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Removal of toxic tellurium (IV) compounds via bioreduction using flucloxacillin in aqueous acidic medium: A kinetic and mechanistic approach

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ABSTRACT

This paper describes a novel method for the removal of potassium tellurite (Te^{IV}), a toxic tellurium (IV) compound, via its bioreduction using the drug flucloxacillin (Flx) in an aqueous sulfuric acid solution. The kinetics of the bioreduction process were monitored using UV–Vis absorption spectra at an ionic strength of 2.0 mol dm^{-3} and 298 K. The reaction between Te^{IV} and Flx was set at a 1:1 stoichiometry. The reduction reaction followed first-order kinetics for [Flx] and fractional-first-order kinetics for [Te^{IV}] and [H^+]. The effects of ionic strength and relative permittivity of the reaction medium were also explored. Supplementation with divalent transition metal ions enhanced the reduction rate. The reaction products were identified, in order of their stoichiometric results, spot tests and FT-IR spectra as 3-(2-chloro-6-fluorophenyl)-5-methylisoxazol-4-carbocylic acid, 5,5-dimethyl-thiazolidine-2,4-dicarboxlic acid, ammonium ion, carbon dioxide and elemental tellurium (Te^0). The reaction rate dependence on temperature was studied, and the activation and thermodynamic parameters were assessed and discussed. The derived rate-law expression was found to be in excellent accordance with the acquired investigational outcomes. A conceivable reaction mechanism has been provided, which includes a reaction between the protonated flucloxacillin (Flx^+) and tellurous acid (H_2TeO_3) as the essential reactive species, resulting in the construction of an intermediate complex. Such complex decays in the rate-determining step to yield the final reaction products.

1. Introduction

Tellurium is a harmful and essential rare metalloid present in a trace amounts in the earth's crust [1]. It exists in nature in several forms, including the nontoxic, elemental state (Te^0), telluride (Te^{2-}), and as the oxyanions tellurite (TeO_3^{2-}) and tellurate (TeO_4^{2-}), which are toxic for a variety of life forms [2,3]. In humans, tellurium is one of the most abundant trace elements in bone. It is a critical element utilized in energy and defence applications [4]. Tellurium compounds have several applications in the manufacture of ceramics, glass, semiconductors, and metals [3]. Tellurium oxyanions are strong oxidants that can be produced by their reductive precipitation to form insoluble elemental tellurium (Te^0) [5]. Tellurium oxyanions have also been investigated as potential antibacterial agents [6,7]. Tellurite ($Te^{IV}O_3^{2-}$) is highly toxic to a variety of microorganisms [4] and is an extremely stable compound, although it can be reduced to Te^0 by electrolysis, by using a powerful reducing agent [2,4,8], by living cells [9] or by some bacteria [10]. The reduction of highly toxic soluble tellurite, which has detrimental impacts on the environment and human health, to the nontoxic insoluble Te^0 is important due to the increasing employment of tellurium in several industries. Additionally, this process could be a treatment for the removal of toxic tellurite from polluted areas to address serious pollution problems. Therefore, the development of a biochemical reduction method for toxic tellurite for environmental clean-up purposes is of interest.

Antibiotics are a group of pharmaceutical drugs used to treat bacterial and fungal infections in both humans and animals. They are not only used in medicine but also in food industries and in scientific research activities [11]. However, antibiotics are chemical substances that are foreign to the human body; hence, the body eliminates them through drug metabolism processes, which may result in pharmacologically active, inactive, or toxic metabolites. Antibiotics are introduced into the environment through many routes, including human or animal excreta, wastewater effluent and industrial wastes and processes [12,13]. The presence of such chemicals, which contain complex organic compounds, even at low environmental concentrations may negatively affect the ecosystem and human health and have toxic impacts on the soil, water resources and organisms. Therefore, they are designated as a dangerous environmental pollutant [13]. There has been increasing concern for the removal of these compounds to protect the human health and the environment [14]. Several well-known methods or

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techniques have previously been utilized for the removal of different pollutants, including adsorption techniques using various adsorbents [15–17]. However, conventional biological treatment methods still do not satisfy all requirements and are not effective as a stand-alone method due to the complicated chemical structures of pharmaceuticals [18]. However, new treatment methods have been proposed [18–21]. One of the most significant methods is the chemical oxidation of antibiotics, which is a broad pathway for their degradation and plays a major role in water treatment processes and in understanding the metabolism of medical drugs in pharmacokinetics studies [22–26]. During the oxidation process, oxidizing agents transform toxic substances to less harmful compounds that can be safely discharged to the environment [25,26].

Despite the pharmaceutical significance of antibiotics, a careful literature review revealed very few kinetic investigations on the oxidative degradation of antibiotics in aqueous media, and the reported investigations gave poor mechanistic information [22–26]. The current study was undertaken in view of the limited knowledge of the oxidation kinetics and mechanisms of such biologically and medically serious molecules. This investigation deals with the kinetic, mechanistic and thermodynamic aspects of the redox reaction between the well-known bioreductant flucloxacillin (Flx) and the highly toxic tellurite ion $Te^{IV}O_3^{2-}$ in aqueous acidic medium (sulfuric acid). Flucloxacillin is a narrow-spectrum beta-lactam antibiotic of the penicillin class and is commonly employed to treat bacterial infections. This study presents an unprecedented treatment method, with a dual benefit for the human health and the environment which can be applied for removal or degradation of flucloxacillin antibiotic and conversion of the highly toxic tellurite to a non-toxic valuable tellurium metalloid. This method is expected to be more convenient, simple, rapid, inexpensive and safe procedure that provides more benefit for the environment and human health than previously reported methods. The study elucidates the reactive species in such system, explores the selectivity of flucloxacillin bioreductant towards tellurite and identifies the reaction products. This study also delineates the redox reaction mechanism and establishes a rate-law expression that is based on the kinetic outcomes.

2. Experimental

2.1. Materials

All chemicals were purchased from Sigma or Merck in spectroscopic grade and were employed as received without further processing. Double-distilled water was used to prepare all solutions. A stock solution of flucloxacillin sodium (Sigma, purity >95%) was prepared by dissolving it in water. The solution of potassium tellurite (Sigma, purity = 95%) was freshly prepared in water and was normalized using spectrophotometry. The stock solutions of the acidic medium (H_2SO_4) and the sulfate salts of zinc, cobalt and cadmium were from Merck (Germany). Sodium sulfate and acetic acid were employed to maintain and study the impact of the ionic strength (I) and to explore the impact of the relative permittivity of the medium, respectively.

2.2. Kinetic measurements

Kinetic measurements were ascertained in pseudo–first-order circumstances, whereas the concentration of potassium tellurite oxidant was in large excess with respect to flucloxacillin bioreductant. The ionic strength, I, of the reaction medium was attained at 2.0 mol dm^{-3}. The absorbance readings were performed with a Shimadzu UV-VIS-NIR-3600 double-beam spectrophotometer. The advance of the redox reaction was monitored by assaying the decay of flucloxacillin absorbance over time at $\lambda = 342$ nm, because potassium tellurite does not absorb at this wavelength. First-order graphs of ln Abs. vs. time were set to be linear (up to >80% of the reaction performance), and the observed pseudo-first-order rate constant values (k_{obs}) were obtained as the mean value of three runs. The reaction order (n) of the tellurite oxidant and sulfuric acid medium was obtained from the slopes of log k_{obs} vs. log Consn. graphs.

