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# The role of selected anions in the photodegradation of vancomycin in the aquatic environment

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## ABSTRACT

The efficiency of micropollutant photodegradation in aquatic matrices depends on several factors, including the presence of anions. They can act as radical scavengers and therefore inhibit the removal rate of micropollutants. Understanding the mechanisms of these interactions is crucial for the further development of advanced treatment technologies of water. Taking this into account, the main objective of the present study was to evaluate the effect of selected anions, such as $Cl^-$, $SO_4^{2-}$, $NO_3^-$, and $HCO_3^-$, on the photolytic and photocatalytic degradation of vancomycin (VAN) in an aqueous matrix. The experiments were carried out in a solar simulator (Solarbox) using $TiO_2$ and ZnO as photocatalysts and Milli-Q water as an aquatic matrix. Additional tests were performed in the presence of peroxymonosulfate (PMS) and sulfate ions ($SO_4^{2-}$) to assess their influence on VAN degradation efficiency in the sulfate radical-based advanced oxidation process. The results demonstrated that vancomycin photodegradation efficiency was significantly influenced by the type of anions present in the solution. The scavenging effects of reactive oxygen species increase in the following order: $HCO_3^- > NO_3^- > Cl^- > SO_4^{2-}$. Moreover, the presence of sulfate ions adversely affected the PMS-assisted photodegradation, with a marked decrease in efficiency in most cases, except for $TiO_2$-based photocatalysis, where comparable removal was still achieved.

**Keywords:** photodegradation, vancomycin, anions, peroxymonosulfate.

## INTRODUCTION

The presence of antibiotics in the environment might have adverse effects on living organisms and lead to their bioaccumulation in soil or in the organisms' tissues (Felis et al., 2019; Zhang et al., 2022). However, the most hazardous effect of the presence of antibiotics in different environmental matrices is contributing to the emergence and spread of the phenomenon of antimicrobial resistance (AMR). European Centre for Disease Prevention and Control (ECDC) estimates that each year throughout countries of European Union (EU), Iceland and Norway, more than 35 000 deaths are related to infections caused by antibiotic-resistant bacteria (ARB) (ECDC, 2024). For decades, vancomycin (VAN) has been classified as a "last-resort antibiotic" (i.e. "reserve"), although it is currently classified as a "watch" according to the WHO classification system. It should be mentioned here that the group of "reserve antibiotics" includes medicines that should be reserved for treatment of confirmed or suspected infections due to multidrug-resistant organisms and only in hospital conditions (WHO, 2023). The "Watch list" comprises antibiotic classes with a high potential to drive antimicrobial resistance. It includes many of the highest-priority agents classified as Critically Important Antimicrobials for Human Medicine, as well as antibiotics considered to pose an elevated risk for selecting resistant bacterial strains. Despite the recommendation, Snodgrass et al. (2023) reported that only 51.7% of patients receiving VAN truly had indications for its use based on the suspected diagnosis, highlighting substantial overuse. Environmental overuse of VAN and the resulting excessive environmental exposure, often alongside third-generation cephalosporins, vancomycin-resistant enterococci (VRE) have emerged (Siegel, 2012). For this reason, VAN has been detected in the wastewater outflows from urban hospitals with a very high frequency of its occurrence (Rossmann et al., 2014; Zuccato et al., 2010). Conventional wastewater treatment plants are unable to completely remove this type of micropollutant (Deng et al., 2026). Given these concerns, the development of efficient wastewater treatment methods for the removal of such micropollutants has become a pressing priority (Szymańska et al., 2019).

Photocatalytic degradation is recognized as an effective method to remove persistent organic micropollutants. The photocatalysis begins when a semiconductor absorbs light with energy exceeding its band gap, promoting electrons ($e^-$) to the conduction band (CB) and generating holes ($h^+$) in the valence band (VB). These charge carriers ($e^-$, $h^+$) initiate oxidation and redox reactions that produce reactive oxygen species (ROS). ROS are capable of degradation of the micropollutants from the aquatic matrix (Figure 1) (Puga et al., 2024). Among various photocatalysts, titanium dioxide ($TiO_2$) pays special attention due to its excellent chemical stability, efficient generation of electron hole ($e^-/h^+$) pairs, and a band gap energy between 3.20 and 3.55 eV (Qi et al., 2025). $TiO_2$-based photocatalysis has demonstrated high efficiency in degrading contaminants of emerging concern (CECs) in aquatic matrices, owing to their strong oxidative capacity, chemical stability, and effective generation of reactive oxygen species (Bayan et al., 2021; Silerio-Vázquez et al., 2024). Researchers are also increasingly investigating zinc oxide (ZnO), which offers comparable photocatalytic efficiency. Moreover, comparing the above-mentioned photocatalysts ZnO is more cost-effective, exhibits greater biocompatibility, and remains stable in environmental conditions (Bujaldón et al., 2024; Kowalska et al., 2022).

