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Degradation of rosuvastatin by UV/persulfate and UV/persulfate/Fe^{2+} processes: Kinetics, mechanism, toxicity and economic evaluations

Abstract

Rosuvastatin (RS), a blood cholesterol lowering medicine, was degraded by sole UV, UV/PS and UV/PS/Fe^{2+} processes. Under UV irradiation, the degradation of RS was 63.50% after 20 min of irradiation at pH 6, employing RS (20 mg/L). The addition of PS (0.2 mM) with UV irradiation significantly improved the removal effectiveness, achieving complete removal of RS, after 20 min. Similarly, UV/PS/Fe^{2+} process was more efficient than UV/PS, obtaining 100% degradation of RS, after 15 min, employing Fe^{2+} (0.1 mg/L), RS (20 mg/L) at pH 3. The efficacy of UV/PS process was adversely impacted by the presence of alkalinity and organic matter in natural water samples. Furthermore, the degradation efficiency was negatively impacted by inorganic ions and humic acid (HA). Similarly, the obtained TOC removal was 68.45 and 85.10%, for UV/PS and UV/PS/Fe^{2+} processes, after 180 min of irradiation. Furthermore, the calculated total cost for UV/PS process was 0.30351 \$ m^{-3}, for one order removal (90% removal) of RS. Moreover, four degradation products (DPs) were detected by GC-MS. One of the DPs showed higher acute and chronic toxicities than parent RS. Nevertheless, it is proposed that UV/PS and UV/PS/Fe^{2+} methods can be used for the effective removal of RS and other emerging organic contaminants from water bodies.

Keywords: Rosuvastatin; Degradation; UV; Persulfate; AOPs; Water treatment.

1. Introduction

Water is an essential element for supporting ecosystem. This finite resource is being continuously depleted by the use of water in industries, transportation, and agriculture [1]. The need for clean water has increased as a result of the expanding population and fast industrial development [2]. Furthermore, advances in medical treatments have resulted in a significant rise in the utilization of pharmaceutical products. Pharmaceutical compounds (PCs) are produced and consumed, and as a result, their content in water bodies has risen significantly in recent years. The PCs are mostly composed of analgesics, antibiotics, antiparasitics, antivirals and cardiovascular medications [3]. Their presence has a negative impact on the ecosystem, despite of their low amount (ng/L) in water bodies [4]. The effluent from the pharmaceutical industry, human and animal excreta, discharges from healthcare facilities, improper disposal of expired medications, and PCs used in agricultural, home, hospitals, and veterinary practices are all ways that PCs reach the aquatic system[5, 6].

Among pharmaceuticals, statins are one of the most commonly utilized medicine. Statins are a class of drugs that lower blood cholesterol and are frequently given to people who already have heart related diseases [7]. Because of its refractory nature, rosuvastatin (RS), a commonly employed statin, has been detected in surface waters at levels as high as 979 ng L^{-1} [8]. In aquatic bodies, about 77% of RS is removed unchanged [9]. RS causes endocrine disruption [10], muscle toxicity [11], and reproductive problems [12-14], including various impacts on human health, aquatic ecosystems, and the environment. Consequently, it is crucial to remove RS from aquatic habitats effectively.

Various traditional techniques are used for the removal of pharmaceutical from waste water, including the coagulation, membrane filtration, activated sludge process and biological treatment

[15]. These traditional techniques are efficient at reducing wastewater that contains large concentrations of organic chemicals, but they are ineffective at reducing wastewater that contains modest concentrations [16-19]. Although each conventional method has advantages and limitations, the primary downside is that they all produce secondary pollutants [4, 20]. Therefore, advanced oxidation processes (AOPs) are effective techniques for removal of toxic pollutants from waste water.

AOPs are potential alternatives to traditional water treatment methods, especially in terms of their broad applicability, quick processing, and largely complete conversion of pollutants to safe end products rather than merely phase transformation [21-23]. The AOPs remove organic contaminants from water by using highly reactive $^{\bullet}OH$ and $SO_4^{\bullet-}$. Among the various AOPs, UV/persulfate (UV/PS) and UV/PS/Fe^{2+} are the commonly used techniques for water treatment. Like $^{\bullet}OH$, $SO_4^{\bullet-}$ can be regarded as a robust reactive species for the degradation of organic contaminants owing to its elevated redox potential (E_0 = 2.60 to 3.10 V). $SO_4^{\bullet-}$ functions as a selective oxidant. Due to its comparable redox potential, $SO_4^{\bullet-}$ interacts with many organic contaminants quickly, with second-order rate constant ranging from 10^5 M^{-1} s^{-1} to 10^9 M^{-1} s^{-1} [24]. The benefits of $SO_4^{\bullet-}$ compared to $^{\bullet}OH$ include its extended half-life (i.e., 30 to 40 µs for $SO_4^{\bullet-}$ vs. < 1 µs for $^{\bullet}OH$), a higher redox potential in neutral conditions, and its selectivity for specific applications. Due to the superior mass transfer and extended contact time with target contaminants, more $SO_4^{\bullet-}$ are expected to diffuse inside the solution reaching easily the target compounds to degrade and mineralize them [24].

The aim of this study is to effectively remove RS by UV, UV/PS and UV/PS/Fe^{2+} AOPs. The effect of various factors, such as pH, RS, PS, and Fe^{2+} concentrations, on RS elimination was investigated. This study also investigates the impact of inorganic ions and humic acid on RS

degradation. Additionally, GC-MS was used to identify degradation products (DPs). Lastly, the so-called Ecological Structure Activity Relationship (ECOSAR) Program was applied to investigate the toxicity of RS and its identified/detected DPs.

2. Experimental

2.1 Chemical and reagents

Rosuvastatin ($C_{22}H_{28}FN_3O_6S$, MW = 481.5 g/mol), HCl, H_2SO_4, NaOH, Na_2CO_3 and $NaHCO_3$, KCl, were purchased from Sigma-Aldrich. Sodium persulfate, humic acid and ferrous sulfate ($FeSO_4.7H_2O$) were supplied by Merck. All compounds were of analytical quality and required no further purification. The natural water samples were collected from Stepa Canal Gohati (SCG), June 10, 2024 and Sheikh Maltoon water plant (SMWP), September 14, 2024.

2.2 Treatment of rosuvastatin and analysis

A stock solution (50 mg/L) of rosuvastatin (RS) was prepared in distilled water. All studies were conducted at room temperature. When required, the pH of the solution was changed with either 1 M NaOH or 1 M HCl. A Philips 35-watt, UV-C lamp (wavelength of emission = 254 nm) from Holland was employed as a radiation source. The samples were obtained after a specific period of time. A 100 mL beaker was used as a photochemical reactor. The volume of reaction mixture/solution was 50 mL. This reaction solution was kept under continuous stirring while irradiation. The distance of the reactor/beaker from the UV lamp was about 12 cm. The experiments/tests were performed three times. The standard deviations of the triplicate results are given in the form of errors bars in the figures.

High performance liquid chromatography (HPLC, Agilent 1200 series) was used to measure the concentration of RS after treatment in the irradiated water samples. The detail information

about the method of analysis regarding the stationary and mobile phases, detector, sample volume, column temperature and detector wavelength etc. has been given in the supporting information.

The irradiated samples were analyzed by Gas chromatography-mass spectrometry (GC Agilent-8890, MS Agilent-5977) to determine the DPs of RS. Further information about the method of analysis for determination of DPs of RS can be seen in supporting information.

TOC analyzer (Shimadzu VCSH-ASI) was employed for quantification of the total organic carbon (TOC) in treated RS solutions. The sample volume used for TOC analysis was 20 mL. The % degradation of RS was calculated from Equation 1.

$$\% \text{ Removal of RS} = \frac{(C_0 - C)}{C_0} \times 100 \quad (1)$$

The computational analysis of RS and its DPs for acute and chronic toxicities were evaluated by ECOSAR tool (ECOSAR, 2014). The ECOSAR program is recognized as a useful approach for predicting the ecotoxicity of toxic chemicals [25]. This tool assesses the risk of RS and its DPs towards daphnia, fish, and green algae in terms of EC50 and LC50.