3. Results

3.1. Time-resolved spectra

Fig. 1 presents the time-resolved spectra for the reduction of tellurite ion (Te^{IV}) by flucloxacillin (Flx) in H_2SO_4. The recorded spectra of the reacting mixture exhibited a decreasing Flx band at its absorption maximum ($\lambda = 342$ nm) as the reaction advanced due to its oxidation by Te^{IV}, with a noticeable bathochromic shift of 6 nm. Furthermore, the presence of two isosbestic points at ($\lambda = 303$ and 265 nm) suggests that an equilibrium was established between Flx and the probable constructed Flx - Te^{IV} intermediate complex.

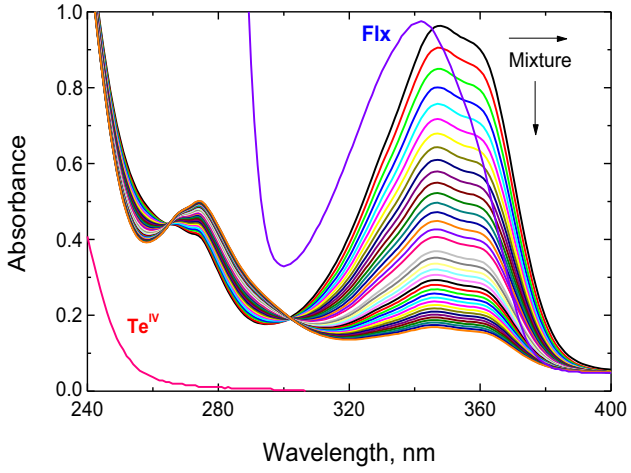
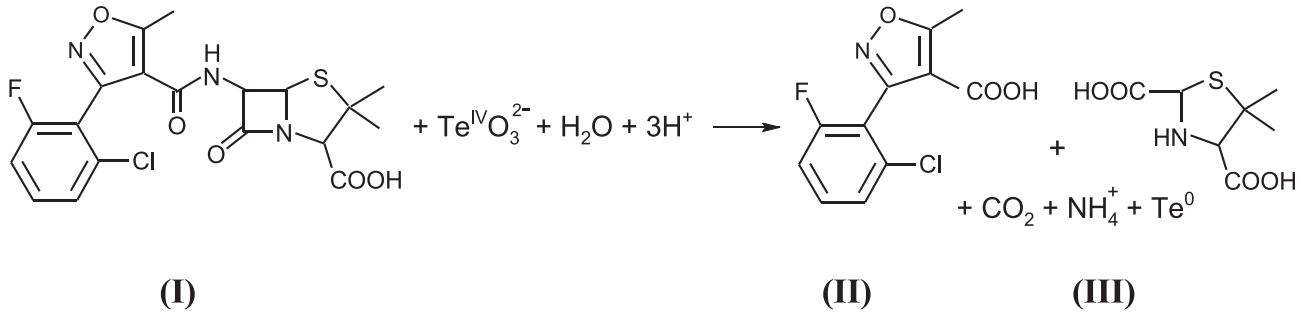


Fig. 1. Time-resolved spectra for the reduction of tellurite ion by flucloxacillin in H_2SO_4 solution. [Flx] = 5.0×10^{-4}, [Te^{IV}] = 6.0×10^{-3}, [H^+] = 1.0 and I = 2.0 mol dm^{-3} at 298 K.

3.2. Stoichiometry and product description

A variety of reaction mixtures containing several ratios of [Flx] / [Te^{IV}] at fixed [H^+] = 1.0 and I = 2.0 mol dm^{-3} at room temperature were allowed to react for 24 h until reaction completion in all mixtures. A spectrophotometric estimation of the unconsumed [Flx] at λ = 348 nm identified a 1:1 stoichiometry, as presented in the following equation:



(I) (II) (III) (1)

This stoichiometric equation is in full agreement with the product description, where the compounds (I), (II) and (III) are flucloxacillin and its oxidation products 3-(2-chloro-6-fluorophenyl)-5-methylisoxazol-4-carbocylic acid and 5,5-dimethyl-thiazolidine-2,4-dicarboxlic acid, respectively. The oxidation products of flucloxacillin drug were identified by spot tests and FT-IR spectra. FT-IR spectra of flucloxacillin (**1**) and its oxidation products (**2**) are illustrated in Fig. 2 which showed different fingerprints in both. The spectrum of the oxidation products (**2**) showed disappearance of the sharp absorption peak which was located at 1768 cm^{-1} (due to amidic ketone C═O stretch) in the spectrum of flucloxacillin (**1**). Appearance of a broad peak at 3375 cm^{-1} (due to carboxylic OH with N—H stretching) is in consistent with the product 5,5-dimethyl-thiazolidine-2,4-dicarboxlic acid. In addition, appearance of a peak at 1652 cm^{-1} is due to carboxylic C═O stretch. The by-products were characterized by spot tests as ammonium ion and CO_2. The formation of elemental tellurium, Te^0, was indicated by the dense black precipitate that formed by the reaction, which was soluble in an aqueous bromine solution [9,10].

3.3. Effect of [Flx] on the reduction rate

The impact of the flucloxacillin reductant concentration, [Flx], on the reduction rate was explored at [Te^{IV}] = 6.0 × 10^{-3}, [H^+] = 1.0, ionic strength, I = 2.0 mol dm^{-3}, T = 298 K and at several [Flx] ranging from 1.0 × 10^{-4} to 9.0 × 10^{-4} mol dm^{-3}. The graphs of ln Abs. vs. time yielded straight lines for approximately 80% of the reactions, and the values of k_{obs} were found to be unaffected when the concentration of Flx was varied, as shown in Table 1. The results indicated that the reduction rate was independent of the reductant concentration and that there was a first-order reaction regarding the reductant.

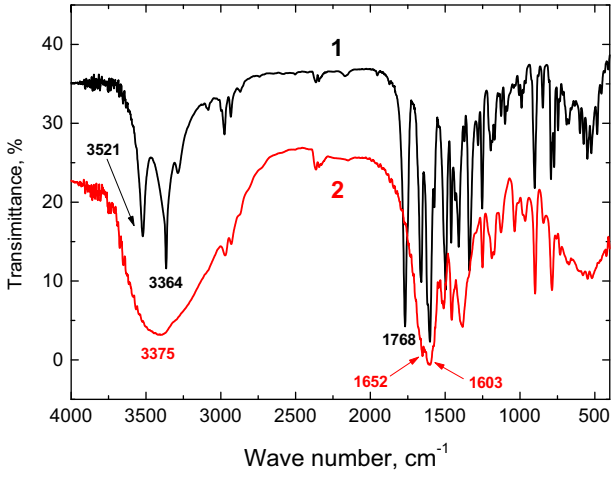


Fig. 2. FT-IR spectra of flucloxacillin (**1**) and its oxidation products (**2**).

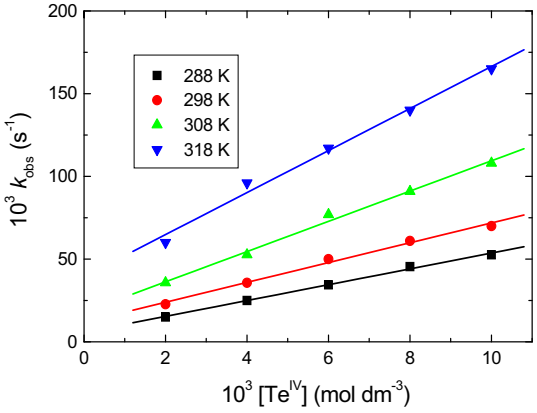


Fig. 3. Effect of $[Te^{IV}]$ on the value of k_{obs} in the reduction of tellurite ion by flucloxacillin in H_2SO_4 solution. $[Flx] = 5.0 \times 10^{-4}$, $[H^+] = 1.0$ and $I = 2.0$ mol dm^{-3} at several temperatures.

