–photodegradation of ritonavir

Process	Volume of H_2O_2 (µL)	Water matrices	*Kt* [a], min^{-1}	½ t [b], min^{-1}	R^2
PhotolysiS	-	MQ	0.0009	770	0.8995
		TW	0.0026	267	0.8199
Photolysis + H_2O_2	125	MQ	0.1274	5.44	0.9843
	250		0.0764	9.07	0.9595
	500		0.1439	4.82	0.9844

Note: [a] pseudo first order reaction constant, [b] half-life of the reaction.

for this investigation. The effectiveness of the degradation process can be significantly impacted by the concentration of hydrogen peroxide (H_2O_2) when utilized alongside UV light. H_2O_2 possesses a strong oxidation potential of 1.78 eV, that makes H_2O_2 an effective agent for enhancing degradation in RTR solutions (Wang et al., 2022). In the presence of UV light, H_2O_2 decomposes, producing extremely reactive hydroxyl radicals (•OH). These •OH radicals are essential for breaking down the organic pollutants especially antivirals and antibacterials drugs present in water environment. The mechanism of degradation for RTR under the combined influence of UV light and H_2O_2 is shown below (Equations 5–12):

$$H_2O_2 + light \rightarrow 2\,{}^{\bullet}OH \quad (5)$$

$$H_2O + light \rightarrow {}^{\bullet}H + {}^{\bullet}OH \quad (6)$$

$${}^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2 \quad (7)$$

$${}^{\bullet}OH + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \quad (8)$$

$${}^{\bullet}OH + HO_2^{\bullet} \rightarrow H_2O + O_2 \quad (9)$$

$$H_2O_2 + HO_2^{\bullet} \rightarrow {}^{\bullet}OH + H_2O + O_2 \quad (10)$$

$${}^{\bullet}OH + RTR \rightarrow CO_2 + H_2O + \text{degradation products} \quad (11)$$

$$H_2O_2 + RTR \rightarrow CO_2 + H_2O + \text{degradation products} \quad (12)$$

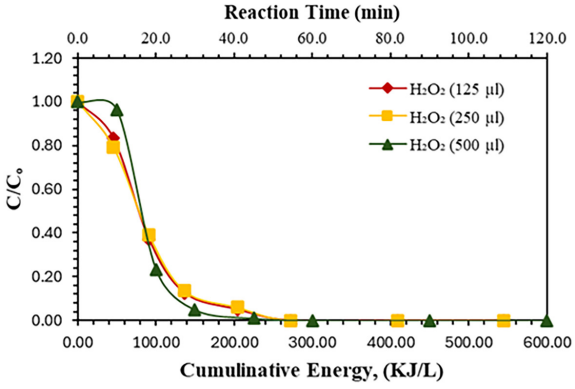

Figure 2. Photodegradation of ritonavir in Milli-Q assisted with H_2O_2

The combination UV/H_2O_2 or solar light/ H_2O_2 performs a significant role in enhancing the degradation process of pharmaceutical pollutants in water (Lester et al., 2011). In a reported study, researchers examined the degradation of group of pharmaceuticals, including metformin, which exhibits antiviral activity against RNA viruses, such as (SARS-CoV-2), and pentoxifylline, has strong antiviral properties against herpes simplex, vaccinia, rotavirus, and tick-borne encephalitis viruses. The study investigated the degradation of these compounds through a UV (solar light)/H_2O_2 process under various conditions, with most pharmaceuticals degrading by up to 90% (Wols et al., 2013).

UV (solar light)/H_2O_2 process significantly accelerates the breakdown of various contaminants, such as organic compounds, by producing reactive species that facilitate their decomposition. As a result, the overall efficiency of removing these harmful substances from the aqueous environment is greatly improved. This advancement contributes not only to more effective wastewater treatment strategies but also promotes healthier and more environmentally friendly water resources for humans as well as the environment. By harnessing the synergistic effects of UV (solar light)/H_2O_2, wastewater treatment facilities can achieve higher levels of contaminant removal, ultimately leading to a more sustainable approach to water management.

Removal of ritonavir in solar light driven TiO_2 photocatalysis

In order to confirm or exclude the interaction of the tested drug with the potential photocatalyst, it is necessary to conduct tests with the photocatalyst alone (without the participation of light) to assess the percentage of the drug that can be adsorbed on the photocatalyst molecule. The photocatalytic activity of pure TiO_2 (10.0 mg/L) on the selected compound (RTR) was examined in MQ water under dark conditions. The experiment was performed

in a beaker securely covered with aluminium foil to prevent light interference. It turned out that the tested drug has a strong affinity for sorption and the sorption process turned out to be the dominant process, and not, as was assumed at the beginning of the study, the photodecomposition process of the tested drug. The results revealed an immediate and complete adsorption of RTR, reaching 100% on the surface of TiO_2, as illustrated in Figure 3a.

In a parallel experiment, solar light irradiance of 500 W/m² was used. After a reaction period of 120 minutes, the amount of RTR adsorbed onto the TiO_2 surface reached 72%. The initial dose of RTR was fixed at 2.0 mg/L, which remained stable for the first 45 minutes. However, it decreased rapidly thereafter, with the equilibrium point established at 60 minutes into the reaction (Figure 3b). Most likely, sunlight caused a cycle of sorption and desorption processes of the tested drug on the titanium dioxide surface until the process stabilized and an equilibrium state was reached. Therefore, it was decided to calculate the efficiency of the adsorption process on the TiO_2 surface, which seems to be the dominant process. To calculate the amount of drug adsorbed on the TiO_2 surface following equation is used:

$$q_e = (C_o - C_e) \cdot V/m \quad (13)$$

where: q_e is amount of drug adsorbed per unit mass of TiO_2 (mg/g), C_o is initial concentration of the drug (before adding TiO_2) and C_e is a quantity of the drug in the solution at time t (after adsorption), V is volume of the solution (L), and m is an amount of catalyst used (g).