3. Results and discussion

3.1 Direct photolysis of rosuvastatin

The generation of hydroxyl radicals and hydrated electron by the photolysis of water occurs only at wavelengths less than 190 nm [26, 27]. As a result, any breakdown of RS at 254 nm (UV-C light) is caused by the production of excited state RS (RS*) species following the absorption of photons at this wavelength, i.e., 254 nm (reaction (2)) [28]. Either RS molecules in their excited states are directly degraded (reaction (3)) or leading to the production of singlet oxygen ($^1O_2$) (reaction (4)) that subsequently attack and degrade the RS (reaction (5)).

$$RS + h\nu \rightarrow RS^* \quad (2)$$

$RS^* \rightarrow$ Degradation products (3)

$RS^* + {}^3O_2 \rightarrow RS + {}^1O_2$ (4)

$RS + {}^1O_2 \rightarrow$ Degradation products (5)

Figure 1 shows direct photolysis of RS at different initial concentrations. The degradation efficiency of RS was 87.55, 80.4 and 57.1%, respectively at pH 6 after 45 min of irradiation for 10, 20 and 30 mg/L of RS, respectively. Similarly, the values of observed rate constant (k_{obs}) were calculated as 0.0539, 0.0406 and 0.0255 min^{-1} for 10, 20 and 30 mg/L of RS, respectively. The increase in RS concentration decreases the degradation efficiency because the number of available photons causing the direct photolysis are constant while the concentration of RS increases. The degradation rate of RS by photolysis in the well-mixed batch reactor can be modeled by the pseudo first-order rate law:

$$-r_{RS} = \phi\kappa_\lambda C_{RS} < I > = k_{obs} C_{RS} \quad (6)$$

which represents the transformation of RS as a result of photon absorption. In Eq 6, $< I >$ is the average light intensity in the reactor, κ_λ is the specific absorption coefficient of RS at wavelength λ, φ is the quantum efficiency and C_{RS} is the concentration of RS in the reactor. The observed rate constant (k_{obs}) can be evaluated recalling Beer-Lambert law and by averaging the photon flux in the well-mixed batch reactor as shown in Eq. 7.

$$k_{obs} = \phi\kappa_\lambda < I > = \phi\kappa_\lambda I_o \frac{1}{L}\int_0^L \exp(-\kappa_\lambda C_{RS} z)\, dz = -\phi\kappa_\lambda I_o \frac{1}{L}[\exp(-\kappa_\lambda C_{RS} L) - 1] \quad (7)$$

Here, I_o is the incident photon flux at the reactor surface ($z = 0$) and L is the reactor depth.

The RS degradation profiles shown in Fig. 1 can therefore, be modelled by combining the rate law of RS degradation by photolysis, as illustrated in Eq. 8.

$$-r_{RS} = \phi\kappa_\lambda C_{RS} < I > = -\phi\kappa_\lambda I_o \frac{1}{L}[\exp(-\kappa_\lambda C_{RS} L) - 1] C_{RS} \quad (8)$$

With the mole balance in the well mixed batch reactor to yield, as in Eq. 9.

$$\frac{dC_{RS}}{dt} = \phi \kappa_\lambda I_o \frac{1}{L}[\exp(-\kappa_\lambda C_{RS} L) - 1] C_{RS} \quad (9)$$

Equation 6 was solved numerically with Matlab to yield the quantum efficiency of the degradation of RS by photolysis.

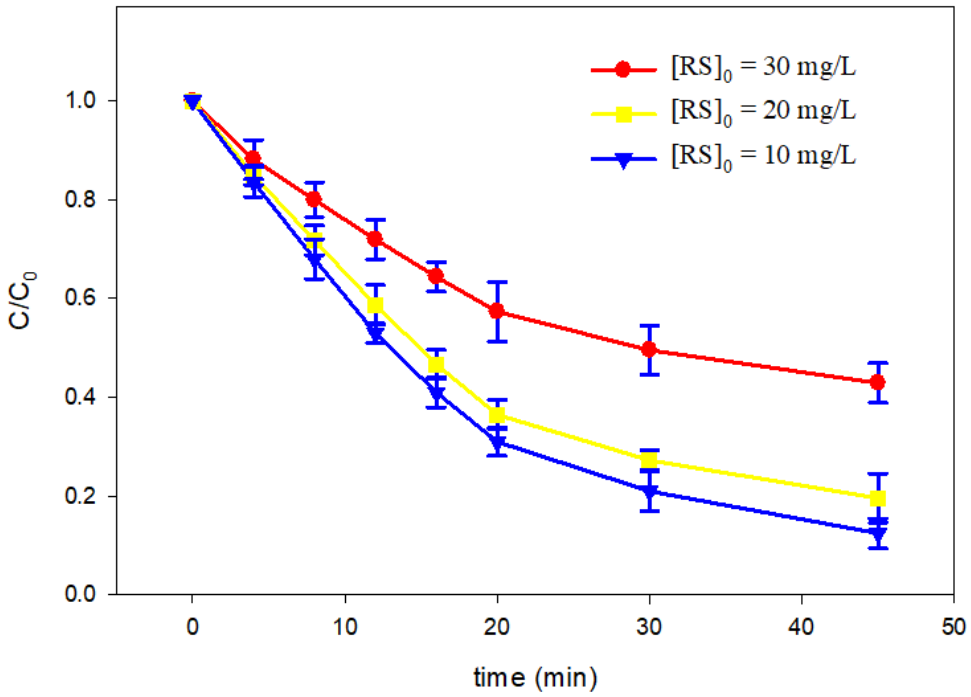


Figure 1. Effect of RS concentration on its photolytic degradation. pH = 6.

3.2 Degradation of rosuvastatin by UV/persulfate and UV/persulfate/Fe^{2+}

3.2.1 Impact of initial persulfate concentration

Both UV/persulfate (UV/PS) and UV/persulfate/Fe^{2+} (UV/PS/Fe^{2+}) processes are called sulfate radicals-based AOPs because both processes lead to the generation of $SO_4^{\bullet-}$ (reactions (10) and (12)) [29, 30].

$$S_2O_8^{2-} + h\nu \rightarrow 2\ SO_4^{\bullet-} \qquad \Phi = 1.8 \qquad (10)$$

$$S_2O_8^{2-} + Fe^{2+} \rightarrow SO_4^{\bullet-} + Fe^{2+} + SO_4^{2-} \quad (11)$$

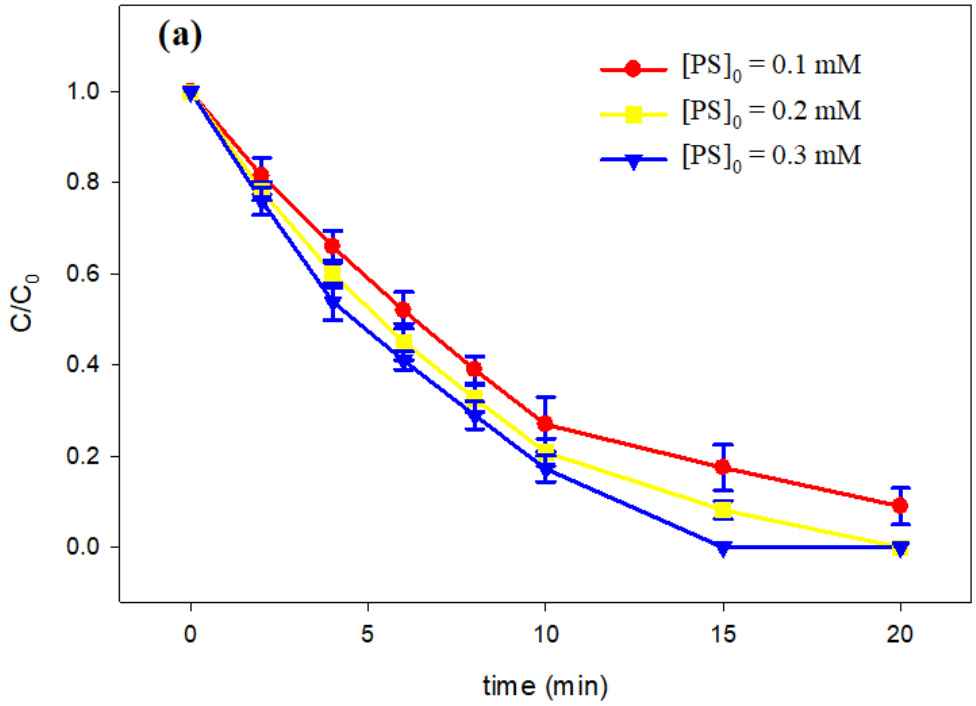
$$SO_4^{\bullet-} + H_2O \rightarrow SO_4^{2-} + {}^{\bullet}OH + H^+ \quad (12)$$