3.4. Effect of $[Te^{IV}]$ on the reduction rate

The reduction rate was assessed at several concentrations of tellurite ion oxidant (Te^{IV}), $2.0 \times 10^{-3} < [Te^{IV}] < 10.0 \times 10^{-3}$ mol dm^{-3}, with fixed [Flx], $[H^+]$ and I, and at four temperatures (288, 298, 308 and 318 K). Increasing the tellurite ion concentration increased the reduction rate, as shown in Table 1. Graphs of k_{obs} vs. $[Te^{IV}]$ at various temperatures were obviously linear with positive intercepts (Fig. 3) demonstrating that the reduction reaction was less than unit order (n) in $[Te^{IV}]_T$ ($0 < n < 1$).

3.5. Effect of $[H^+]$ on the reduction rate

The consequence of varying $[H^+]$ on the reduction rate was explored to further investigate the reduction mechanism. Kinetic experiments were carried out at a variety of $[H_2SO_4]$ from 0.4 to 1.8 mol dm^{-3} while maintaining the other constituents and the four studied temperatures. Increasing the sulfuric acid concentration enhanced the reduction rate (Table 1), indicating that the redox reaction was acid-catalyzed. Graphs of k_{obs} vs. $[H^+]$ at several temperatures were linear, with presumed positive slopes designating fractional-first order reliance with reverence to $[H^+]$ (Fig. 4).

3.6. Effect of ionic strength and relative permittivity of the reaction medium

The impact of the reaction medium's ionic strength on the reduction rate was studied to better understand the nature of the reactive species in the rate-limiting step of the redox reaction. This was accomplished by the addition of known concentrations of Na_2SO_4 solution to fixed concentrations of the other reaction ingredients. The results showed that varying the ionic strength did not significantly alter the reduction rate.

Additionally, the influence of the relative permittivity of the reaction medium was explored by altering the acetic acid–water content (vol%) in the reaction medium (up to 40% acetic acid) while maintaining all other conditions. The reduction rate was unaffected by altering the relative permittivities of the acidic medium.

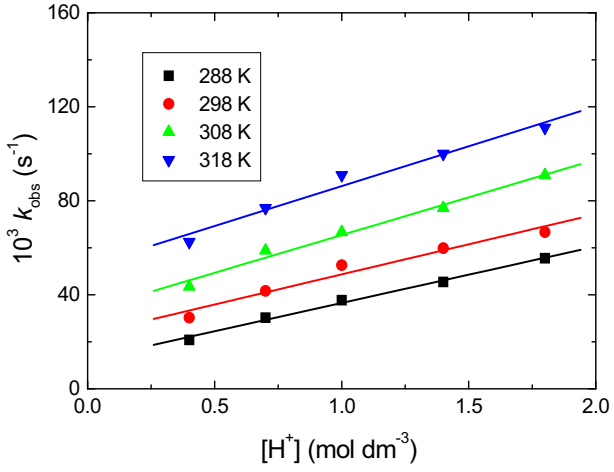


Fig. 4. Effect of $[H^+]$ on the value of k_{obs} in the reduction of tellurite ion by flucloxacillin in H_2SO_4 solution. $[Flx] = 5.0 \times 10^{-4}$, $[Te^{IV}] = 6.0 \times 10^{-3}$ and $I = 2.0$ mol dm^{-3} at several temperatures.

Table 1
Effect of [Flx], [Te^{IV}], [H^+] and I on k_{obs} in the reduction of tellurite ion by flucloxacillin in H_2SO_4 solution at 298 K.

10^4 [Flx] mol dm^{-3}	10^3 [Te^{IV}] mol dm^{-3}	[H^+] mol dm^{-3}	I mol dm^{-3}	$10^3 k_{obs}$ s^{-1}
1.0	6.0	1.0	2.0	49.9
3.0	6.0	1.0	2.0	51.3
5.0	6.0	1.0	2.0	51.0
7.0	6.0	1.0	2.0	52.1
9.0	6.0	1.0	2.0	50.6
5.0	2.0	1.0	2.0	23.2
5.0	4.0	1.0	2.0	33.9
5.0	6.0	1.0	2.0	51.0
5.0	8.0	1.0	2.0	61.3
5.0	10.0	1.0	2.0	70.0
5.0	6.0	0.4	2.0	29.8
5.0	6.0	0.7	2.0	41.2
5.0	6.0	1.0	2.0	51.0
5.0	6.0	1.4	2.0	59.9
5.0	6.0	1.8	2.0	67.3
5.0	6.0	1.0	2.0	51.0
5.0	6.0	1.0	2.5	51.5
5.0	6.0	1.0	3.0	53.4
5.0	6.0	1.0	3.5	52.2
5.0	6.0	1.0	4.0	52.5

Experimental error ± 4%.

3.7. Effect of divalent transition metal ions on the reduction rate

The rate of the reduction reaction was assayed at several concentrations of certain divalent metal ions, namely, Co^{II}, Zn^{II} and Cd^{II}, in the range of 2.0–10.0 × 10^{-4} mol dm^{-3}, with the other reactants being fixed, and at 298 K. The resulting reduction rates increased with increasing concentrations of the supplemented metal ions, as presented in Fig. 5.

3.8. Effect of temperature

To estimate the activation and thermodynamic parameters, the reduction rate was recorded at four temperatures ranging between 283 and 313 K with various concentrations of tellurite ion and H_2SO_4 and at [Flx] = 5.0 × 10^{-4} and I = 2.0 mol dm^{-3}. The results showed that raising the temperature increased the reduction rate. The rate constant activation parameters of the slow step (k_1) and the thermodynamic parameters of the equilibrium constants (K_1 and K_2) included in the reaction mechanism were assessed and are presented in Tables 2 and 3, respectively.

3.9. Polymerization study

The appearance of free radicals throughout the redox reaction was assessed by supplementing the reaction mixture with acrylonitrile for approximately 4 h in an inert atmosphere, followed by diluting the mixtures with methanol. The test was negative, i.e., no white precipitate was formed, signifying the absence of free radical production in the present redox reaction.

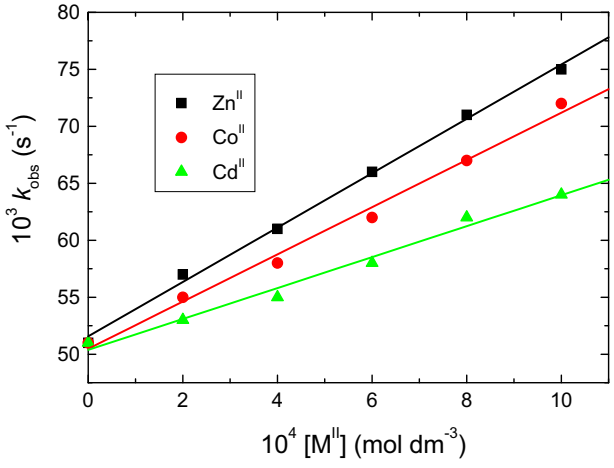


Fig. 5. Effect of divalent transition metal ions on k_{obs} in the reduction of tellurite ion by flucloxacillin in H_2SO_4 solution. [Flx] = 5.0 × 10^{-4}, [Te^{IV}] = 6.0 × 10^{-3}, [H^+] = 1.0 and I = 2.0 mol dm^{-3} at 298 K.