To enhance photocatalytic efficiency, the process can be coupled with sulfate radical-based advanced oxidation processes (SR-AOPs), which generate highly reactive sulfate radicals ($SO_4^{\bullet-}$) in the reaction medium. SR-AOPs have been attracting increasing attention because of their strong oxidation ability and mineralization efficiency (Long et al., 2022). Compared with HO•, $SO_4^{\bullet-}$ exhibit higher selectivity, extended stability, and equal or even higher redox potential under neutral pH conditions (Li et al., 2021; Milh et al., 2021). Peroxymonosulfate ($HSO_5^-$, PMS) is an unsymmetrical oxidant that can partially oxidize some organic compounds. However, its direct reaction toward most pollutants is relatively low. Therefore, activation of PMS to generate $SO_4^{\bullet-}$ is necessary to achieve effective degradation (Li et al., 2021). PMS has been found as the sulfate radical precursor owing to its strong oxidative potential (2.5–3.1), making it an environmentally friendly reagent for solar-driven degradation processes. A wide range of reactive species generated during, e.g. $SO_4^{\bullet-}$, HO•, $\bullet O_2^{\ -}$, and $^1O_2$ photochemical activation degrade organic micropollutants to by-products, $CO_2$, $H_2O$, and other mineral products as well (Jiang et al., 2022; Tian et al., 2023).

Although reaction kinetic depends on solution pH, it is also crucial to evaluate the photodegradation of VAN under various water treatment conditions, including the presence of various ions naturally occurring in aqueous matrices or extensively released through human activities. Therefore, this study aimed to investigate the impact of common anions such as nitrate ($NO_3^-$), chloride ($Cl^-$), bicarbonate ($HCO_3^-$), and sulfate ($SO_4^{2-}$), on the VAN degradation. They might inhibit photocatalysis by scavenging reactive species or interfering with the formation and subsequent reactions of radicals (e.g., hydroxyl radical (HO•), and sulfate radical ($SO_4^{\bullet-}$) (He and O'Shea, 2020). Conversely, the presence of sulfate anions may enhance the degradation efficiency in persulfate-based systems. However, the influence of $SO_4^{2-}$ on photocatalytic degradation strongly depends on the sulfate concentration and the concentration of the sulfate radical precursor as well (Honarmandrad et al., 2023).

Despite the increasing concern regarding the presence of VAN in aquatic environments, studies addressing its degradation using advanced oxidation processes (AOPs) are limited. To the best of authors' knowledge, systematic investigations on VAN removal via conventional AOPs or SR-AOPs have not yet been reported. The application of solar-driven photolysis and photocatalysis, both in the absence and presence of PMS, remains unexplored. Therefore, this study aims to fill this research gap by evaluating the efficiency and mechanisms of VAN degradation in solar-driven system using PMS as a sulfate anion radicals' precursor.

This study focused on evaluating VAN removal efficiency by solar-driven photolysis and

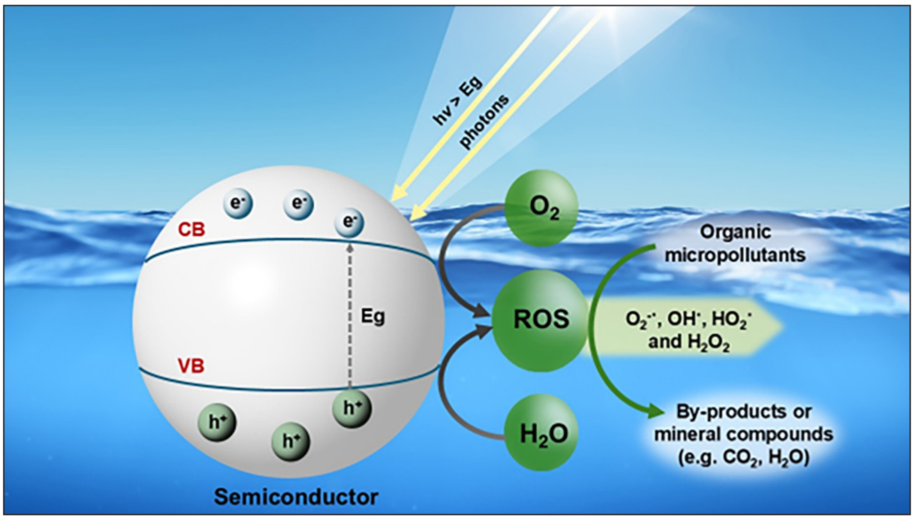

**Figure 1.** The schematic diagram of the photocatalytic mechanism (based on Qi et al., 2025)

photocatalysis in the presence of various anions. $TiO_2$-P25 and ZnO were used as photocatalysts, where $TiO_2$-P25 was used as a reference photocatalysts. Experiments were performed without PMS and with PMS at two concentrations (20 mg $L^{-1}$ and 200 mg $L^{-1}$), as well as with and without an additional sulfate source to assess the influence of $SO_4^{\bullet -}$ on the VAN degradation efficiency in PMS-assisted systems.

## MATERIALS AND METHODS

The present methodology builds on and extends the approach applied in our previous works (Sowik et al., 2025a, Sowik et al., 2025b).

### Reagents and chemicals

The analytical standard of VAN-HC was purchased from Sigma Aldrich (China). Peroxymonosulfate (PMS), supplied as Oxone® salt ($KHSO_5 \cdot 0.5KHCO_5 \cdot 0.5K_2SO_4$), was purchased from Sigma Aldrich (USA). Acetonitrile (ACN; HPLC grade, 99.9%) and formic acid (FA, ≥99.9%) for HPLC were obtained from VWR Chemicals (Poland). The photocatalysts: $TiO_2$-P25 (Titandioxid P25, 99.9%) and ZnO (99.9%), were purchased from Degussa (Germany) and Sigma Aldrich (China), respectively. $TiO_2$-P25 refers to the commercial Degussa (Evonik) P25 titanium dioxide – photocatalysts composed of a mixed-phase structure of anatase (~80%) and rutile (~20%). As a source of selected anions: sodium chloride (>99%) (Warchem, Poland), sodium bicarbonate (98.8%), sodium nitrate (>99%) (Avantor, Poland), and sodium sulfate (99.9%) (Standard, Poland) were used. The mobile phase solution was prepared using ultrapure Milli-Q water (18.2 MΩ.cm) produced by a Synergy® Water Purification System (Merck, Germany).