In UV/PS process, three different PS concentration such as 0.1, 0.2 and 0.3 mM, respectively, were used to investigate the degradation of RS using RS = 20 mg/L, and pH 6. The findings indicated that the efficacy of RS degradation increases as the concentration of PS increases. The degradation efficiency was 91% for 0.1 mM PS, while complete removal of RS occurs at 0.2 and 0.3 mM PS after 20 min of irradiation **(Figure 2a)**. Similarly, the observed rate constant (k_{obs}) for 0.1, 0.2, and 0.3 mM PS were 0.1186, 0.1561 and 0.1654 min^{-1}, respectively. The increase in concentration of PS increases the number of $SO_4^{\bullet-}$ and ${}^{\bullet}OH$ (reaction (10 and 12)), which results in higher degradation of RS. Moreover, it has been reported that at relatively higher concentration of PS, the PS in solution can scavenge $SO_4^{\bullet-}$ via reaction (13) that negatively impact the degradation process [30]. However, in this study, the quenching effect of PS was not observed.

$$S_2O_8^{2-} + SO_4^{\bullet-} \rightarrow SO_4^{2-} + S_2O_8^{\bullet-} \qquad k = 6.1 \times 10^5\ M^{-1}\ s^{-1} \quad (13)$$

In photo-Fenton like technique (i.e., UV/PS/Fe^{2+}), the same amount of PS was used as in UV/PS, i.e., 0.1, 0.2 and 0.3 mM. The degradation efficiency was found to be 97.5% for 0.1 mM PS employing RS (20 mg/L), pH 3, after 20 min of irradiation. Similarly, the % degradation of RS at 0.2 and 0.3 mM PS was 100% under the same experimental conditions **(Figure 2b)**. The k_{obs} was 0.1637, 0.2145 and 0.2445 min^{-1}, respectively, for 0.1, 0.2 and 0.3 mM PS. The degradation of RS linearly increased with increase in PS concentration. Compared to UV/PS, higher k_{obs} was recorded for UV/PS/Fe^{2+} process, indicating the higher efficiency in terms of RS degradation of the later process than the former one. This is because, PS is activated by both UV and Fe^{2+} in UV/PS/Fe^{2+} process in contrast to only UV activation of the PS in UV/PS process. The dual

activation of PS led to higher amount of reactive species formation which ultimately resulted in higher removal of RS by the UV/PS/Fe^{2+} [29].



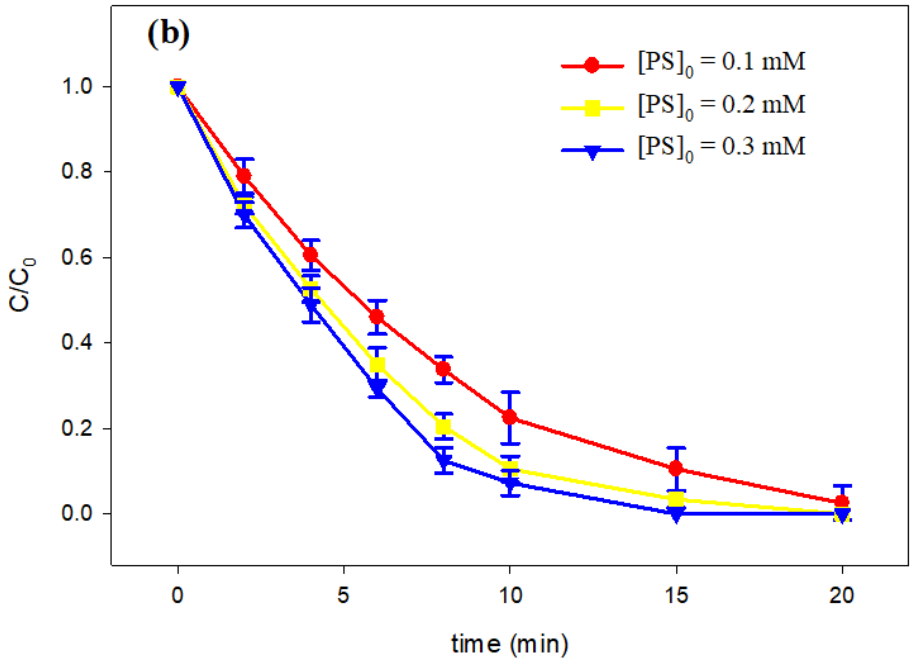


Figure 2. Impact of PS concentration on removal of RS by (a) UV/PS, and (b) UV/PS/Fe^{2+}. Reaction conditions: $[RS]_0$ = 20 mg/L, $[Fe^{2+}]_0$ = 0.1 mg/L, pH = 6 for UV/PS and 3 for UV/PS/Fe^{2+}.

3.2.2 Impact of initial Fe^{2+} concentration in UV/PS/Fe^{2+}

At high concentrations, Fe^{2+} can precipitate, potentially requiring additional secondary treatment, which increases operational costs for large-scale water treatment systems [31]. Therefore, the experiments were performed at low Fe^{2+} concentrations such as 0.05, 0.1 and 0.2 mg/L. The other experimental conditions were: RS = 20 mg/L, pH = 3 and PS = 0.2 mM. As the concentration of Fe^{2+} rises from 0.05 to 0.2 mg/L, the degradation efficiency of RS increases. The removal of RS was 83.0, 89.5 and 94.0%, respectively, for 0.05, 0.1 and 0.2 mg/L of Fe^{2+}, after 10 min of irradiation. Complete removal of RS occurred at 20 min **(Figure 3)**. Similarly, the k_{obs} was 0.1717, 0.2145 and 0.2414 min^{-1} for 0.05, 0.1 and 0.2 mg/L of Fe^{2+}, respectively. The enhancement in removal efficiency with rising Fe^{2+} concentration is attributed to the catalytic activation of PS by Fe^{2+} and the generation of $SO_4^{\bullet-}$ **(reaction (11))** **[29]**.

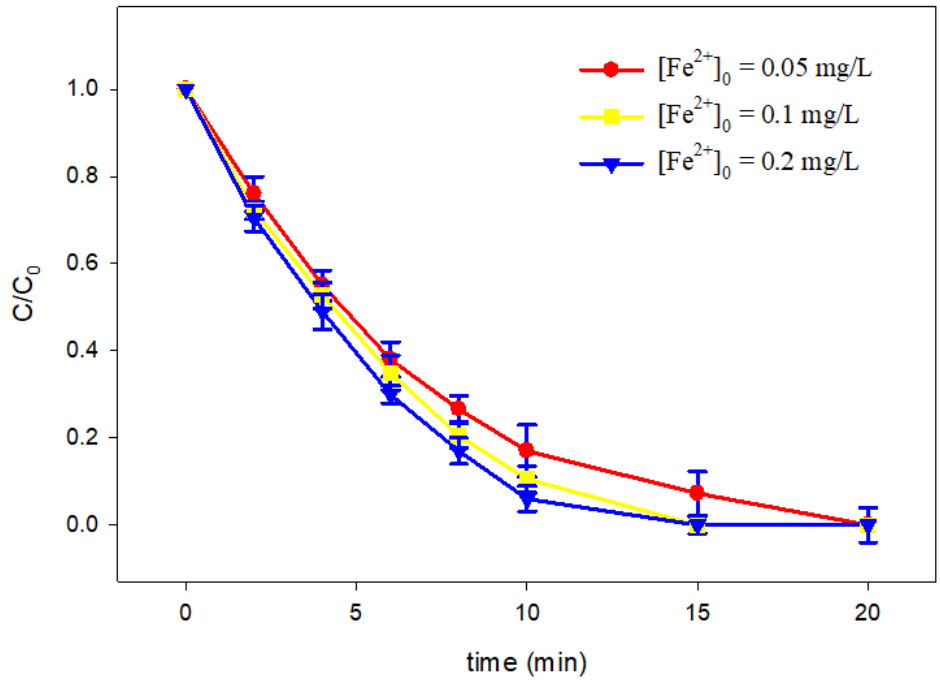


Figure 3. Effect of $[Fe^{2+}]_0$ on removal of RS by UV/PS/Fe^{2+} technique. Conditions: $[RS]_0$ = 20 mg L^{-1}, $[PS]_0$ = 0.2 mM, pH = 3.

