# Methods for water treatment

1. 12. 2 Effect of chlorination of water

Chlorine is toxic not only for microorganisms, but for human being also. For humans, chlorine is an irritation to the nasal passages eye, and respiratory system. Chlorine gas must be cautiously handled because it may cause severe health problem. Although, chlorine gas is also the low rate form of chlorine for water treatment, It makes use choice in spite of the health problem.

In drinking water, the concentration of chlorine is usually very low and is thus not a concern in acute exposure. More of a concern is the long term risk of cancer due to chronic exposing to chlorinated water. This is mainly due to the halo alkanes and other products and chlorinated products. These are carcinogenic and have been the substance of concern in chlorinated drinking water. Chlorinated water has been related with increased risk of bladder, colon and rectal cancer. In the case of bladder cancer, the risk may be doubled.

Chlorination is a very popular method of water disinfection that has been used from several years. It has proved to be efficient for destroying bacteria and viruses, but not for some carcinogenic disinfection by-product, many communities have become hesitant in the continuation of this process. Although chlorination does have some disadvantages, it continues to be the most conventional, useful, and consistent method of water disinfection.

1. 13 Oxidation by potassium permanganate

Most treatment plants, uses potassium permanganate for the oxidation and subsequent removal of iron, follow the chemical addition with manganese greensand filtration. Manganese treated greensand can exchange electrons and therefore oxidizes iron and manganese to their insoluble, filterable states [[1]–[2]].

When the filter is completely regenerated the excess $KMnO_4$ will break through the filter bed leaving a pink color in the water. The greensand filter bed is usually capped with anthracite to first remove insoluble compounds, which helps prevent the filter from becoming clogged. Most filters are equipped with an air wash system to enhance the greens and backwashing process. Major disadvantages to the use of the potassium permanganate – greens and filtration process for iron removal include high chemical costs and filter bed deterioration when the pH falls below 7. 0. In some treatment plants, $KMnO_4$ is used to oxidize iron and manganese without greensand filtration[[3]]and analytical chemistry [[4]] and also as a disinfectant. Among the six oxidation states of manganese from +2 to +7, permanganate, Mn(VII) is the most pervasive oxidation state in acid, with reduction potentials of [[5]]Oxidation by permanganate finds extensive application in organic synthesis [[6]]. The manganese chemistry involved in these multistep redox reactions is an important source of information as the manganese intermediates are relatively easy to identify when they have sufficiently long lifetimes, and oxidation states of the intermediates permit useful conclusions as to the possible reaction mechanisms, including the nature of intermediates. In acidic medium it exists in the different forms: $HMnO_4$, $H_2MnO_4^+$, $HMnO_3$ and $Mn_2O_7$.

The thesis comprises seven chapters including the general introduction about chemical kinetics as follows.

1. General Introduction

This chapter introduces about the kinetics, mechanisms, disinfection and catalysis of reactions in general.

PART I

Uncatalyzed reactions

2. Transformation of Levofloxacin during Water treatment with chlorine: Kinetics, Mechanism and Pathways

Kinetics and mechanism of removal of fluoroquinolone antibacterial levofloxacin (LFC) by free available chlorine (FAC) during water chlorination processes was investigated for the first time between the pH values 4. 2 and 8. 5. The pH dependent second order rate constants were found to decrease with increase in pH. (e. g. Apparent second order rate constant; $k''_{app} = 20$ dm$^3$ mol$^{-1}$ s$^{-1}$ at pH 4. 2 and $k''_{app} = 1$ dm$^3$ mol$^{-1}$ s$^{-1}$ at pH 8. 5 and at 25 $^o$C). The products of the reaction were determined by Liquid chromatography and high resolution mass spectrometry. There are two plausible pathways for the LFC chlorination. The major channel is electrophilic halodecarboxylation of quinolone moiety in which, HOCl reacts at tertiary N(4) amine to form a reactive chlorammonium intermediate (R$_3$N(4)Cl$^+$) that can catalytically halogenate LFC and the minor channel is chlorination at piperazinyl moiety in which the HOCl reacts at tertiary N(4)

amine to form a reactive chlorammonium intermediate (R $_3$ N(4)Cl $^+$ ) followed by intermediate degradation both at piperazinyl and quinolone moiety with successive chlorination. The effect of temperature on the rate of the reaction was studied at four different temperatures and rate constants were found to increase with increase in temperature and the thermodynamic activation parameters $E_a$ , $\Delta H^{\#}$ , $\Delta S^{\#}$ and $\Delta G^{\#}$ were evaluated for the reaction and discussed.