A stock solution of VAN (10 mg $L^{-1}$) was prepared by dissolving 10 mg of the analytical standard in 1000 mL of Milli-Q water. Working solutions with a concentration of 2 mg $L^{-1}$ were freshly prepared prior to each experiment by diluting 1:5 of the stock solution also in Milli-Q water. The stock solutions were stored at 2 °C in a refrigerator and remained stable for at least three weeks.

### Quantification of VAN

Vancomycin (VAN) was quantified using high-performance liquid chromatography (HPLC) with a UV variable wavelength detector (UltiMate 3000 system; Dionex Corporation, Sunnyvale, CA, USA). Separation was achieved on a C18 Hypersil™ Gold column (250 × 4.6 mm; 5 µm; Thermo Scientific, Polygen, Poland). The mobile phase consisted of 0.1% FA solution and ACN in a 77:23 (v/v) ratio. Detection was carried out at 323 nm and 280 nm, and VAN was identified at a retention time of 5.5 ± 0.8 min. The limit of quantification (LOQ) was 0.1 mg $L^{-1}$, corresponding to the lowest point of the calibration curve (linear regression, $R^2 > 0.98$). Data acquisition and processing were performed using Dionex Chromeleon™ 6.8 software.

## Experimental set-up

Control experiments under dark conditions were conducted to evaluate the removal of VAN due to sorption onto surface of the photocatalysts ($TiO_2$-P25 and ZnO). The experiments were performed in class beakers tightly covered with aluminum foil to prevent any unintended light exposure. Each experiment was carried out with a total solution volume of 250 mL and a photocatalysts concentration of 20 mg $L^{-1}$. Solutions containing VAN and respective photocatalysts were continuously mixed using magnetic stirrers to ensure homogeneity. The sorption experiments were conducted for 60 minutes, with samples collected at the same time intervals as those used in the photodegradation experiments.

Target laboratory-scale experiments were carried out to investigate the removal of VAN and to evaluate the influence of selected anions on VAN degradation efficiency under simulated solar irradiation. A Solarbox 1500e solar simulator (Co.fo.me.gra, Italy), equipped with a 1500 W polychromatic xenon lamp, was used to imitate the solar radiation (Figure 2). Photolytic and photocatalytic degradation of VAN were evaluated under irradiation intensity set at 500 W $m^{-2}$ (400–700 nm).

Photocatalytic experiments were performed using $TiO_2$-P25 and ZnO at a concentration of 20 mg $L^{-1}$ of each. The concentrations of the selected anions were established based on the permissible limits for drinking water quality in Poland (Dz. U. 2017.2294), including 250 mg $L^{-1}$ for $Cl^-$, $SO_4^{2-}$ and $HCO_3^-$ and 50 mg $L^{-1}$ for $NO_3^-$. To assess the influence of the sulfate anion precursor, PMS was used at concentrations of 20 mg $L^{-1}$ and 200 mg $L^{-1}$. The PMS concentrations were selected based on reported ranges in literature, which span from very low to higher concentrations than those used in the present study. These values were chosen to evaluate the effect of PMS dosage on VAN degradation while recognizing further optimization is required to identify the optimal concentration for the process. Tests were also performed in the presence of sulfate ions ($SO_4^{2-}$) at concentrations of 250 mg $L^{-1}$, as one of the main components of the aquatic environmental matrices. This allowed to assess the effect of PMS dosage on VAN removal and its interaction with sulfate ions.

The working volume solution was 250 mL for each experiment. The initial concentration of VAN was 2 mg $L^{-1}$. Although micropollutants are typically present in environmental water at ng $L^{-1}$ – ug $L^{-1}$ levels, locally elevated concentrations in the mg $L^{-1}$ range may occur in specific scenarios, such as pharmaceutical effluents or hospital wastewater. Moreover, the use of higher initial concentration was also necessitated by analytical detection limitations of the available equipment.

**Figure 2.** Solar simulator (Solarbox 1500e)

The reaction solution was placed in a glass beaker positioned inside the Solarbox and continuously stirred using a magnetic stirrer to ensure homogeneity throughout the experiment. The Solarbox is equipped with an internal mirror system that enables multiple reflections of the incident light, allowing uniform irradiation of the sample from all directions. Samples were collected at predetermined time intervals (0, 5, 10, 20, 30, 45, 60, and 90 minutes) which was the same for both photolysis and photocatalysis. All experiments were performed in duplicate.

### Data analysis

The removal efficiency of VAN ($R_{VAN}$) was determined using to Equation 1:

$$R_{VAN} = \left(\frac{C_0 - C_t}{C_0}\right) \cdot 100\% \tag{1}$$

where: $C_0$ and $C_t$ represent the initial and residual antibiotic concentrations (mg L$^{-1}$) at time $t$, respectively.