4. Discussion

It has been stated [27] that tellurite ion (TeO_3^{2-}) is present in solutions as hydrotellurite, also termed hydrogen tellurite ion $HTeO_3^-$. In slightly acidic solutions, $HTeO_3^-$ can be present, but in more acidic solutions tellurous acid, H_2TeO_3, is predominant [10,28]. In aqueous solutions, tellurous acid behaves as a weak acid, as exemplified in the following equilibria [29]:

$$H_2TeO_3 + H_2O \rightleftharpoons H_3O^+ + HTeO_3^- \; K_{a1} = 2.0 \times 10^{-3} \quad (2)$$

$$HTeO_3^- + H_2O \rightleftharpoons H_3O^+ + TeO_3^{2-} \; K_{a2} = 1.0 \times 10^{-8} \quad (3)$$

The dissociation constant (K_{a1} and K_{a2}) values specify that deprotonation occurs first, to a presumed extent, in aqueous acidic medium. However, due to the very low value of K_{a2}, the second deprotonation does not occur under the acidic condition of the present study. Furthermore, the observed increasing reduction rate upon raising $[H^+]$ also signifies that tellerous acid is the predominant reactive species.

On the other hand, flucloxacillin tends to become protonated in acidic medium, as represented by the following equilibrium [30]:

$$Flx + H^+ \; Flx^+ \quad (4)$$

Therefore, the fractional first-order rate constant with reference to $[H^+]$ can be interpreted as the protolytic process of flucloxacillin in an acidic medium, i.e., the protonated species of flucloxacillin may be the reactive species, playing the principle role in the present reaction kinetics.

Flucloxacillin has a good ability to form complexes with transition metal ions [31]. The findings of the current work showed that adding certain divalent transition metal ions (Co^{II}, Zn^{II} and Cd^{II}) increased the rate of the redox reaction. These findings can be interpreted on the basis of the complexation of transition metal ions with flucloxacillin in such medium. In view of the results found here and in previous studies, the anticipated structure of flucloxacillin-metal complexes (shown in Fig. 6) are of the general formula $M^{II}(Flx)_2(H_2O)_2$, where M is the transition metal ion and Flx^- is the mono anion of flucloxacillin. It is suggested that flucloxacillin coordinates with the transition metal ion through a carbonyl oxygen and forms a covalent bond with the deprotonated nitrogen atom.

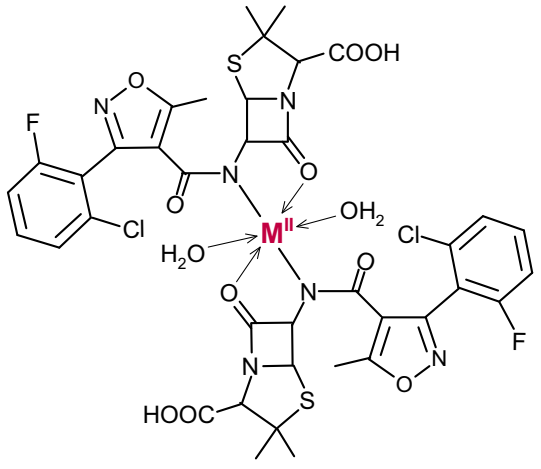


Fig. 6. Suggested molecular structure of flucloxacillin complexes with divalent transition metal ions.

Additionally, the acquired less-than unit order of the reduction rate with respect to the tellurite ion concentration can be ascribed to the formation of complexes among the reactive species (Flx^+ and H_2TeO_3) prior to the rate-limiting step. Additionally, complex formation was confirmed by the acquired non-zero intercepts of $1/k_{obs}$ vs. $1/[Te^{IV}]$ at all the studied temperatures, similar to Michaelis–Menten kinetics for complex formation, as shown in Fig. 7.

Based on the acquired kinetic outcomes and product characterization, a likely reduction mechanism was suggested and is illustrated in Scheme I. The first step of the anticipated mechanism is the protonation of flucloxacillin bioreductant to form the more reactive species, Flx^+, (Eq. (4)), which reacts with tellurous acid, H_2TeO_3, in the second step to form an intermediate complex (C), as represented by the following equation:

$$Flx^+ + H_2TeO_3 \overset{K_2}{\rightleftharpoons} [Flx\text{–}H_2TeO_3]^+ \; (C) \quad (5)$$

This intermediate promptly disintegrates in the rate-limiting step, giving rise to an intermediate oxidation product of flucloxacillin and the very reactive tellurium (II) ion, $HTeO_2^-$. Finally, the latter two intermediate products rapidly interact, forming the final redox products. This can be depicted by the following equation:

$$[Flx\text{–}H_2TeO_3]^+ \underset{slow}{\overset{k_1}{\rightarrow}} Flx \text{ intermediate product} + HTeO_3^- \underset{fast}{\overset{H_2O}{\rightarrow}} Flx \text{ oxidation products} + Te^0 \quad (6)$$

The negligible impact of the ionic strength and the relative permittivity of the reaction medium are in agreement with the reaction occurring between an ion and a neutral molecule [32], i.e., between Flx^+ and H_2TeO_3 (as in the anticipated mechanism).

According to the anticipated mechanism, the following rate-law expression was deduced (see Appendix A),

$$\text{Rate} = \frac{k_1 K_1 K_2 [Flx]\left[Te^{IV}\right][H^+]}{1 + K_1[H^+] + K_1 K_2\left[Te^{IV}\right][H^+]} \quad (7)$$

This equation is in a good agreement with all of the observed orders regarding the existing reactants.

Under pseudo-first order conditions:

$$\text{Rate} = \frac{-d[Flx]}{dt} = k_{obs}[Flx] \quad (8)$$

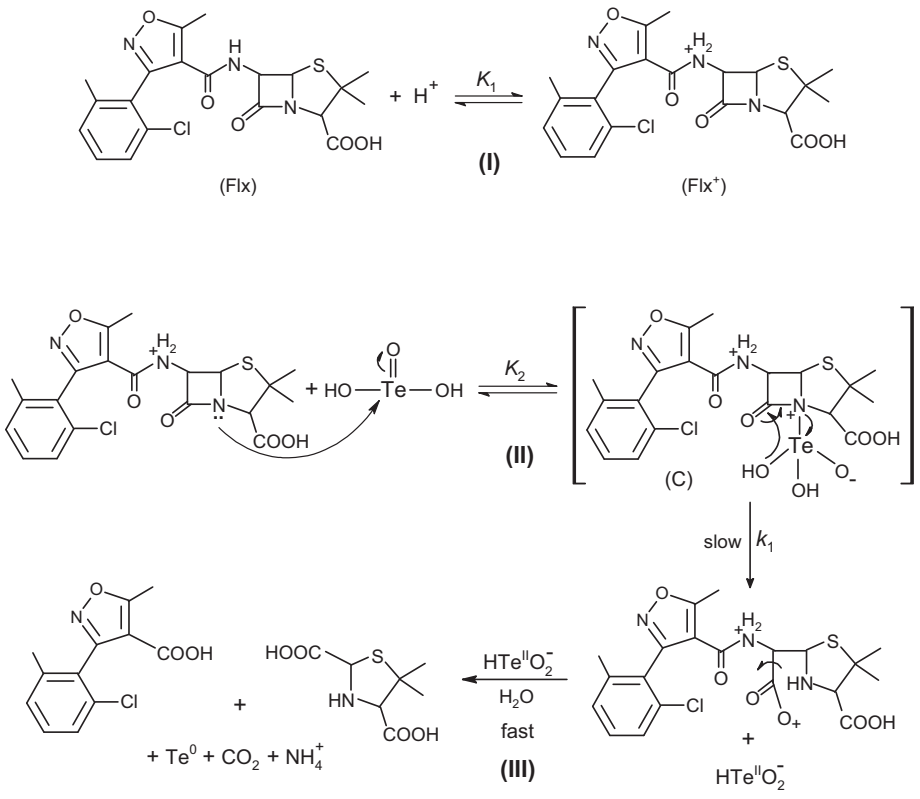
Comparison of Eqs. (7) and (8) gives:

$$k_{obs} = \frac{k_1 K_1 K_2\left[Te^{IV}\right][H^+]}{1 + K_1[H^+] + K_1 K_2\left[Te^{IV}\right][H^+]} \quad (9)$$

and with rearrangement of Eq. (9) results in the following equations:

$$\frac{1}{k_{obs}} = \left(\frac{1 + K_1[H^+]}{k_1 K_1 K_2[H^+]}\right)\frac{1}{\left[Te^{IV}\right]} + \frac{1}{k_1} \quad (10)$$

$$\frac{1}{k_{obs}} = \left(\frac{1}{k_1 K_1 K_2\left[Te^{IV}\right]}\right)\frac{1}{[H^+]} + \frac{1}{k_1 K_2\left[Te^{IV}\right]} + \frac{1}{k_1} \quad (11)$$



Scheme 1. Mechanism of reduction of tellurite ion by flucloxacillin in H_2SO_4 solution.

As stated in Eqs.(10) and (11), graphs of $1/k_{obs}$ vs. $1/[Te^{IV}]$ at a fixed $[H^+]$ and $1/k_{obs}$ vs. $1/[H^+]$ at fixed $[Te^{IV}]$ (at several temperatures) should form straight lines with positive intercepts on the $1/k_{obs}$ axes. This was shown in the investigational outcomes (Figs. 7 and 8, respectively), confirming the validity of the anticipated mechanism. The acquired values of k_1 at several temperatures are listed in Table 2. The activation parameters of k_1 were estimated from Arrhenius and Eyring graphs (Figs. 9a and b, respectively) and are also inserted in Table 2. Similarly, on the basis of Eq. (11), graphs of $1/k_{obs}$ vs. $1/[H^+]$ yielded straight lines. Using the slopes and intercepts of such graphs, the values of K_1 and K_2 at several temperatures were acquired and are presented in Table 3. The Van't Hoff graphs (Fig. 10) were constructed to show the variation of K_1 and K_2 with temperature. The values for enthalpy, entropy, and free energy of the reaction were evaluated and are also presented in Table 3.

The anticipated mechanism and the rate-law expressions are supported by the acquired activation parameters. The high positive values of both enthalpy ($\Delta H^{\neq}$) and free energy ($\Delta G^{\neq}$) signified that the formation of the intermediate complex is endothermic and non-spontaneous, while the acquired negative entropy ($\Delta S^{\neq}$) indicated the establishment

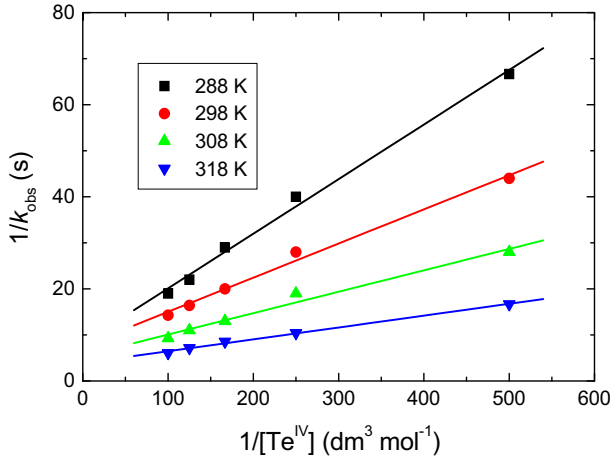


Fig. 7. Graphs of $1/k_{obs}$ vs. $1/[Te^{IV}]$ at several temperatures for the reduction of tellurite ion by flucloxacillin in H_2SO_4 solution. $[Flx] = 5.0 \times 10^{-4}$, $[H^+] = 1.0$ and $I = 2.0$ mol dm^{-3}.

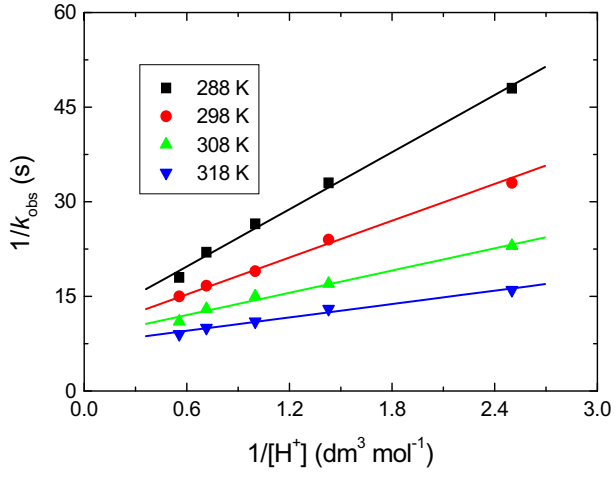


Fig. 8. Graphs of $1/k_{obs}$ vs. $1/[H^+]$ at several temperatures for the reduction of tellurite ion by flucloxacillin in H_2SO_4 solution. $[Flx] = 5.0 \times 10^{-4}$, $[Te^{IV}] = 6.0 \times 10^{-3}$ and $I = 2.0$ mol dm^{-3}.

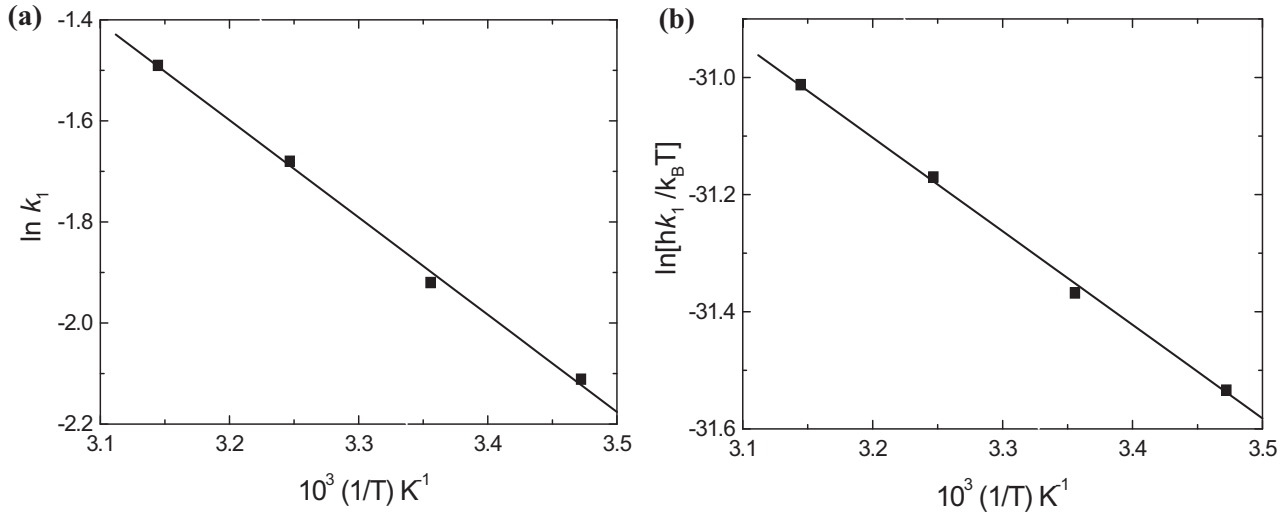


Fig. 9. (a) Arrhenius and (b) Eyring graphs of k_1 in the reduction of tellurite ion by flucloxacillin in H_2SO_4 solution. [Flx] = 5.0×10^{-4}, [Te^{IV}] = 6.0×10^{-3} and I = 2.0 mol dm^{-3}.