3. Transformation of linezolid during water treatment with chlorine: A kinetic study

The experimental studies on transformation of emerging contaminant linezolid during water chlorination process have been carried out using UV-Visible spectrometer. The pseudo-first order rate constants of linezolid reaction with free available chlorine (FAC) at 5. 0 to 8. 8 pH have been determined. The second order rate constants are found to decrease with increase in p $^H$ (e. g. apparent second rate constant; k" $_{app}$ = 2. 88 dm $^3$ mol $^-$ $^1$ s $^{-1}$ at pH 5. 0 and k" $_{app}$ = 0. 076 dm $^3$ mol $^{-1}$ s $^{-1}$ at pH 8. 8 at 298K). Monochlorinated reaction product has been identified by LC/ESI/MS spectra under the experimental conditions. A mechanism involving electrophilic halogenation is proposed based on the kinetic data and LC/ESI/MS spectra. The effect of temperature on the rate of the reaction has been studied at four different temperatures. It is observed that rate constants increase with the increase in temperature and the thermodynamic activation parameters $E_a$ , $\Delta H^{\#}$ , $\Delta S^{\#}$ and $\Delta G^{\#}$ are evaluated for the reaction and discussed. The product of the reaction between linezolid and FAC retains the antibacterial

activity. The geometry optimization of the reactants and the products has been done using dispersion corrected density functional (DFT-D) method. All the DFT calculations are accomplished using the TurboMole-5. 10 package.

4. Transformation of antibacterial agent lomefloxacin by alkaline permanganate: Kinetics and Mechanism

The kinetic and mechanistic investigation of oxidation of emerging contaminant Lomefloxacin (LMF) by alkaline permanganate was carried out spectrophtometrically. The oxidation product 7-amino-1-ethyl-6, 8-difluoro-4-oxo-quinoline-3-carboxylic acid was identified by Agilent 6130 Series Quadrupole LC/MS. The stoichiometry was found to be 1: 2, that is, 1 mol of lomefloxacin reacted with 2 mol manganese (VII). Orders with respect to [LMF] and [OH $^-$ ] were found to be fractional and less that one. The oxidation reaction proceeds via an alkali-permanganate species, that forms a complex with lomefloxacin and the complex then decomposes to give the product. The rate of reaction was found to decrease with decrease in the dielectric constant. The effects of initially added products and ionic strength have also been investigated. The kinetics of the reaction was also studied at four different temperatures and the thermodynamic activation parameters for the reaction were evaluated and discussed. The geometry optimization of reactants and activated complex were carried out using density functional theory (DFT). The DFT calculations were accomplished with the TURBOMOLE program package (Version-6. 4). The activation energy was found to be ~21 kJ/mol at RI-BP86. def 2-TZVPP level of theory.

PART II

CATALYSED REACTIONS

## 5. Silver (I) catalyzed and uncatalyzed oxidation of levofloxacin with aqueous chlorine: A comparative kinetic and mechanistic approach

The kinetics and mechanism of the Ag (I) ion catalyzed reaction of levofloxacin (LFC) by free available chlorine (FAC) during water chlorination processes was investigated for the first time between the pH values 4. 2 and 8. 2. The pH dependent second order rate constants were found to decrease with increase in pH. (e. g. Apparent second order rate constant for Ag (I) catalyzed reaction, $k''_{app}$ = 114. 40 dm $^{-3}$ mol $^{-1}$ sec $^{-1}$ at pH 4. 2 and $k''_{app.}$ = 8. 72 dm $^{-3}$ mol $^{-1}$ sec $^{-1}$ at pH 8. 2 and at 25±0. 2 â„ ƒ). The reaction rates revealed that Ag (I) catalyzed reaction was about six-fold faster than the uncatalyzed reaction. The products of the reaction were determined by Liquid chromatography and high resolution mass spectrometry. The reaction proceeds via formation of intermediate complex between Ag (I) ion and levofloxacin, then HOCl reacts with the complex to form chlorinated product. The effect of catalyst, effect of initially added product, effect dielectric constant and effect ionic strength on the rate of reaction was also studied. The effect of temperature on the rate of the reaction was studied at four different temperatures and rate constants were found to increase with increase in temperature and the thermodynamic activation parameters $E_a$, $\Delta H^{\#}$, $\Delta S^{\#}$ and $\Delta G^{\#}$ were evaluated for the reaction and discussed.