The degradation kinetics of VAN followed a pseudo first-order kinetics model, as described by Equations 2–3 (Sowik et al., 2025a):

$$ln\left(\frac{C_t}{C_0}\right) = exp^{-k_t t} \tag{2}$$

$$t_{1/2} = \frac{ln2}{k_t} \tag{3}$$

## RESULTS AND DISCUSSION

### Photodegradation of VAN without PMS

These experiments were carried out to determine the effect of matrix complexity on the photodegradation of VAN. Selected anions, namely nitrate ($\mathrm{NO_3^-}$), chloride ($\mathrm{Cl^-}$), bicarbonate ($\mathrm{HCO_3^-}$), and sulfate ($\mathrm{SO_4^{2-}}$), were used as chemical scavengers. Comparing the degradation efficiency of VAN in the presence and absence of each scavenger, there is a possibility to evaluate the effect of each anion on the photolytic and photocatalytic degradation of VAN.

Sorption experiments under dark conditions indicated partial removal of VAN, with approximately 22% of the initial concentration adsorbed onto the ZnO surface within 60 minutes. In comparison, $TiO_2$ exhibited slightly higher sorption capacity, achieving about 26% VAN removal within the same time. Photolytic degradation of VAN was inefficient, reaching only 18% removal after 90 minutes of irradiation ($t_{1/2}$ = 301 min, $k$ = 0.002 min$^{-1}$, $R^2$ = 0.88) (Figure 3a). The relatively low efficiency of direct photolysis can be attributed to its high molecular weight and complex polycyclic structure which limits its absorption of solar radiation and reduces the probability of direct bond cleavage. The presence of multiple aromatic rings and functional groups may promote steric hindrance, thereby decreasing the reactivity toward photogenerated species. The addition of anions slightly enhanced the degradation efficiency in the following orders: $\mathrm{HCO_3^-} > \mathrm{NO_3^-} > \mathrm{Cl^-} > \mathrm{SO_4^{2-}}$. The presence of bicarbonates increased the removal efficiency by 48 pp ($t_{1/2}$ = 49 min, $k$ = 0.014 min$^{-1}$, $R^2$ = 0.99). The efficiency increase in the presence of carbonates may be result of the formation of carbonate radicals ($CO_3^{\cdot-}$) by reaction with HO• (Equations 4–6). $CO_3^{\cdot-}$ has been found as powerful oxidant in the degradation of organic pollutants. It has high reactivity and selectivity towards pollutants with electron-rich centers and possesses a lower redox potential than HO•. According to above, carbonates show a dual effect depending on the type of micropollutants (Rayaroth et al., 2023; Wang et al., 2021).These anions act as pH buffers, typically shifting the solution toward alkaline conditions, where many micropollutants, including antibiotics, exist in deprotonated forms that are more susceptible to photochemical transformation (Li et al., 2018). At the same time, at low concentrations, carbonates and bicarbonates act primarily as radical scavengers, converting highly reactive $SO_4^{\cdot-}$ and ·OH into less reactive carbonate radicals ($CO_3^{\cdot-}$), which may reduce degradation efficiency (Ao and Liu, 2017; Liu et al., 2013). Presence of carbonates may reduce non-selective hydroxyl-based oxidation, $CO_3^{\cdot-}$ can still contribute to the degradation of specific compounds, especially under conditions where dissolved oxygen is limited (Li et al., 2018).

$$OH \cdot + CO_3^{2-} \rightarrow OH^- + CO_3^{\cdot-} \tag{4}$$

$$OH \cdot + HCO_3^- \rightarrow OH^- + HCO_3^{\cdot} \tag{5}$$

$$HCO_3^{\cdot} \leftrightarrow OH^+ + CO_3^{\cdot-} \tag{6}$$

Lin et al. (2023) showed that $\mathrm{Cl^-}$, $\mathrm{SO_4^{2-}}$, $\mathrm{NO_3^-}$ had inhibitory effects on the photodegradation of sulfamethoxazole and enrofloxacin. On the other hand, Bian and Zhang (2016) indicate that $NO_3^-$ can be photolyzed to nitroso and negative oxygen ions and later further combined with $H^+$ to form HO• (Equations 7 and 8). The addition of the nitrate to the sulfadiazine solution resulted in enhanced degradation rate from 0.071 to 0.10. Nitrate ions, commonly present in natural waters, can act as effective photosensitizers in photocatalytic and photolytic processes. Upon UV irradiation, nitrates undergo photolysis, leading to the formation of highly reactive HO• through reactions involving excited nitrate species and water molecules. As a result, the degradation rate of various micropollutants often increases with increasing nitrate concentrations, reflecting enhanced HO• generation. However, at elevated nitrate levels, light absorption by $NO_3^-$ may partially compete with target contaminants for photons, introducing a light-screening effect that can limit further efficiency gains (Li et al., 2018).