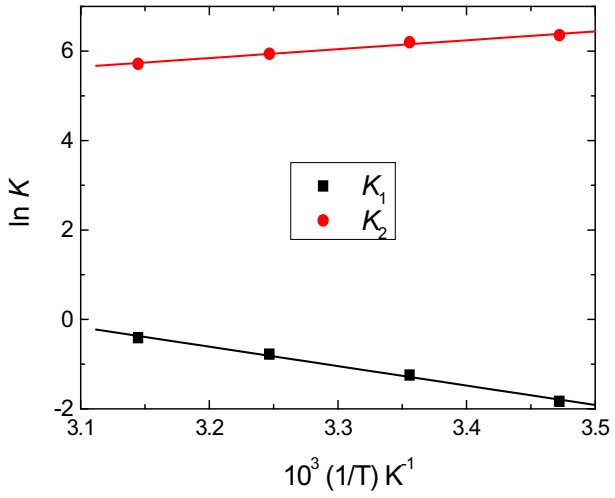


Fig. 10. Van't Hoff graphs of K_1 and K_2 in the reduction of tellurite ion by flucloxacillin in H_2SO_4 solution. [Flx] = 5.0×10^{-4}, [Te^{IV}] = 6.0×10^{-3} and I = 2.0 mol dm^{-3}.

of a rigid associative intermediate complex with diminishing degrees of freedom of the reactant molecules. The values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were both consistent with the electron-transfer process. Furthermore, the higher activation energy ($E_a^{\neq}$) indicates that the slow (rate-limiting) step was due to the intermediate complex decaying into the reaction products [33].

5. Conclusions

1) A novel treatment method for the removal of toxic tellurite ion was described via its bioreduction using flucloxacillin antibiotic in H_2SO_4 solution.
2) This treatment method has a dual benefit for the human health and the environment due to the degradation of flucloxacillin antibiotic and the conversion of highly toxic tellurite to a nontoxic valuable tellurium metalloid.
3) The suggested method is expected to be more convenient, simple, rapid, inexpensive and safe and provides more benefit for the human health and the environment than previously reported methods.
4) The kinetics of the bioreduction process were monitored spectrophotometrically.
5) Supplementation with certain divalent transition metal ions augmented the reaction rate.
6) The redox products were identified as 3-(2-chloro-6-fluorophenyl)-5-methylisoxazol-4-carbocylic acid and 5,5-dimethyl-thiazolidine-2,4-dicarboxlic acid, NH_4^+, CO_2 and Te^0.

Table 2
Values of k_1 at several temperatures and the related activation parameters in the reduction of tellurite ion by flucloxacillin in H_2SO_4 solution. [Flx] = 5.0×10^{-4}, [Te^{IV}] = 6.0×10^{-3} and I = 2.0 mol dm^{-3}.

Rate constant (s^{-1})	Temperature (K)				Activation parameters			
	288	298	308	318	$\Delta S^{\neq}$ [8] (Jmol^{-1} K^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta G^{\neq}_{298}$ (kJ mol^{-1})	$E_a^{\neq}$ (kJ mol^{-1})
10^2 k_1	12.11	14.95	18.50	22.53	−37.83	13.26	24.53	15.96

Experimental error ± 4%.

Table 3
Values of K_1 and K_2 at several temperatures and their thermodynamic quantities in the reduction of tellurite ion by flucloxacillin in H_2SO_4 solution. [Flx] = 5.0×10^{-4}, [Te^{IV}] = 6.0×10^{-3} and I = 2.0 mol dm^{-3}.

Equilibrium constant (dm^3 mol^{-1})	Temperature (K)				Thermodynamic parameters		
	288	298	308	318	ΔH^o (kJ mol^{-1})	ΔG^o_{298} (kJ mol^{-1})	ΔS^o (Jmol^{-1} K^{-1})
10^2 K_1	16.02	28.79	46.05	66.43	36.17	3.07	−111.07
10^{-2} K_2	5.76	4.92	3.81	3.04	−16.51	−15.36	3.86

Experimental error ± 5%.

7) The activation and thermodynamic parameters were estimated and confirmed.
8) The probable reaction mechanism presents the protonated flucloxacillin and tellurous acid as the reactive species.
9) The derived rate-law expression was found to be in good agreement with the acquired investigational outcomes.

Appendix A. Derivation of the rate-law expression

As stated in Scheme 1:

$$K_1 = \frac{[\mathrm{Flx}^+]}{[\mathrm{Flx}][\mathrm{H}^+]}, [\mathrm{Flx}^+] = K_1[\mathrm{Flx}][\mathrm{H}^+] \quad (A.1)$$

and

$$K_2 = \frac{[\mathrm{C}]}{[\mathrm{Flx}^+]\left[\mathrm{Te}^{\mathrm{IV}}\right]} \quad (A.2)$$

$$[\mathrm{C}] = K_2[\mathrm{Flx}^+]\left[\mathrm{Te}^{\mathrm{IV}}\right] = K_1K_2[\mathrm{Flx}]\left[\mathrm{Te}^{\mathrm{IV}}\right][\mathrm{H}^+]$$

From step (III), the rate-law expression can be written as in Eq. (A.3):

$$\mathrm{Rate} = \frac{-d[\mathrm{Flx}]}{dt} = k_1[\mathrm{C}] \quad (A.3)$$

Substituting Eq. (A.2) into Eq. (A.3) results in:

$$\mathrm{Rate} = k_1K_1K_2[\mathrm{Flx}]\left[\mathrm{Te}^{\mathrm{IV}}\right][\mathrm{H}^+] \quad (A.4)$$

Total concentration of Te^{IV} is given by:

$$\left[\mathrm{Te}^{\mathrm{IV}}\right]_{\mathrm{T}} = \left[\mathrm{Te}^{\mathrm{IV}}\right]_{\mathrm{F}} + [\mathrm{C}] \quad (A.5)$$

where 'T' and 'F' indicate total and free.

