Summary

Nitrogen oxides (NO and NO₂) have a proven negative impact on our environment and are involved in the formation of acid rain and smog. The compounds are formed by burning fossil fuels. Road transportation, power plants and other industrial activities are major contributors to the emissions of nitrogen oxides. According to the Gothenburg protocol, the NOx emissions in Europe, estimated 9.5 million ton in 2002, need to be reduced to 6 million ton in the year 2010. Commercial technologies for NOx emission reductions for stationary sources range from combustion modifications to flue gas treatments. Flue gas treatment concepts offer the highest NO removal efficiencies. The most widely used technology is Selective Catalytic Reduction (SCR), able to achieve NO removal efficiencies up to 90%. The SCR technology is based on the reaction of NO gas with ammonia in presence of a catalyst to form nitrogen and water. Drawbacks of this technology are the relatively high costs involved and environmental concerns about the use of ammonia. Alternative flue gas treatment technologies have been proposed and are currently under investigation. Particularly promising are wet removal technologies, where the NO is absorbed in aqueous solutions with a suitable reactant. NO is poorly soluble in water, leading to low absorption rates. In the presence of a suitable reactant, the absorption rate of NO is enhanced considerably due to chemical reaction. In particular, Fe²⁺ chelates based on ethylene-diamine-tetraacetic acid (EDTA) and related compounds like nitrilotriacetic acid (NTA) rapidly react with the absorbed NO gas to form stable metal-nitrosyl complexes (see reaction (1)).

\[ Fe^{II} (EDTA) + NO \rightleftharpoons Fe^{II} (EDTA)(NO) \]  \hspace{1cm} (1)

To be economically viable, efficient regeneration methods for the metal-chelate solutions are necessary. A novel biotechnological approach has been described recently to regenerate the loaded iron-chelate solution. In this so-called BiodeNOx process, the loaded iron-chelate solution is contacted with specific micro-organisms that convert the nitrosyl complex back to the original Fe²⁺(EDTA) complex and N₂ gas in presence of an electron donor (ethanol). Fe³⁺(EDTA), also formed in the absorption process due to the presence of oxygen in the flue gas and unable to bind NO, is also reduced to the original Fe²⁺(EDTA) complex:

\[ 12Fe^{III} (EDTA) + C_2H_5OH + 3H_2O \rightarrow 12Fe^{II} (EDTA) + 2CO_2 + 12H^+ \]  \hspace{1cm} (2)

A schematic representation of the BiodeNOx process is shown in Figure 1. Successful pilot plant studies have shown that the BiodeNOx process is capable of NO removal efficiencies of up to 65%. However, it is expected that a better fundamental understanding of the process and optimization of the process parameters will result in a significant improvement of the BiodeNOx process performance and lead to a substantial lowering of the NO removal cost. A multidisciplinary research group with researchers from three different Dutch Universities and input from industry has been instituted with the support of the Netherlands Technology Foundation (STW). The University of Wageningen has focused on the fundamentals of the bio-regeneration process, the microbiological aspects of the BiodeNOx process.
have been investigated at the University of Delft, whereas the RijksUniversiteit of Groningen has focused on the design and optimization of the absorber unit. The results of the latter activities are described in this thesis.

Figure 1. Schematic representation of the BiodeNOx process.

In Chapter 2, an experimental- and modelling study on NO absorption in aqueous Fe\textsuperscript{II}(EDTA) solutions in a stirred cell reactor is reported. The experimental results imply that the reaction is first order in NO and iron chelate. The reaction is an exothermic equilibrium reaction and the reverse reaction has to be taken into account. The equilibrium constant of the reaction at various temperatures has been determined. In addition, the ratio of the diffusion coefficients of Fe\textsuperscript{II}(EDTA) and NO, an important physical property for the design of a reactive absorber unit has been established. Due to the exothermicity of the reaction, the equilibrium constant decreases at higher temperature. This results in significant reductions of the absorption rates of NO at the high end of the temperature range of the study.