$$NO_3^- + hv \rightarrow \cdot NO_2 + O^{\cdot -} \tag{7}$$

$$O^{\cdot -} + H^+ \leftrightarrow \cdot OH \tag{8}$$

The highest removal efficiency of VAN among all studied processes was achieved by photocatalysis with $TiO_2$, where complete VAN removal was observed after only 20 minutes ($t_{1/2} = 2.93$ min, $k = 0.237$ min$^{-1}$, $R^2 = 0.97$) (Figure 3b). A comparable result was obtained in the presence of $NO_3^-$, indicating that nitrate slightly affect the process ($t_{1/2} = 5.04$ min, $k = 0.138$ min$^{-1}$, $R^2 = 0.95$). In contrast, other anions (Cl, $HCO_3^-$, $SO_4^{2-}$) reduced the photodegradation rate, and complete removal was observed after 45 minutes. Chlorides ions can act as effective scavengers of photogenerated charge carriers and reactive oxygen species, including valence band holes ($h^+$), HO•, and $•O_2^-$, leading to the formation of reactive chlorine speciec (RCS) such as $Cl_2$ or $HOCl^{•-}$ (Equations 9–11). While these reactions often reduce the availability of highly reactive HO• and slow overall mineralization, the generated RCS may selectively oxidize electron-rich organic micropollutants, what can result in faster removal of certain parent compounds. However, chloride ions may also compete with pollutants for active sites on the photocatalysts surface, further limiting degradation efficiency (Sun et al., 2024; Chi et al., 2020). For example, presence of $Cl^-$ at certain value enhanced removal of dye pollutants. But decreasing the overall photodegradation efficiency occurred when the $Cl^-$ concentration was below the appropriate value (Wang et al., 2011). Moreover, at low pH values, chloride ions can form inner-sphere surface complexes with $TiO_2$. According to that, $Cl^-$ competes with hydroxyl ions and water molecules for active sites on the $TiO_2$ surface, leading to reduced HO• radical generation (Puga et al., 2024; Villegas-Guzman et al., 2017).

$$2Cl^- + 2h^+ \rightarrow Cl_2 \tag{9}$$

$$2Cl^- + 2\cdot OH + 2H^+ \rightarrow 2H_2O + Cl_2 \tag{10}$$

$$Cl^- + \cdot OH \rightarrow HOCl^{\cdot -} \tag{11}$$

ZnO-based photocatalysis showed a significant decrease in VAN removal efficiency compared to $TiO_2$-based processes ($t_{1/2} = 8.57$ min, $k = 0.081$ min$^{-1}$, $R^2 = 0.86$) (Figure 3c). Complete removal was achieved after 90 minutes. The presence of $SO_4^{2-}$ further decreased efficiency, resulting in only 89% removal of VAN ($t_{1/2} = 27$ min, $k = 0.025$ min$^{-1}$, $R^2 = 0.97$). Conversely, the presence of the other anions ($Cl^-$, $HCO_3^-$ and $NO_3^-$) positively influenced the photocatalytic degradation of VAN, where complete removal was obtained after 45 minutes for $Cl^-$ ($t_{1/2} = 9.16$ min, $k = 0.076$ min$^{-1}$, $R^2 = 0.86$) and $HCO_3^-$ ($t_{1/2} = 11.99$ min, $k = 0.058$ min$^{-1}$, $R^2 = 0.93$) and after 60 minutes for $NO_3^-$ ($t_{1/2} = 11.46$ min, $k = 0.0605$ min$^{-1}$, $R^2 = 0.94$). The presence of $NO_3^-$ in photocatalysis with ZnO process slightly improved VAN degradation, which may be attributed to nitrate photolysis under irradiation, generating $\cdot NO_2$ and $O^-$ radicals that can further react to form ·OH (Bian and Zhang, 2016). However, previous studies have reported other effects of nitrate, with Lin et al. (2023) showing inhibitory behavior. Therefore, the observed enhancement should be considered as a process-specific effect and interpreted with caution. Lower efficiency of ZnO-based photocatalysis in the presence of $SO_4^{2-}$ might be result of too high concentration of $SO_4^{2-}$ beyond the optimum value. Under such conditions, $SO_4^{2-}$ can interact with the ZnO surface, contributing to catalyst site deactivation and as result reduce the degradation efficiency of organic contaminants (Mirzaei et al., 2016). In turn, increased efficiency in other cases may be the result of the formation of new reactive radicals.

The presence of $Cl^-$ and other ions, such as $SO_4^{2-}$, $NO_3^-$ and $HCO_3^-$ are commonly studied as interfering species, where their presence together with the micropollutant, can influence the efficiency