3.2.3 Effect of pH

In chemical processes, one of the most important environmental elements influencing the removal of pollutants is the initial pH of the solution. pH have direct impact on the stability of oxidants, the kind of iron species, the generation, and redox potential of $SO_4^{\bullet-}$ and $^{\bullet}OH$ in solution during the advanced oxidation process [32, 33]. The degradation efficiency of RS was investigated at pH 3, 6 and 11 for UV/PS process and pH 3 and 6 for UV/PS/Fe^{2+} technique. In case of UV/PS/Fe^{2+}, the experiment at pH 11 was not performed. Because at alkaline pH the Fe^{2+} converted into ferric oxyhydroxide species, which cannot effectively activate PS [32]. Using UV/PS, the degradation of RS was 100% at pH 3 and 6, and 92.75% at pH 11, after 20 min of irradiation. The experimental conditions were: RS = 20 mg/L and PS = 0.2 mM. The calculated k_{obs} was observed to be 0.1739, 0.1561 and 0.1305 min^{-1} at pH 3, 6 and 11, correspondingly. The k_{obs} decreases from 0.1739 to 0.1305 min^{-1} as pH increases from 3 to 11. At pH 3, $SO_4^{\bullet-}$ is the main specie for degradation of RS [34]. Similarly, enhancement of RS degradation at acidic pH may be due to the formation of more $SO_4^{\bullet-}$ (**reactions (14 and 15)**) [35].

$$S_2O_8^{2-} + H^+ \rightarrow HS_2O_8^- \quad (14)$$

$$HS_2O_8^- \rightarrow SO_4^{\bullet-} + H^+ + SO_4^{2-} \quad (15)$$

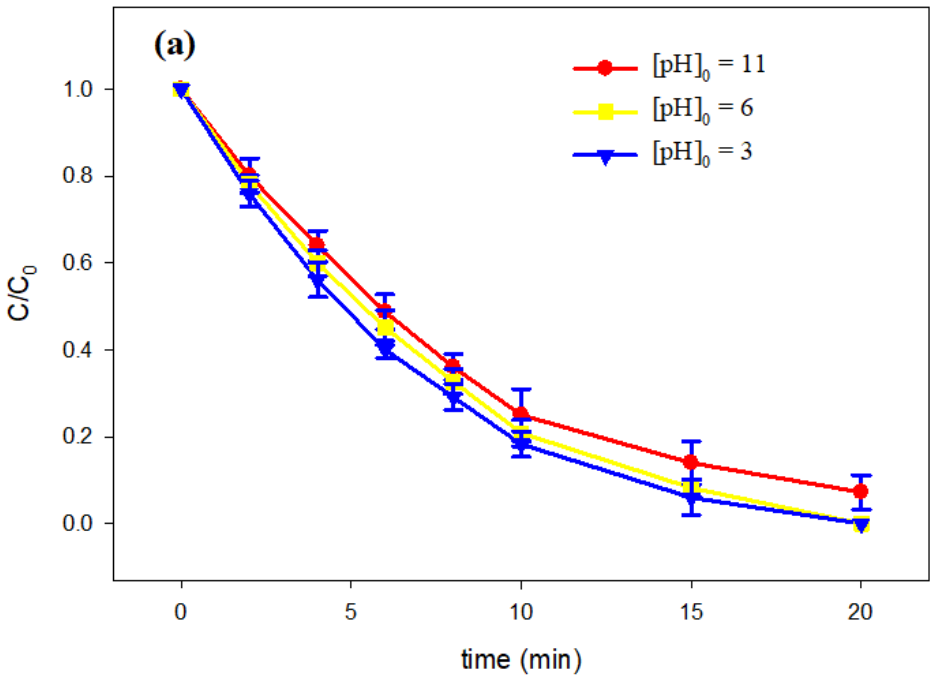
At pH 11, the $^{\bullet}OH$ and $SO_4^{\bullet-}$ are substantially scavenged by OH^- (reactions (16) and (17)), causing an inhibition in degradation efficiency of RS at alkaline pH conditions [36]. However, it is important to note that the redox potential (E^o) of $^{\bullet}OH$ fluctuates in accordance to the system's pH. Consequently, the decline/reduction in the degradation of RS at pH 11 could be due the

decrease in E^o of $^{\bullet}OH$ (approximately 2.0 V) in alkaline conditions, compared to acidic pH (2.7 V) [37, 38].

$$OH^- + SO_4^{\bullet-} \rightarrow SO_4^{2-} + {}^{\bullet}OH \qquad k = 8.3 \times 10^7\ M^{-1}\ s^{-1} \qquad (16)$$

$$OH^- + {}^{\bullet}OH \rightarrow H_2O + O^{\bullet-} \qquad k = 61.2 \times 10^{10}\ M^{-1}\ s^{-1} \qquad (17)$$

In UV/PS/Fe^{2+} process, the removal efficiency of RS was 100 and 95.10% at pH 3 and 6, employing $[39]_0$, $[9]_0$, $[Fe^{2+}]_0$, and pH as 20 mg/L, 0.2 mM, and 0.1 mg/L, and 3, respectively, after 20 min of irradiation **(Figure 4b)**. Similarly, the k_{obs} were 0.2145 and 0.163 min^{-1}, for pH 3 and 6, accordingly. The optimum pH for UV/PS/Fe^{2+} technique is 2.5 – 3.0 [40]. As the pH increases from 3 to 6, the Fe^{3+} get precipitated due to which the catalytic activity of iron decreases [40]. Therefore, the degradation efficiency of RS decreases at pH 6 in UV/PS/Fe^{2+} process.



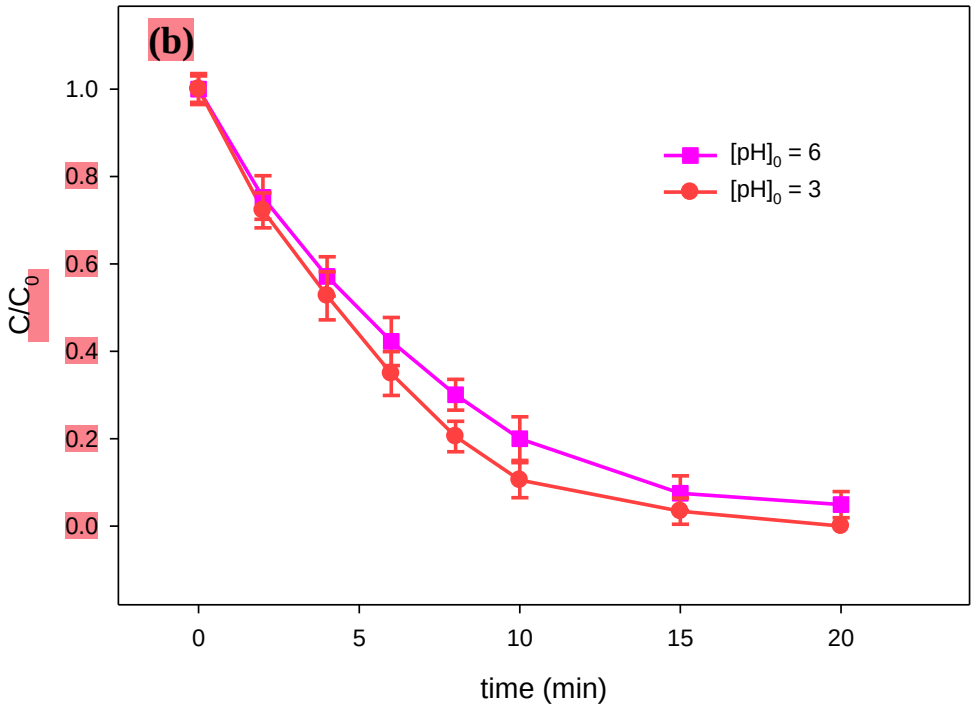


Figure 4. Impact of solution's pH on removal of RS by (a) UV/persulfate, and (b) UV/persulfate/Fe^{2+}. Conditions: $[RS]_0$ = 20 mg/L, $[Fe^{2+}]_0$ = 0.1 mg/L, and persulfate = 0.2 mM.