To characterize the adsorption equilibrium, Langmuir adsorption isotherms model was used (Equation 14):

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{q \max k_L c_e} \quad (14)$$

where: qe represents the quantity of drug deposited at equilibrium (mg/g), Ce is equilibrium concentration of drug in solution (mg/L), q_{max} is a maximal adsorption capacity (mg/g), and K_L is the Langmuir constant.

Adsorption of RTR on the surface of TiO_2 showed KL value of 1330.5 and 12515 in dark and with solar light irradiance respectively, indicates a highly favorable adsorption process (Araújo et al., 2018), with the adsorbent showing a strong affinity for the adsorbate (Table 2).

Adeola et al. (2021) investigated the removal of the antiretroviral drugs efavirenz and nevirapine from water. Their findings revealed that the maximum adsorption capacities for efavirenz and nevirapine were 899 mg/g and 5.547 mg/g, respectively. The suitability of efavirenz adsorption suggests that the interaction between these drugs and graphene wool (GW) is complex and exhibits significant heterogeneity, which contributes to the observed high level of variability. RTR can potentially form a coordination complex with the surface of titanium dioxide (TiO_2), because RTR contains functional groups such as: Thiazole ring with nitrogen atoms, Hydroxyl (-OH) groups, Amide (-CONH-) groups, and Ether (-O-) linkages. However, the extent and nature of the interaction depend on its functional groups, the surface chemistry of TiO_2, and environmental conditions such as pH and solvent (Natarajan et al., 2022). To confirm the formation of a complex, further research is needed for example FTIR analysis that shifts in characteristic vibrational bands (e.g., C=O, N-H, O-H) can indicate binding, XPS analysis

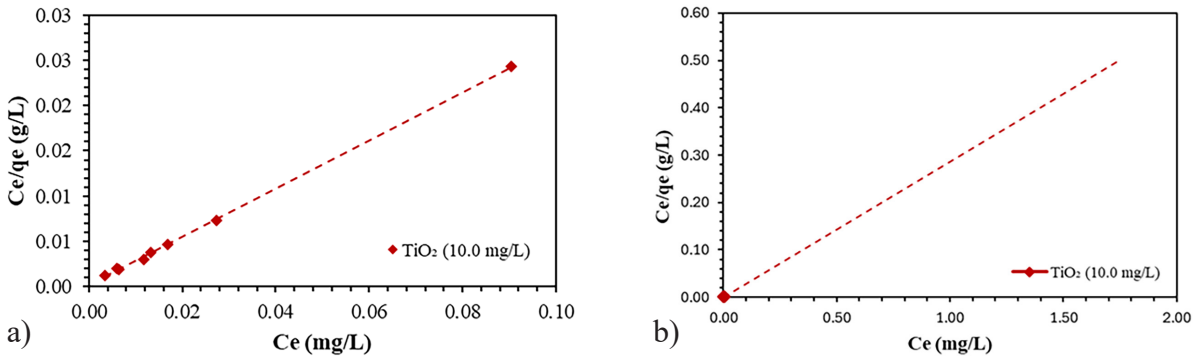

Figure 3. (a) Adsorption of ritonavir on the surface of TiO_2 in dark experiment; (b) adsorption of ritonavir on the surface of TiO_2 with solar light

Table 2. Kinetic parameters−adsorption of ritonavir

Process	Pseudo first rate constant of drug degradation rate (k), 1/min	R^2	KL	q_{max} (mg/g)
TiO_2 + Dark reaction	0.2862	0.9997	12515	3.9952
UV + TiO_2 (500 W/m²)	0.2661	0.9995	1330.5	3.7580

that can change in binding energy of titanium or elements in ritonavir (e.g., nitrogen, oxygen) can reveal coordination.

CONCLUSIONS

The study investigated the effects of hydrogen peroxide (H_2O_2) and pure titanium dioxide (TiO_2) on the degradation of ritonavir in two types of water under artificial solar irradiation. The results indicated that during the photolysis process, the degradation rates of ritonavir in the two different water matrices – Milli-Q (MQ) and tap water (TW) – were 0.0009 min^{-1} and 0.0026 min^{-1}, respectively. In contrast, the UV/H_2O_2 process proved to be the most effective, achieving a complete degradation rate after just 45 minutes of exposure, using three different concentrations of H_2O_2 (125 µL, 250 µL, and 500 µL). The photocatalytic reactions were observed to follow pseudo-first-order kinetics across all experiments. Regarding the process conducted in the presence of TiO_2, it turned out that the dominant process in the removal of the tested drug from the aqueous environment was adsorption, not photochemical decomposition. Therefore, in order to calculate the parameters of the adsorption process, the Langmuir isotherm was used, which showed a very good fit to the obtained research results. The Langmuir constant (KL) recorded in the UV/TiO_2 process was 1330.5 in MQ water, with a maximum adsorption capacity (q_{max}) of 3.7580 mg/g. Rapid adsorption was noted, suggesting that ritonavir may form a coordination complex with the surface of titanium dioxide (TiO_2). However, additional research, including FTIR and XPS analyses, is needed to confirm the existence of this coordination complex.

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