Substituting Eq. (A.1) into Eq. (A.5) leads to:

$$\left[\mathrm{Te}^{\mathrm{IV}}\right]_{\mathrm{T}} = \left[\mathrm{Te}^{\mathrm{IV}}\right]_{\mathrm{F}} + K_1K_2[\mathrm{Flx}]\left[\mathrm{Te}^{\mathrm{IV}}\right][\mathrm{H}^+] \quad (A.6)$$

$$\left[\mathrm{Te}^{\mathrm{IV}}\right]_{\mathrm{T}} = \left[\mathrm{Te}^{\mathrm{IV}}\right]_{\mathrm{F}}(1 + K_1K_2[\mathrm{Flx}][\mathrm{H}^+]) \quad (A.7)$$

Thus,

$$[\mathrm{Flx}]_{\mathrm{F}} = \frac{\left[\mathrm{Te}^{\mathrm{IV}}\right]_{\mathrm{T}}}{1 + K_1K_2[\mathrm{Flx}][\mathrm{H}^+]} \quad (A.8)$$

Due to the low [Flx] used, the term $K_1K_2[\mathrm{Flx}][\mathrm{H}^+]$ in the denominator can be neglected. Hence,

$$\left[\mathrm{Te}^{\mathrm{IV}}\right]_{\mathrm{F}} = \left[\mathrm{Te}^{\mathrm{IV}}\right]_{\mathrm{T}} \quad (A.9)$$

The total concentration of flucloxacillin is given by:

$$[\mathrm{Flx}]_{\mathrm{T}} = [\mathrm{Flx}]_{\mathrm{F}} + [\mathrm{Flx}^+] + [\mathrm{C}] = [\mathrm{Flx}]_{\mathrm{F}} + K_1[\mathrm{Flx}][\mathrm{H}^+] + K_1K_2[\mathrm{Flx}] \times \left[\mathrm{Te}^{\mathrm{IV}}\right][\mathrm{H}^+] \quad (A.10)$$

$$[\mathrm{Flx}]_{\mathrm{T}} = [\mathrm{Flx}]_{\mathrm{F}}\left(1 + K_1[\mathrm{H}^+] + K_1K_2\left[\mathrm{Te}^{\mathrm{IV}}\right][\mathrm{H}^+]\right) \quad (A.11)$$

Then,

$$[\mathrm{Flx}]_{\mathrm{F}} = \frac{[\mathrm{Flx}]_{\mathrm{T}}}{1 + +K_1[\mathrm{H}^+] + K_1K_2\left[\mathrm{Te}^{\mathrm{IV}}\right][\mathrm{H}^+]} \quad (A.12)$$

Because of the low $[Te^{IV}]$ used, the term $K_1K_2[Te^{IV}][H^+]$ in the denominator can be neglected. So,

$$[\mathrm{Flx}]_{\mathrm{F}} = \frac{[\mathrm{Flx}]_{\mathrm{T}}}{1 + K_1[\mathrm{H}^+]} \quad (A.13)$$

Based on high $[H^+]$, we can write:

$$\left[\mathrm{H}^+\right]_{\mathrm{F}} = \left[\mathrm{H}^+\right]_{\mathrm{T}} \quad (A.14)$$

Substituting Eqs. (A.9), (A.13) and (A.14) into Eq. (A.4) gives:

$$\mathrm{Rate} = \frac{k_1K_1K_2[\mathrm{Flx}]\left[\mathrm{Te}^{\mathrm{IV}}\right][\mathrm{H}^+]}{1 + K_1[\mathrm{H}^+] + K_1K_2\left[\mathrm{Te}^{\mathrm{IV}}\right][\mathrm{H}^+]} \quad (A.15)$$

Under pseudo-first-order circumstances:

$$\mathrm{Rate} = \frac{-d[\mathrm{Flx}]}{dt} = k_{\mathrm{obs}}[\mathrm{Flx}] \quad (A.16)$$

Comparing Eqs. (A.15) and (A.16), the following relationship is acquired:

$$k_{\mathrm{obs}} = \frac{k_1K_1K_2\left[\mathrm{Te}^{\mathrm{IV}}\right][\mathrm{H}^+]}{1 + K_1[\mathrm{H}^+] + K_1K_2\left[\mathrm{Te}^{\mathrm{IV}}\right][\mathrm{H}^+]} \quad (A.17)$$

With rearrangement, the following essential equations are obtained:

$$\frac{1}{k_{\mathrm{obs}}} = \left(\frac{1 + K_1[\mathrm{H}^+]}{k_1K_1K_2[\mathrm{H}^+]}\right)\frac{1}{\left[\mathrm{Te}^{\mathrm{IV}}\right]} + \frac{1}{k_1} \quad (A.18)$$

$$\frac{1}{k_{\mathrm{obs}}} = \left(\frac{1}{k_1K_1K_2\left[\mathrm{Te}^{\mathrm{IV}}\right]}\right)\frac{1}{[\mathrm{H}^+]} + \frac{1}{k_1K_2\left[\mathrm{Te}^{\mathrm{IV}}\right]} + \frac{1}{k_1} \quad (A.19)$$

References

[1] M. Wagner, A.D. Toews, P. Morell, Tellurite specifically affects squalene epoxide: investigations examining the mechanism of tellurium-induced neuropathy, J. Neurochem. 64 (1995) 2169–2176.
[2] J.M. Sandoval, P. Leveque, B. Gallez, C.C. Vasquez, P.B. Calderon, Tellurite-induced oxidative stress leads to cell death of murine hepatocarcinoma cells, Biometals 23 (2010) 623–632.
[3] T. Girard, C. Derie, E. Fuentes, J. Carlos, T. Claudio, C. Vásquez, Tellurite: history, oxidative stress, and molecular mechanisms of resistance, FEMS Microbiol. Rev. 33 (2009) 820–832.
[4] A. Ramos-Ruiz, J. Sesma-Martin, R. Sierra-Alvarez, J.A. Field, Continuous reduction of tellurite to recoverable tellurium nanoparticles using an upflow anaerobic sludge bed (UASB) reactor, Water Res. 108 (2017) 189–196.
[5] A. Fleming, M.Y. Young, The inhibitory action of potassium tellurite on coliform bacteria, J. Pathol. Bacteriol. 51 (1980) 29–35.
[6] H. Moscoso, C. Saavedra, C. Loyola, S. Pichuantes, C. Vásquez, Biochemical characterization of tellurite-reducing activities of Bacillus Stearothemophilus V, Res. Microbiol. 149 (1998) 389–397.
[7] J.P. O'Gara, M. Gomelsky, S. Kaplan, Identification and molecular genetic analysis of multiple loci contributing to high-level tellurite resistance in Rhodobacter sphaeroides 2.4.1, Appl. Environ. Microbiol. 63 (1997) 4713–4720.
[8] E. Wiberg, A.F. Holleman, Nils Wiberg (Eds.), Inorganic Chemistry. Translated by Mary Eagleson, Academic Press 2001, p. 588.
[9] K. Dong-Hun, K. Min-Gyu, S. Jiang, L. Ji-Hoon, H. Hor-Gil, Promoted reduction of tellurite and formation of extracellular tellurium nanorods by concerted reaction between iron and shewanella oneidensis MR-1, Environ. Sci. Technol. 47 (2013) 8709–8715.