3.2.4 Effect of RS concentration

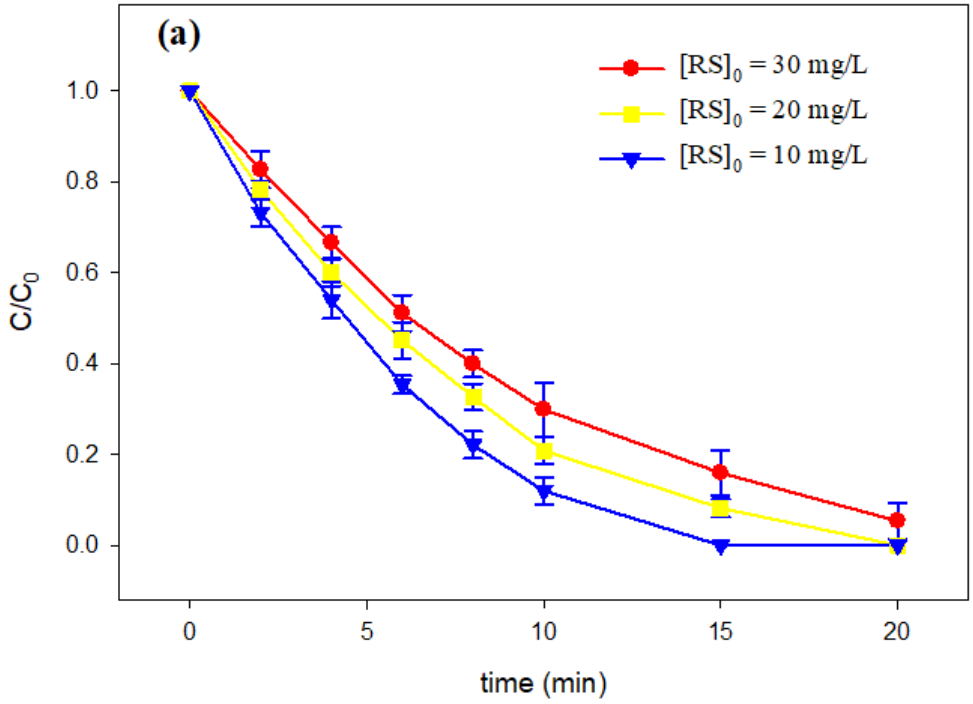
It is more important to investigate how different initial concentrations of target pollutants affect the effectiveness of a water treatment method in removing them because natural water has varying concentrations of these contaminants. It will aid in the development of effective water treatment technology for naturally contaminated waters under various conditions. Consequently, to evaluate the influence of starting RS concentration on both UV/PS and UV/PS/Fe^{2+}, experiments/tests were performed at varying initial RS concentrations of 10, 20, and 30 mg/L. The degradation efficiency of RS was 100% for 10 and 20 mg/L RS, while 94.67% for 30 mg/L RS, respectively, after 20 min of irradiation **(Figure 5a)**. The other experimental conditions were kept

constant at PS = 0.2 mM and pH = 6. Similarly, the observed rate constants for 10, 20 and 30 mg/L RS were 0.1936, 0.1561 and 0.1191 min^{-1}, respectively.

In UV/PS/Fe^{2+} process, the % degradation of RS for 10 and 20 mg/L RS was 100%, while 95.87% for 30 mg/L RS, respectively (**Figure 5b**). Similarly, the observed pseudo first order rate constants were 0.2556, 0.2145 and 0.1557 min^{-1}, for 10, 20 and 30 mg/L RS, respectively. The removal efficiency of both UV/PS and photo-Fenton like techniques decreases with increase in RS concentration. As both of these processes depend on $SO_4^{\bullet-}$, therefore the reason for decrease in degradation of RS with increase in RS concentrations are the same for both processes [41]. Likewise, the quantity of photons required to generate $SO_4^{\bullet-}$ and $^{\bullet}OH$ remains constant; however, the concentration of RS rises in comparison to $SO_4^{\bullet-}$ and $^{\bullet}OH$, resulting in a reduction in RS degradation. In addition, the concentration of degradation products rises as the concentration of RS increases, therefore the $SO_4^{\bullet-}$ likely to react with degradation products rather than RS, which cause decrease in degradation efficiency. However, as the concentration of RS increases so the degradation rate also increases. Therefore, more molecules of RS are exposed to $SO_4^{\bullet-}$, increasing the likelihood of a collision between $SO_4^{\bullet-}$ and RS molecules at higher RS concentration, which results in degradation of RS at higher number per unit time [42, 43]. The degradation rates for UV/PS process were 0.779, 1.583 and 2.103 mg/L/min, for 10, 20 and 30 mg/L, respectively, after 10 min (Table 1). Similarly, the calculated degradation rate for 10, 20 and 30 mg/L of RS were 0.942, 1.79 and 2.402 mg/L/min, for UV/PS/Fe^{2+} process, after 10 min of reaction time (Table 1).

Table 1. Effect of initial RS concentration on degradation rate (initial 10 min). PS = 0.2 mM, Fe^{2+} = 0.1 mg/L, pH = 6.0 for UV/PS and 3.0 for UV/PS/Fe^{2+}.

RS concentration (mg L^{-1})	Degradation rate (mg/L/min) for UV/PS	Degradation rate (mg/L/min) for UV/PS/Fe^{2+}
10	0.779	0.942
20	1.583	1.79
30	2.103	2.402



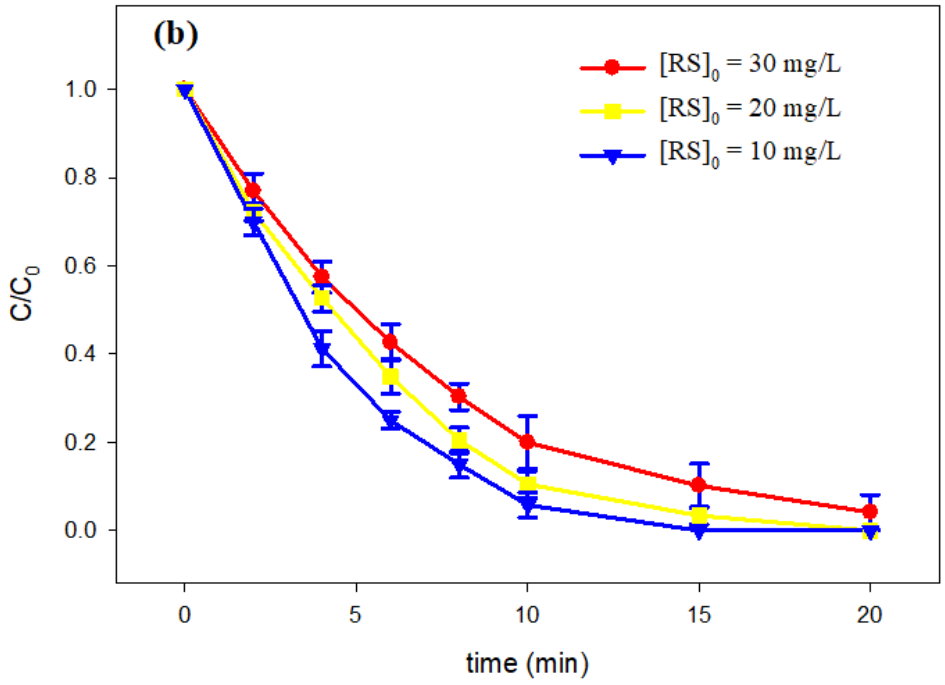


Figure 5. Influence of $[RS]_0$ on removal efficiency of RS in (a) UV/persulfate, and (b) UV/persulfate/Fe^{2+} processes. [Persulfate]$_0$ = 0.2 mM, $[Fe^{2+}]_0$ = 0.1 mg/L, pH = 6 for UV/persulfate process and 3 for UV/persulfate/Fe^{2+} process.

3.2.5 Degradation of RS in natural water samples

The majority of treatment systems were examined using distilled water to remove hazardous organic contaminants. Experiments conducted in natural waters are necessary to make practical suggestions for treatment technologies, as water matrices might impact efficiency [28, 44]. Therefore, the removal efficiency of RS was checked by US/PS technique in natural water samples. The % removal of RS was 100% in distilled water compared to SCG and SMWP field water samples which were 67.0 and 60.5%, respectively, using RS = 20 mg/L and PS = 0.2 mM, after 20 min of irradiation (**Figure 6**). The decrease in degradation of RS in natural water samples may be due to the reactive species scavenging properties of alkalinity and dissolved organic matter. Furthermore, the dissolved inorganic and organic materials/substances may function as screens

and/or filters to scatter and/or absorb UV light instead of the oxidants absorbing the UV radiation for the generation of radicals or the pollutants absorbing them for direct photolysis [28]. Therefore, the degradation of RS is negatively impacted. In addition, it is challenging to determine which component contributed more negatively to the removal of organic pollutants by AOPs since real water exhibits as a complex combination of inorganic and organic components. As a result, more research is necessary to determine the impact of each component of water including pH, natural organic matter, and inorganic anions, on the effectiveness of AOPs in degrading contaminants.