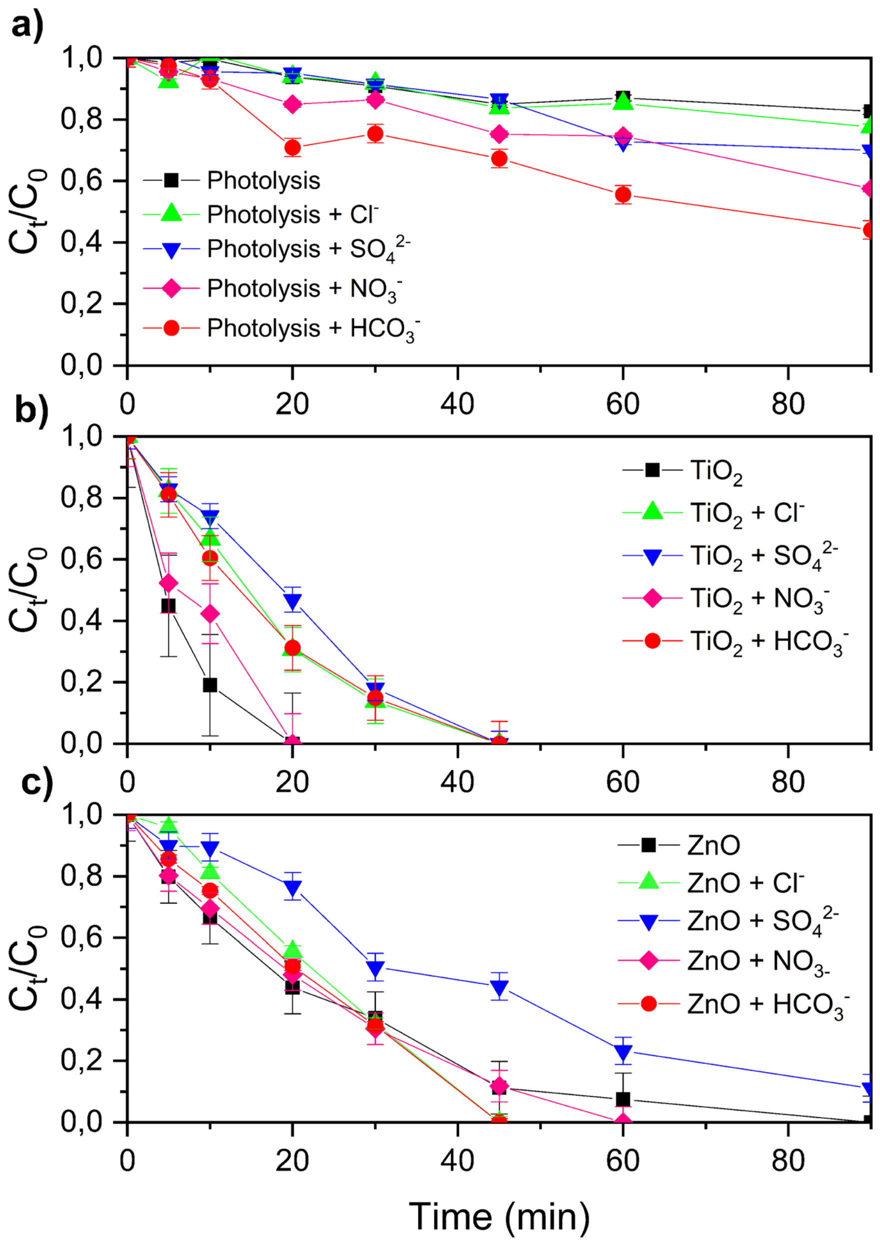

**Figure 3.** Photodegradation of VAN a) photolysis; b) $TiO_2$-based photocatalysis; c) ZnO-based photocatalysis without and in the presence of studied anions ($Cl^-$= 250 mg $L^{-1}$; $SO_4^{2-}$ = 250 mg $L^{-1}$; $NO_3^-$ = 50 mg $L^{-1}$ and $HCO_3^-$ = 250 mg $L^{-1}$)

of photocatalytic degradation. Confirming photocatalytic activity in the presence of these ions is critical for the development of applications in wastewater treatment systems (Hong et al., 2022).

The error bars represent standard deviations calculated from duplicate experiments and are provided to indicate experimental reproducibility.

## Photodegradation of VAN with PMS

Anions might affect the efficiency of antibiotic photodegradation using PMS in aquatic matrices in different ways. Understanding their impact is crucial, as these anions naturally occurred in aquatic environments can either inhibit or enhance micropollutants removal. The overall effect depends on several factors, including the type of process, the concentration of the target micropollutant, the type and dosage of oxidant, and concentration of present anions. Many studies have examined the effects of $Cl^-$, $NO_3^-$, $H_2PO_4^-$, and $HCO_3^-$ on photodegradation of CECs (He and O’Shea, 2020; Nie et al., 2019; Raczak et al., 2025; Yang et al., 2018).

However, there is still incomplete knowledge of the influence of $SO_4^{2-}$ on PMS-based photodegradation processes that rely on the generation of sulfate radical anions ($SO_4^{\bullet-}$).

The presence of $SO_4^{\bullet-}$ negatively affects the photodegradation of VAN. In all cases, the removal efficiency decreased in comparison to PMS alone, with the lowest degradation rate observed for the photolysis. Complete VAN removal was achieved after 60 and 20 minutes for PMS concentrations of 20 mg L$^{-1}$ (PMS20) ($t$ = 14.75 min, $k$ = 0.047 min$^{-1}$, $R^2$ = 0.96) and 200 mg L$^{-1}$ (PMS200) ($t$ = 4.74 min, $k$ = 0.146 min$^{-1}$, $R^2$ = 0.97), respectively (Figure 4a). Addition of sulfates results in lower degradation efficiency, where complete degradation was obtained after 45 minutes with PMS200 ($t$ = 9.43 min, $k$ = 0.074 min$^{-1}$, $R^2$ = 0.93), while approximately 73% of removal was achieved within 90 minutes at the lower PMS concentration ($t$ = 52.12 min, $k$ = 0.013 min$^{-1}$, $R^2$ = 0.96). The smallest differences between processes were observed for the $TiO_2$-based photocatalysis, where the presence of $SO_4^{\bullet-}$ caused only a minor decrease in efficiency, especially at the higher PMS concentration (Figure 4b). In contrast, the greatest differences occurred in the ZnO-based processes, where $SO_4^{\bullet-}$ reduced degradation efficiency at both PMS levels, indicating a stronger inhibitory effect on ZnO than on $TiO_2$. Moreover, increasing the PMS concentration significantly enhanced VAN removal during all processes. However, the highest improvement was for the photolytic and ZnO-based processes, which showed much efficient degradation at PMS200 compared to PMS20. In contrast, photocatalysis with $TiO_2$, already highly efficient at the lower PMS concentration, exhibited the smallest relative enhancement upon increasing PMS dosage.