[10] N. Mor, M. Resnick, F. Silbaq, H. Bercovier, L. Levy, Reduction of tellurite and deesterification of fluorescein diacetate are not well correlated with the viability of mycobacteria, Ann. Inst. Pasteur Microbiol. 139 (1988) 279–288.
[11] D. Ann-Marie, Pharmaceuticals in Industrial Wastewater and their Removal Using Photo-Fenton's xidation, Ph.D. Research Thesis School of Biotechnology Dublin City University, Dublin 9 Ireland, 2011.
[12] B. Halling-Sorensen, S.N. Nielsen, P.F. Lankzky, F. Ingerslev, H.C. Holten Lützhoft, S.E. Jorgensen, Occurrence, fate and effects of pharmaceutical substances in the environment, Chemosphere 36 (1998) 357–393.
[13] K. Kümmerer, A. Al-Ahmad, V. Mersch-Sundermann, Biodegradability of some antibiotics, elimination of the genotoxicity and affection of wastewater bacteria in a simple test, Chemosphere 40 (2000) 701–710.
[14] E. Gurtekin, N. Şekerdag, An advanced oxidation process: Fenton process, J. Eng. Sci. (2008) 229–239.
[15] (a) Z.A. AL-Othman, R. Ali, M. Naushad, Hexavalent chromium removal from aqueous medium by activated carbon prepared from peanut shell: adsorption kinetics, equilibrium and thermodynamic studies, Chem. Eng. J. 184 (2012) 238-247.
(b) M. Naushad, Surfactant assisted nano-composite cation exchanger: development, characterization and applications for the removal of toxic Pb^{2+} from aqueous medium, Chem. Eng. J. 235 (2014) 100-108.
(c) M. Naushad, T. Ahamad, G. Sharma, A.H. Al-Muhtaseb, A.A. Ghfar, Synthesis and characterization of a new starch/SnO_2 nanocomposite for efficient adsorption of toxic Hg^{2+} metal ion, Chem. Eng. J. 300 (2016) 306-316.
(d) M. Naushad, T. Ahamad, B.M. Al-Maswari, A.A. Alqadami, S.M. Alshehri, Nickel ferrite bearing nitrogen-doped mesoporous carbon as efficient adsorbent for the removal of highly toxic metal ion from aqueous medium, Chem. Eng. J. 330 (2017) 1351-1360.
[16] A.A. Alqadami, M. Naushad, Z.A. Alothman, A.A. Ghfar, Novel metal–organic framework (MOF) based composite material for the sequestration of U(VI) and Th(IV) metal ions from aqueous environment, ACS Appl. Mater. Interfaces 9 (2017) 36026–36037.
[17] A.A. Alqadami, M. Naushad, M.A. Abdalla, T. Ahamad, A.A. Ghfar, Efficient removal of toxic metal ions from wastewater using a recyclable nanocomposite: a study of adsorption parameters and interaction mechanism, J. Clean. Prod. 156 (2017) 426–436.
[18] A.G. Trovó, R.F.P. Nogueira, A. Agüera, A.R. Fernandez-Alba, C. Sirtori, S. Malato, Degradation of sulfamethoxazole in water by solar photo-Fenton. Chemical and toxicological evaluation, Water Res. 43 (2009) 3922–3931.
[19] P. Demirden, Treatability of Pharmaceutical Industry Wastewaters Containing Antibiotic in Anaerobic/Aerobic Sequential Processes, PhD-thesis, Izmir 2005.
[20] T. Oppenlander, Photochemical Purification of Water and Air (Weinheim, Germany: Wiley-VCH Verlag (2003); C.B. Ozkala, A. Koruyucub, S. Merica, Heterogeneous photocatalytic degradation, mineralization and detoxification of ampicillin under varying pH and incident photon flux conditions, Desalin. Water Treat. 57 (2016) 18391–18397; A.M. Garcıa, P.G. Navarro, P.J. Martınez, de las Parras, Degradation of ampicillin in the presence of cadmium(II) ions, Talanta 46 (1998) 101–109.
[21] F.J. Beltran, O.S. Keen, K.G. Linden, Ozone Reaction Kinetics for Water and Wastewater Systems, Lewis Publishers, Boca Raton, FL, 2003Degradation of antibiotic activity during UV/H_2O_2 advanced oxidation and photolysis in wastewater effluent, Environ. Sci. Technol. 47 (2003), pp. 13020–13030.
[22] A.K. Singh, M. Singh, S. Rahmani, J. Srivastava, J. Singh, A.K. Singh, R. Negi, B. Jain, Y. Katre, S.P. Singh, V.K. Sharma, Kinetics of the oxidation of tetracycline hydrate by copper(II) complexed with bipyridyl in alkaline medium using chloro-complex of palladium(II) as homogeneous catalyst, Ind. Eng. Chem. Res. 51 (2012) 5728–-5736Kinetics and mechanism of Ru(III)-catalyzed oxidation of paracetamol by chloramine-T in aqueous acidic medium, Catal. Lett. 132 (2012) 285–291.
[23] R.V. Hosahalli, K.S. Byadagi, S.T. Nandibewoor, S.A. Chimatadar, Kinetics and mechanism of ruthenium(III) catalyzed oxidation of chloramphenicol - an antibiotic drug by diperiodatocuprate(III) in aqueous alkaline medium, Kinet. Catal. (2012) 65–74.
[24] A.K. Durgannavar, M.B. Patgar, S.A. Chimatadar, Oxidation of amoxicillin by hexacyanoferrate(III) in aqueous alkaline medium - a kinetic and mechanistic approach, Indian J. Chem. (2015) 1085–1091.
[25] A.K. Singh, R. Yadav, J. Srivastava, R.S. Bala, R. Pradhan, S. Rahmani, N.P.S. Rajesh, S.T. Nandibewoor, Kinetics of Ir(III)-catalysed oxidation of ampicillin by cu$(Bip)_2^{2+}$ in alkaline medium: a spectrophotometric study, Int. J. ChemTech Res. 10 (2017) 514–-524Structure reactivity and thermodynamic analysis on the oxidation of ampicillin drug by copper(III) complex in aqueous alkaline medium (stopped-flow technique), J. Mol. Struct. 930 (2017) 180–186.
[26] R.R. Hosamani, N.P. Shetti, S.T. Nandibewoor, Mechanistic investigation on the oxidation of ampicillin drug by diperiodatoargentate (III) in aqueous alkaline medium, J. Org. Phys. Chem. 22 (2009) 234–240.
[27] S.E. Ramadan, A.A. Razak, A.M. Ragab, M. El-Meleigy, Incorporation of tellurium into amino acids and proteins in a tellurium-tolerant fungi, Biol. Trace Elem. Res. 20 (1989) 225–232.
[28] S.L. Chua, K. Sivakumar, M. Rybtke, M. Yuan, J.B. Andersen, T.E. Nielsen, M. Givskov, T. Tolker-Nielsen, B. Cao, S. Kjelleberg, L. Yang, C-di-GMP regulates Pseudomonas aeruginosa stress response to tellurite during both planktonic and biofilm modes of growth, Sci. Rep. 5 (10052) (2015) 1–13.
[29] C.E. Housecroft, A.G. Sharpe, Chapter 16: the group 16 elements, Inorganic Chemistry, 3rd ed.Pearson 2008, p. 524.
[30] V.F. Chemie, PhD Thesis, Duisburg University, Germany, 2005.
[31] R.S. Gujral, S.M. Haque, P. Shanker, A sensitive validated spectrophotometric method for the determination of flucloxacillin sodium, E-J. Chem. 6 (2009) S397–S405.
[32] A.A. Frost, R.G. Person, Kinetics and Mechanism, Wiley Eastern, New Delhi, 1973.
[33] F. Freeman, C.O. Fuselier, C.R. Armstead, C.E. Dalton, P.A. Davidson, E.M. Karchesfski, D.E. Krochman, M.N. Johnson, N.K. Jones, Permanganate ion oxidations. 13. Soluble manganese (IV) species in the oxidation of 2,4(1H,3H)-pyrimidinediones (uracils), J. Am. Chem. Soc. 103 (1981) 1154–1159.