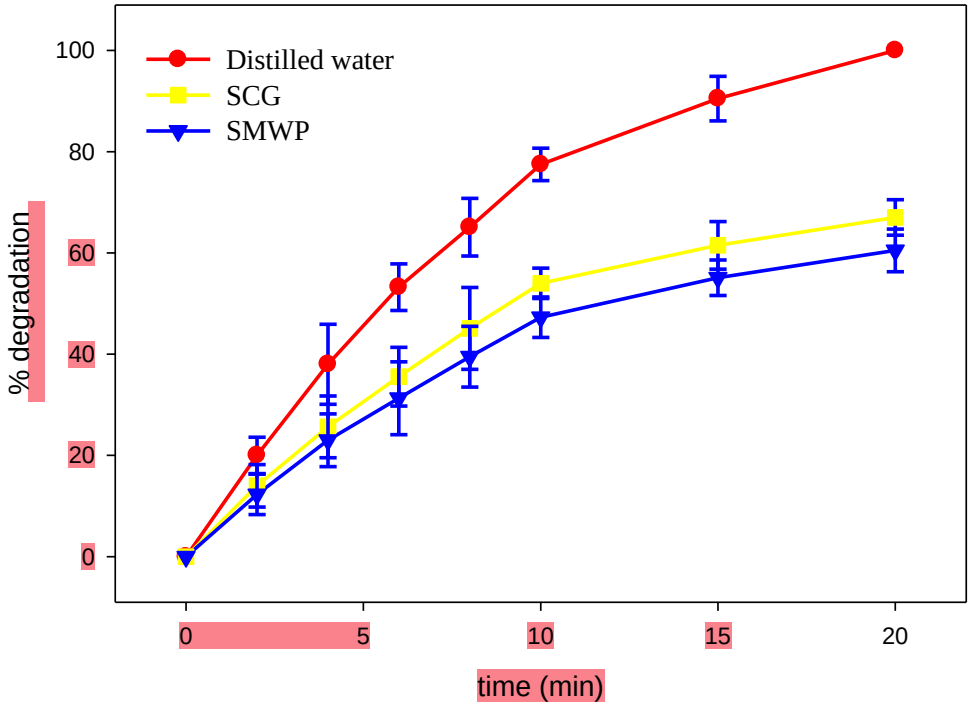


Figure 6. Influence of natural/real water matrices on RS degradation using UV/PS method. Reaction conditions: $[RS]_0$ = 20 mg/L, $[PS]_0$ = 0.2 mM, and pH = 6 for distilled water, whereas for SCG and SMWP the pH was not adjusted.

3.2.6 Effect of inorganic ions and humic acid

The advanced oxidation process was thought to be impacted by a number of commonly coexisting species, such as CO_3^{2-}, Cl^-, HCO_3^-, and natural organic matters (NOMs). Therefore, in UV/PS technique the influence of CO_3^{2-}, Cl^-, HCO_3^- and humic acid (HA) was investigated, while in UV/PS/Fe^{2+} method the influence of HA and Cl^- was studied. The effect of carbonates and bicarbonate was not investigated in UV/PS/Fe^{2+}process, as it increases the pH of solution and **Fe^{2+}** precipitates at alkaline pH. Similarly, the activity of iron to activate PS decreases at alkaline pH. The % degradation of RS decreases from 100% to 88.4, 82.3, 75.07 and 66% by the addition of chloride, carbonates, bicarbonates and HA, employing RS (20 mg/L), PS (0.2 mM), after 20 min of irradiation, respectively (**Figure 7a**). Similarly, k_{obs} decreases from 0.1561 to 0.1053, 0.087, 0.0747 and 0.0582 min^{-1} in presence of no scavenger, chloride, carbonate, bicarbonate and HA. The degradation efficiency of RS decreases by the addition of carbonate and bicarbonate ions, as it scavenge both $^{\bullet}OH$ and $SO_4^{\bullet-}$ and convert into weak carbonate radicals (**reactions (18 – 21)**) [45, 46]. In addition, $SO_4^{\bullet-}$ and $^{\bullet}OH$ quench each other at alkaline pH (reaction 22), which can also cause decrease in degradation of RS [45].

$$SO_4^{\bullet-} + HCO_3^- \rightarrow HCO_3^{\bullet} + SO_4^{2-} \qquad k = 1.6 \times 10^6\ M^{-1}\ s^{-1} \qquad (18)$$

$$SO_4^{\bullet-} + CO_3^{2-} \rightarrow SO_4^{2-} + CO_3^{\bullet-} \qquad k = 6.1 \times 10^6\ M^{-1}\ s^{-1} \qquad (19)$$

$$CO_3^{2-} + {}^{\bullet}OH \rightarrow CO_3^{\bullet-} + OH^- \qquad k = 3.9 \times 10^8\ M^{-1}\ s^{-1} \qquad (20)$$

$$HCO_3^- + {}^{\bullet}OH \rightarrow CO_3^{\bullet-} + H_2O \qquad k = 8.5 \times 10^6\ M^{-1}\ s^{-1} \qquad (21)$$

$$SO_4^{\bullet-} + {}^{\bullet}OH \rightarrow HSO_5^- \qquad k = 1 \times 10^{10}\ M^{-1}\ s^{-1} \qquad (22)$$

In case of UV/PS/Fe^{2+} process, the degradation efficiency decreases from 100% to 86.72 and 61.55% by the addition of 5 mM chloride and 10 mg/L HA, after 20 min of irradiation (**Figure 7b**). The other experimental conditions were kept constant at, RS (20 mg/L), **Fe^{2+}** (0.1 mg/L), PS (0.2 mM) and pH 3. Similarly, the observed rate constant decreases from 0.2145 to 0.0976 and

0.0516 min^{-1}, in presence of no scavenger, chloride and HA. The degradation of RS in both processes, i.e., UV/PS and UV/PS/Fe^{2+}, decreased by the addition of chloride because it scavenge both $SO_4^{\bullet-}$ and $^{\bullet}OH$ and convert it into weak chloride radicals (reactions (23)-(26)) [47].

$$SO_4^{\bullet-} + Cl^- \rightarrow SO_4^{2-} + Cl^{\bullet} \qquad k = 2.7 - 6.6 \times 10^8\ M^{-1}\ s^{-1} \qquad (23)$$

$$Cl^{\bullet} + Cl^- \rightarrow Cl_2^{\bullet-} \qquad k = 8.5 \times 10^9\ M^{-1}\ s^{-1} \qquad (24)$$

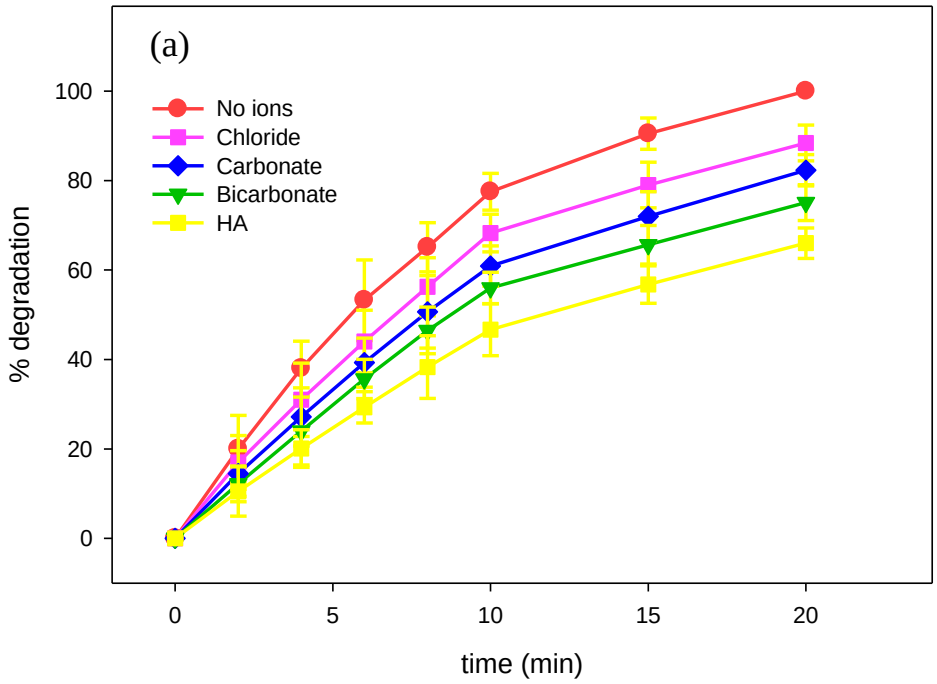
$$^{\bullet}OH + Cl^- \rightarrow ClHO^{\bullet-} \qquad k = 4.3 \times 10^9\ M^{-1}\ s^{-1} \qquad (25)$$

$$ClHO^{\bullet-} + H^+ \rightarrow H_2O + Cl^{\bullet} \qquad k = 3.0 \times 10^{10}\ M^{-1}\ s^{-1} \qquad (26)$$

The decrease in degradation of RS by HA in both UV/PS and UV/PS/Fe^{2+} processes is due to following reasons. One is that, HA absorb UV light, hence it compete with RS for its direct photolysis by UV light [48]. Secondly, HA scavenge $SO_4^{\bullet-}$ and thus have negative impact on degradation of RS (reaction (27)) [34].

$$SO_4^{\bullet-} + NOM \rightarrow Products \qquad (27)$$

In addition, NOM is a powerful UV light absorber, competing with PS for UV photons (i.e., radiant flux) and potentially reducing reactive radical concentrations [49]. In UV/PS/Fe^{2+} process more sulfate radicals are generated which can be scavenged more by NOM. Therefore, the inhibitory effect of HA is more in UV/PS/Fe^{2+} compared to UV/PS process.