Error bars represent standard deviations calculated from duplicate experiments and are provided to indicate experimental reproducibility. The highest efficiency of VAN removal was achieved by photocatalysis using $TiO_2$ and PMS at a concentration of 200 mg L$^{-1}$ ($t_{1/2}$ = 2.62 min, $k$ = 0.264 min$^{-1}$, $R^2$ = 0.93). Decrease of removal efficiency was observed only at the lower PMS concentration in the presence of sulfates ($t_{1/2}$ = 6.94 min, $k$ = 0.099 min$^{-1}$, $R^2$ = 0.98). In turn, in any case of the ZnO-based process, the presence of $SO_4^{2-}$ reduces the efficiency of the VAN photodegradation process. The observed effects in ZnO/PMS processes are likely related to PMS activation, although the contribution of $Zn^{2+}$ release cannot be excluded and was not directly investigated (Kong et al., 2021). In the process with a lower PMS concentration (20 mg L$^{-1}$), complete VAN removal occurred after 30 and 45 minutes, respectively. However, in the processes with PMS at a concentration of 200 mg L$^{-1}$, complete removal was achieved within 20 and 30 minutes, both for the process without and in the presence of $SO_4^{2-}$.

The enhanced degradation efficiency observed in PMS-assisted photocatalytic processes may suggests that VAN removal is predominantly ruled by non-selective radical reactions, involving $SO_4^{\bullet-}$, which are more effective in attacking structurally complex antibiotic molecules. Moreover, pH is one of the most influential parameters in PMS-based processes, as it rules PMS stability, speciation, and the relative contribution of reactive radicals, directly affecting antibiotics degradation efficiency. Under acidic conditions (pH < 7) – like in our case, where pH of most of the processes is in de range 3.4–6.1, $SO_4^{\bullet-}$ are the dominant reactive species. However, at very low pH values, excess $H^+$ may act as radical scavengers, potentially reducing degradation rates. In neutral and mildly alkaline conditions can be converted into HO• may coexist, whereas at higher pH values (pH > 9), sulfate radicals can be converted into hydroxyl radicals through reactions with $OH^-$, often resulting in lower oxidation efficiency due to the weaker oxidizing potential and shorter lifetime of HO•. Additionally, alkaline conditions may promote PMS decomposition pathways leading to the formation of $H_2O_2$, $O_2^{\bullet-}$, 1O2, which can further modify degradation mechanisms. pH also affects catalysts behavior, including metal speciation, surface hydroxylation, and the formation of secondary radical scavengers such as bicarbonate and carbonate ions. Therefore, although PMS-based processes can operate over a wide pH range, the balance between $SO_4^{\bullet-}$ and HO• and degradation efficiency are strongly process-dependent, highlighting the need for pH-specific optimization tailored to the target antibiotic (Ghanbari et al., 2016; Honarmandrad et al., 2023 Wang et al., 2018).

Sulfate ions exhibit a limited influence on degradation efficiency in PMS-based processes. Previous studies on the degradation of pharmaceuticals such as sulfamethoxazole and atenolol have shown that $SO_4^{2-}$ neither significantly inhibits nor promotes pollutant removal. This behavior may be attributed to the relatively low reactivity of sulfate ions toward both sulfate and hydroxyl radicals