## 6. Ag (I) catalyzed chlorination of linezolid during water treatment: Kinetics, mechanism

The kinetics and mechanism of the Ag (I) ion catalyzed reaction of linezolid (LNZ) by free available chlorine (FAC) during water chlorination processes was investigated for the first time between the pH values 4. 0 and 9. 0. The pseudo-first order rate constants of linezolid reaction with free available chlorine (FAC) at 4. 0 to 9. 0 pH have been determined. The pH dependent second order rate constants were found to decrease with increase in pH. Apparent second order rate constant for uncatalyzed reaction, e. g. $k''_{app}$ = 8. 15 dm$^{-3}$ mol$^{-1}$ sec$^{-1}$ at pH 4. 0 and $k''_{app.}$ = 0. 076 dm$^{-3}$ mol$^{-1}$ sec$^{-1}$ at pH 9. 0 and at 25±0. 2 â„ƒ and for Ag (I) catalyzed reaction total apparent second order rate constant, e. g. $k''_{app}$ = 51. 50 dm$^{-3}$ mol$^{-1}$ sec$^{-1}$ at p$^{H}$ 4. 0 and $k''_{app.}$ = 1. 03 dm$^{-3}$ mol$^{-1}$ sec$^{-1}$ at pH 9. 0 and at 25±0. 2 â„ƒ. The reaction rates revealed that Ag (I) catalyzed reaction was about five to ten-fold faster than the uncatalyzed reaction. Monochlorinated reaction product has been identified by LC/ESI/MS spectra under the experimental conditions. A mechanism involving electrophilic halogenation is proposed based on the kinetic data and LC/ESI/MS spectra. The reaction rates revealed that Ag (I) catalyzed reaction was about ten-fold faster than the uncatalyzed reaction. The reaction proceeds via formation of intermediate complex between Ag (I) ion and linezolid, then HOCl reacts with the complex to form chlorinated product. The effect of temperature on the rate of the reaction has been studied at four different temperatures. It is observed that rate constants increase with the increase in temperature and the thermodynamic activation parameters $E_a$, $\Delta H^{\#}$, $\Delta S^{\#}$ and $\Delta G^{\#}$ are evaluated for the reaction and discussed. The effect of catalyst, effect of initially added product, effect dielectric constant and effect ionic strength on the rate of reaction. The

product of the reaction between linezolid and FAC retains the antibacterial activity.

7. Transformation of linezolid during water treatment with permanganate: Kinetics, mechanism and Pd (II) catalysis

The uncatalyzed and Pd (II) catalyzed transformation of Linezolid (LNZ) with permanganate in acidic medium was carried out between the pH values 3. 0 and 6. 0. The pH dependent second order rate constants were found to decrease with increase in pH. Apparent second order rate constant for uncatalyzed reaction, e. g. $k''_{app}$ = 6. 32 dm$^{-3}$ mol$^{-1}$ sec$^{-1}$ at pH 3. 0 and $k''_{app.}$ = 2. 64 dm$^{-3}$ mol$^{-1}$ sec$^{-1}$ at pH 6. 0 and at 25±0. 2 â„ƒ and for Pd (II) catalyzed reaction total apparent second order rate constant, e. g. $k''_{app}$ = 75. 5 dm$^{-3}$ mol$^{-1}$ sec$^{-1}$ at p$^H$ 3. 0 and $k''_{app.}$ = 45. 66 dm$^{-3}$ mol$^{-1}$ sec$^{-1}$ at pH 6. 0 and at 25±0. 2 â„ƒ. The reaction rates revealed that Pd (II) catalyzed reaction was about ten-fold faster than the uncatalyzed reaction. The products of the reaction were determined by Liquid chromatography and high resolution mass spectrometry. The reaction proceeds via formation of complex between Pd (II) and linezolid, then complex reacts with acidic permanganate to form intermediate compound, which then form oxidized products. The effect of catalyst, effect of initially added product, effect dielectric constant and effect ionic strength on the rate of reaction were also studied. The effect of temperature on the rate of the reaction was studied at four different temperatures and rate constants were found to increase with increase in temperature and the thermodynamic activation parameters $E_a$, $\Delta H^{\#}$, $\Delta S^{\#}$ and $\Delta G^{\#}$ were evaluated for the reaction and discussed.

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