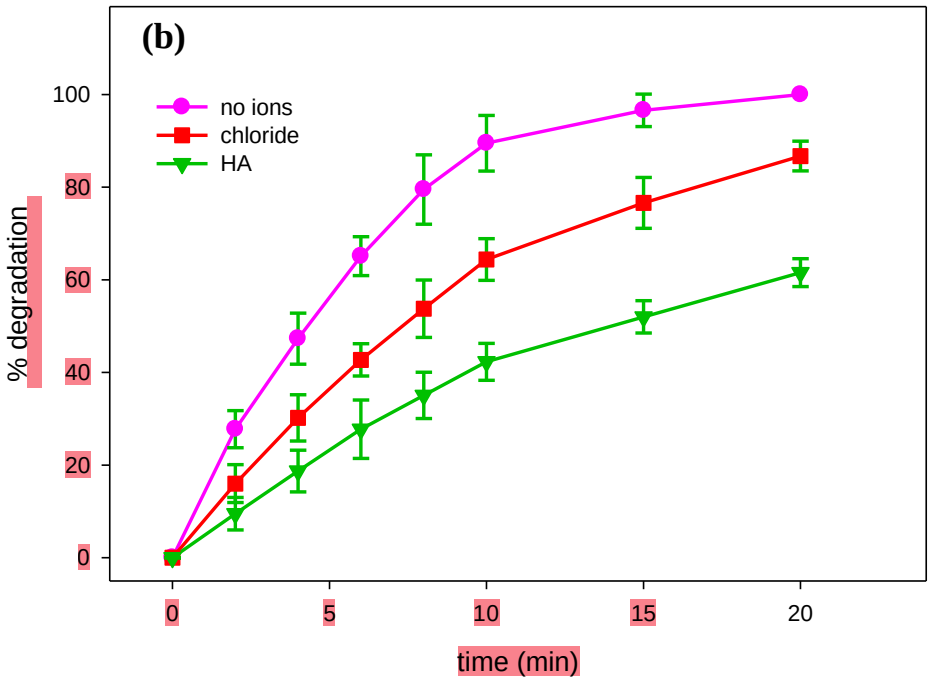


Figure 7. Influence of ions (Cl^-, HCO_3^- and CO_3^{2-}) and HA on removal of RS by (a) UV/persulfate, and (b) UV/persulfate/Fe^{2+}. $[RS]_0$, = 20 mg/L, $[Fe^{2+}]$= 0.1 mg/L, $[persulfate]_0$ = 0.2

mM respectively, [Each ion]$_0$ = 5 mM, [HA]$_0$ = 10 mg/L, pH = 6.0 (UV/PS technique) and 3 (UV/PS/Fe^{2+} technique). In case of HCO_3^{2-} and CO_3^{2-}, pH = 8.1, for UV/PS process.

3.3 TOC analysis

The primary objective of water treatment technology is to eliminate or diminish the hazardous organic contaminants from polluted water. Consequently, it is necessary to examine the efficacy of a given water treatment method in reducing the total organic carbon (TOC) of a particular contaminant [47]. In this context, the removal of TOC from RS solution by UV/PS and UV/PS/Fe^{2+} systems were examined. The elimination of the TOC required more time than the complete RS deterioration. Additionally, the TOC removal was examined at pH 6.0 for the UV/PS method in order to be more applicable to natural water conditions. The elimination of TOC was examined at pH 3.0 for the UV/PS/Fe^{2+} process, since Fe^{2+} exhibits a greater catalytic activity at acidic pH. The obtained TOC removal was 68.45 and 85.10%, respectively for UV/PS and UV/PS/Fe^{2+} processes, after 180 min (Figure 8). In addition, the increased TOC removal of RS in UV/PS/Fe^{2+} process is due to the activation of PS by both UV and Fe^{2+}, which results in the formation of more $SO_4^{\bullet-}$ (reactions (10 and 11)).

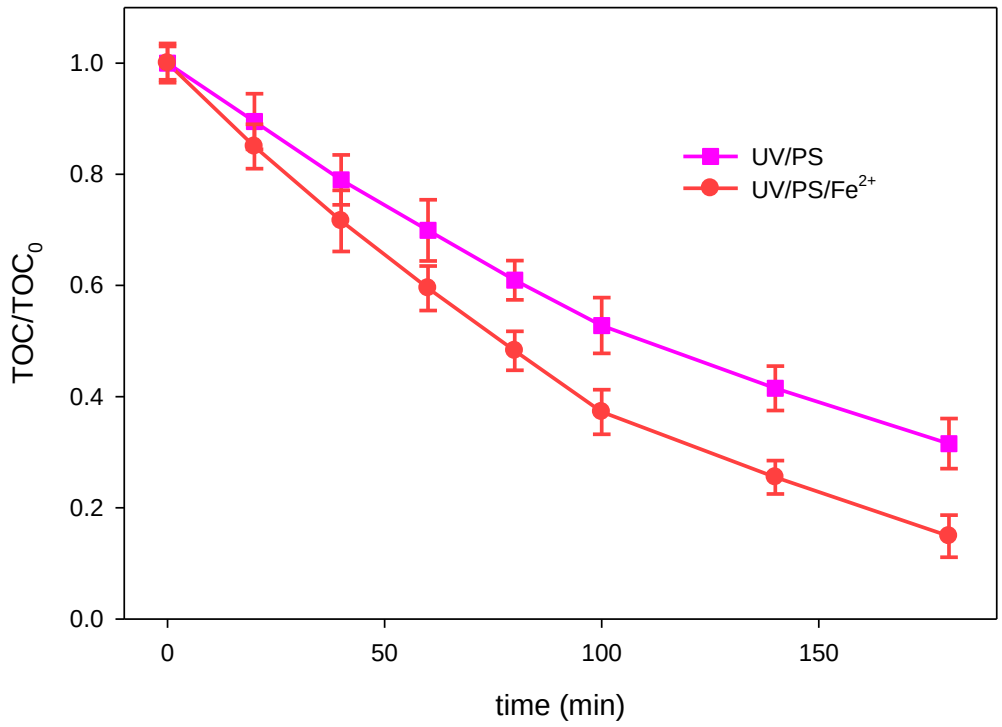


Figure 8. Removal of TOC during RS degradation by UV/persulfate and UV/PS/Fe^{2+}. Conditions: $[RS]_0$ = 20 mg/L, $[Fe^{2+}]_0$ = 0.1 mg/L, $[persulfate]_0$ = 0.2 mM, pH was 6 UV/PS and 3 for UV/PS/Fe^{2+}.

3.4 Economic comparison

The efficiency of the UV/PS technique was investigated in terms of economic cost. This calculation only included the UV/PS process cost. Since Fe^{2+} was utilized as a catalyst for PS activation, very little Fe^{2+} must be supplied to the water in order to purify it. Furthermore, there is no need to add Fe^{2+} from an outside source because natural water already contains a little amount of it. Consequently, the Fe^{2+} was excluded from economic computations. The UV/PS process economic estimate was determined on basis of electrical energy per order (EE/O). EE/O may be stated as the electrical energy (measured in kilowatt hours) needed to remove/degrade 90% of a pollutant/contaminant from 1 m^3 of contaminated air or water (equation (28)) [50].