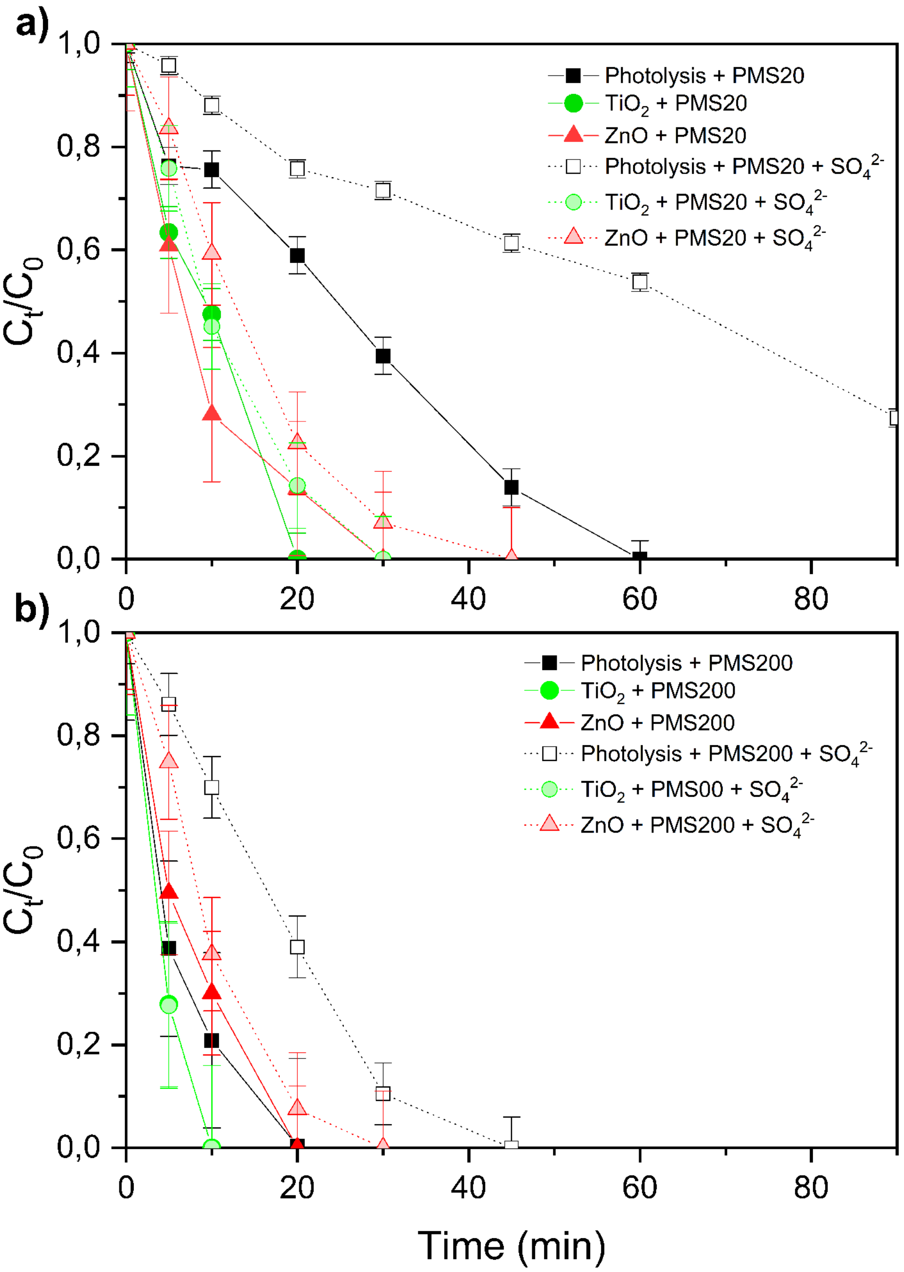

**Figure 4.** Photodegradation of VAN in the absence and presence of $SO_4^{2-}$ with PMS concentration at a) 20 mg $L^{-1}$ and b) 200 mg $L^{-1}$

compared to other common inorganic anions. Consequently, $SO_4^{2-}$ is not considered an effective radical scavenger under typical UV/PMS conditions, and its presence does not substantially deteriorate process performance. Only in specific systems and at low concentrations may $SO_4^{2-}$ slightly enhance degradation, whereas higher concentrations tend to exhibit a neutral or mildly inhibitory effect (Ao and Liu, 2017; Liu et al., 2013). From the other hand, Honarmandrad et al. (2023) reported that sulfate ions negatively affect $SO_4^{\bullet-}$ and HO•, because $SO_4^{2-}$ can suppress those radicals and may also chelate metal oxide. Moreover, the scavenging effect of $SO_4^{2-}$ might become stronger with increasing $SO_4^{2-}$ concentration, which in turn led to the reduction of micropollutants degradation rate at high $SO_4^{2-}$ concentration. Similar results were observed during the degradation of cefixime using a UV/PMS system, where low concentrations of $SO_4^{2-}$ ions decreased the photodegradation efficiency (Khazaei et al., 2019). Nevertheless, our recent work demonstrated that the PMS/Vis system achieved much higher removal of VAN in a more complex matrix, such as real municipal wastewater effluent (MWWE). It is highlighting that, despite the potential inhibitory role of $SO_4^{2-}$, processes using PMS as oxidant can perform very effectively under realistic environmental conditions (Sowik et al., 2025). Although direct reactions between anions and PMS were not assessed in this study, we recognize their potential significance for PMS activation and radical generation.

## CONCLUSIONS

VAN photodegradation in the solar light spectrum is influenced by several factors such as the type of process, photocatalysts and its concentration, and the dosage of oxidant. Increasing PMS concentration enhanced the photodegradation rate of VAN, due to higher generation of more reactive oxygen species. However, the presence of $SO_4^{2-}$ negatively affected the photodegradation of VAN, leading to a significant depletion of removal efficiency. In case of photocatalysts examined, $TiO_2$ outperforms ZnO, showing higher photodegradation efficiency under artificial sunlight. Moreover, the study confirms that anions naturally present in aquatic environments can inhibit or promote photodegradation, based on their concentration and chemical characteristics. These effects do not follow a simple trend. Anions interact with oxidant like PMS and compete for reactive sites on the catalysts, potentially altering the entire degradation mechanism. In real environmental matrices, the coexistence of various ions and organic matter introduces additional competitive and synergistic reactions, leading to results that may differ from those obtained with single-ion model systems. According to the complexity of relations between reactions, it is necessary to evaluate advanced oxidation processes in the environmental samples, such as real wastewater, to properly assess and understand the possibility of implementation of photocatalytic technologies for micropollutants removal in wastewater treatment plants. Overall, the results indicate that the proposed PMS-based process operating under visible-light irradiation has strong potential for application in wastewater treatment plants due to its high efficiency and low energy demand, as it does not require UV light. Nevertheless, further studies should include analysis of transformation products, toxicity assessment of post-process solutions, and a systematic evaluation of pH and anion synergy. Those are necessary to fully assess practical applicability of the technology.

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