(28)

Here, P stands for the total electrical flux or power inflowing the reaction mixture/solution, t for irradiation period, and V is the volume of the treated solution in units of m^3. The UV/PS process and electrical energy costs were calculated using equations (29) and (30), respectively, with a maintenance cost of 45% of the total electricity cost and an electricity cost of 0.008 $/kWh. **Table 2** shows the total cost and electrical energy of the UV/PS procedure for the one-order elimination of RS. The cost of PS was 0.00636 $/g [51].

$$\text{Electrical energy cost (\$ m}^{-3}\text{)} = \text{Power cost (\$/KW h)} \times \text{EE/O (KW h m}^{-3}\text{)} \quad (29)$$

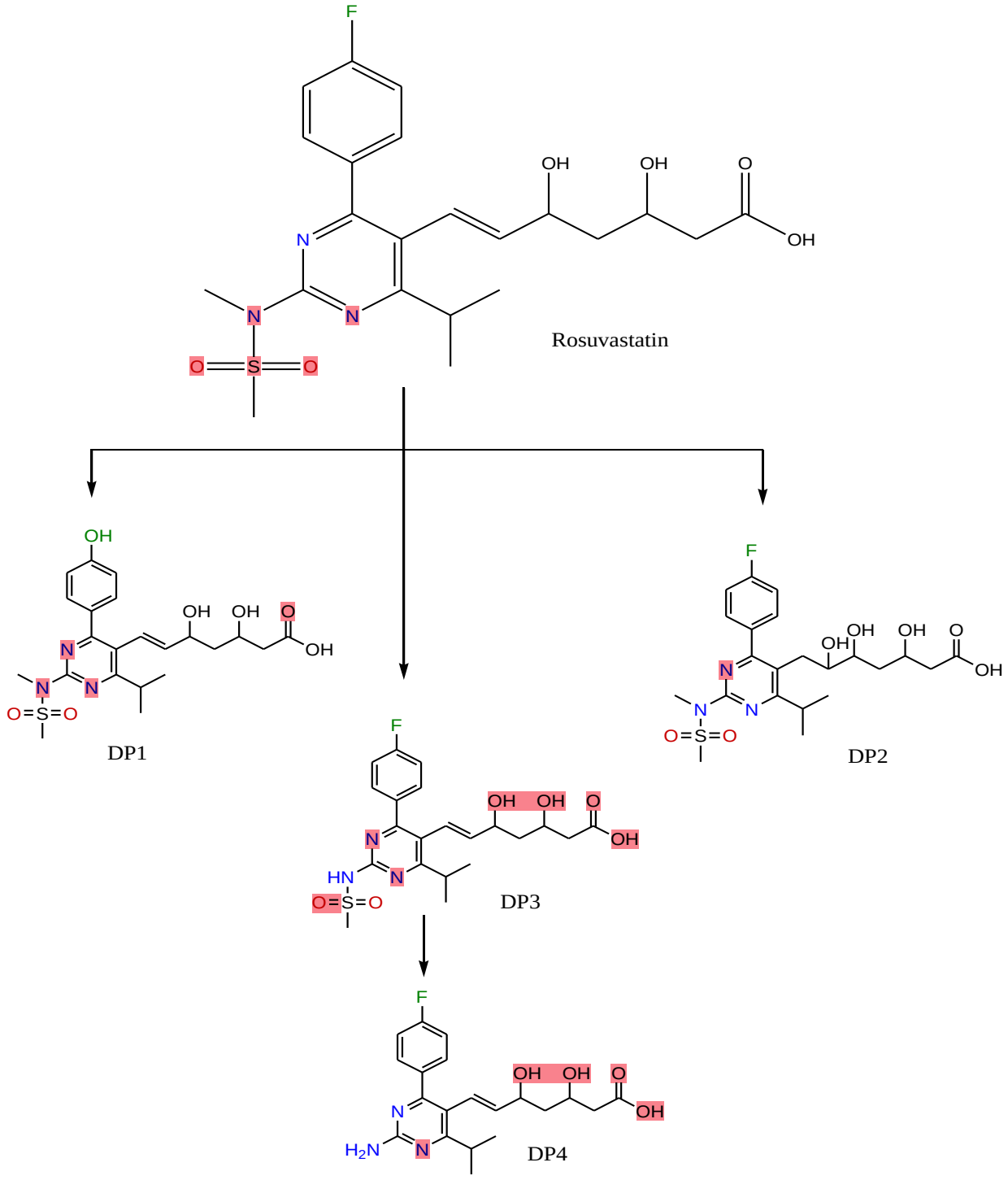
$$\text{Total system cost (\$ m}^{-3}\text{)} = (1.45 \times \text{electrical energy cost}) + \text{reagent cost} \quad (30)$$

Table 2. Economic calculations for UV/PS process for degradation of RS = 20 mg/L, persulfate = 0.2 mM and pH was 6.

Oxidation process	**UV/PS**
k_{obs} (cm^2/mJ)	0.0307
UV fluence needed for one-order removal of RS (mJ/cm^2)	75.02
EE/O (kW h m^{-3}/order)	6.95 × 10^{-3}
Electricity cost (\$ m^{-3})	5.56 × 10^{-4}
Reagent cost (\$ g^{-3})	0.00636
Total cost (\$ m^{-3})	0.30351

3.5 Identification of degradation products

Although the removal of the target pollutant is frequently used to assess the effectiveness of the treatment procedure, but the generation of DPs during the process presents some significant issues. These DPs can be more resistant to breakdown and increase the toxicity of treated water. As a result, it is required to consider information about the DPs of target pollutants [39]. In current study, four DPs were identified by GC-MS as a result of RS treatment by UV/PS method. The degradation products of RS in UV/PS may be due to both $^{\bullet}OH$ and $SO_4^{\bullet-}$, because both radical are formed in this process. The DP1 is formed by the addition of $^{\bullet}OH$ at C12 at flourobenzene ring of RS, a favorable position for $^{\bullet}OH$ addition [52]. Similarly, DP2 is formed by the addition of $^{\bullet}OH$ to unsaturated C atom (C15), a preferable position for the $^{\bullet}OH$ addition. Moreover, DP1 and DP2 have been identified earlier by Doncevic et al. [52]. However, DP3 is formed by the breaking of methyl group from the amine side of RS, which is further converted to the DP4 by the loss of Sulfonyl group. Both DP3 and DP4 were also identified by Mandic et al. [53].



Scheme 1. Degradation pathways of RS by UV/PS technique.

3.6 Ecotoxic assessment

The continuous and escalating release/entrance of emerging environmental contaminants (EECs) into natural aquatic ecosystems might be considered a catalyst for the advancement of remediation techniques [28]. There have been numerous endeavors to effectively eliminate these EECs. The primary objective of water treatment technique is to provide safe and clean water for the public. [28]. For this purpose, the ECOSAR program was used to examine the theoretical acute toxicity and chronic toxicity of the RS and it's identified DPs towards aquatic organisms in order to evaluate the examined AOPs. The acute and chronic toxicities of the identified DPs are presented in **Table 3**. Only DP4 show higher acute and chronic toxicity than RS (**Table 3**).

Table 3. Aquatic toxicity of RS and its DPs (unit = mg L^{-1}).

Compound	**Acute Toxicity**			**Chronic Toxicity**		
	Fish (LC_{50})	**Daphnia (LC_{50})**	**Green Algae (EC_{50})**	**Fish (ChV)**	**Daphnia (ChV)**	**Green Algae (ChV)**
RS	1480	879	785	152	96.8	227
DP1	6030	3360	2310	576	311	580
DP2	2370	1250	6710	2110	976	1480
DP3	4460	2520	1820	433	241	470
DP4	153	27.1	63.1	1.17	0.354	13.0

4. Conclusion

In present study, the removal of RS was performed by UV, UV/PS and UV/PS/Fe^{2+} methods. The degradation of RS by sole UV was 63.50%, using $[RS]_0$ = 20 mg/L, at pH 6, after 20 min of irradiation. When PS (0.2 mM) was added to direct photolysis the % degradation of RS rises from

63.50 to 100%, employing RS = 20 mg/L, at pH 6, after 20 min. similarly, the addition of homogenous catalyst (Fe^{2+}, 0.1 mg L^{-1}) to the UV/PS system, complete removal of RS was achieved after 15 min, using PS (0.2 mM) and RS (20 mg/L), at pH = 3. The degradation efficiency of RS was more at pH 3 in both processes, i.e., UV/PS and UV/Fe^{2+}/PS. Inorganic ions and HA have inhibitory impact on the degradation of RS in both UV/PS and UV/PS/Fe^{2+} techniques. The removal of RS was decreased from 100.0% to 88.4, 82.3, 75.07 and 66% in presence of chloride, carbonates, bicarbonates and HA, respectively, in UV/PS process. Similarly, in UV/PS/Fe^{2+} process, the removal efficiency of RS decreases from 100% to 86.72 and 61.55% in presence of chloride and HA. Moreover, the TOC removal was observed to be 68.45 and 85.10%, for UV/PS and UV/PS/Fe^{2+} techniques. GC–MS was used for the identification of degradation products. In addition, the toxicity of the DPs towards green algae, fish, and daphnia were assessed by ECOSAR program. One of the DPs showed higher acute and chronic toxicity than parent compound. Although the present study demonstrated that sulfate radical-based AOPs can effectively decompose RS, it is imperative for researchers to guarantee the thorough elimination of all degradation products (DPs) to avert the formation of detrimental DPs that might increase the toxicity of the treated water.

Acknowledgment

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