In Chapter 3, an experimental- and modelling study on NO absorption in Fe\textsuperscript{II}(EDTA) solutions in the presence of typical BiodeNOx sludges is reported. On the basis of these studies, it is expected that the NO absorption rate will be lowered with increasing BiodeNOx sludge loading. The decrease is likely due to partial blockage of the gas - liquid interface by inorganic and organic suspended solids and to a lesser extent to changes in the physical properties of the liquid. However, under particular circumstances, like the presence of small adsorptive solids, the NO absorption rate may be enhanced. A semi-empirical model has been developed, including mass transfer reduction by surface blocking and enhancement by adsorptive particles, to describe the results.

An experimental study on the absorption of oxygen in Fe\textsuperscript{II}(EDTA) solutions in a stirred cell reactor is reported in Chapter 4. The reaction is shown to be an irreversible reaction, first order in oxygen and second order in iron chelate. The oxygen absorption takes place in a regime between fast and instantaneous. The value of the kinetic constant appears to be independent of the pH in the range 5 - 8. In case of NaCl addition to the liquid phase, the kinetic constant is a function of the salt loading.
and a significant increase was observed when performing the reaction in a 15 kg/m³ NaCl solution. The overall stoichiometric coefficient of Fe deviates from the theoretical value of 4, suggesting that other oxygen consuming reactions take place as well. A remarkable step change in the stoichiometric coefficient of Fe as a function of the concentration of oxygen was observed. Higher oxygen concentrations and, to a lesser extent, low pH values promote the side reactions and causes the stoichiometric coefficient of Fe to drop to about 3.

In Chapter 5, the simultaneous absorption of NO and O₂ in Fe²⁺(EDTA) solution in a stirred cell reactor is investigated. The NO absorption rates and the selectivity of the absorption process are affected by the presence of oxygen. Here, the selectivity is defined as the ratio of the average NO flux and the average oxygen flux. High NO and low oxygen concentrations result in higher NO absorption rates and selectivity improvements. The temperature and the initial Fe³⁺(EDTA) concentration have a profound effect on both the absorption rates and the selectivity. To promote NO absorption, it is advantageous to work at low temperatures and high Fe-concentrations. Modelling studies using enhancement factors from the film theory for reactive gas absorption allow prediction of the NO fluxes at various conditions. Agreement between the experimental and modelled NO fluxes is good.

In Chapter 6, a counter-current model spray tower with well defined single drops is used to study the reactive absorption of NO in aqueous Fe²⁺(EDTA) solutions. In this ideal spray tower, the efficiency of the gas absorption is a strong function of the temperature and to a lesser extent the Fe-concentration. The efficiency drops dramatically at high temperatures and low iron chelate concentrations.

In Chapter 7, an experimental study on EDTA degradation in a G-L stirred cell contactor is reported. EDTA degradation takes place when reacting Fe²⁺(EDTA) with molecular oxygen. The degradation process is studied in a range of process conditions relevant for the BiodeNOx process (\( T = 323 \) K, \( C_{Fe}^{Fe(II)(EDTA)} = 10 \) mol/m³, pH = 7, \([EDTA]/[Fe] = 1.1, C_{O2} = 5 \) vol%). One of the possible degradation products, ED3A (ethylenediaminetriacetic acid) is used as a probe to assess the degradation level. The average rate of Fe³⁺(ED3A) formation is increased at higher temperatures, higher oxygen levels and higher initial iron chelate concentrations. However, the integral selectivity remains constant, suggesting that the rate of the oxidation of Fe²⁺(EDTA) to Fe³⁺(EDTA) is coupled to the rate of EDTA degradation. The presence of NO seems to have a positive effect, leading to reduced degradation rates and higher selectivity values. A remarkable reduction of the (average) rate of Fe³⁺(ED3A) formation is observed when performing the reaction with a higher EDTA/Fe ratio. This suggests that performing the BiodeNOx process with an excess of EDTA on Fe will lead to a significant reduction in the EDTA degradation rates. Further studies to determine the impact of the excess of EDTA on bioreactor performance are necessary.

A steady state, rate based reactor model for a packed column reactor configuration is reported in Chapter 8. Various input parameters, like the kinetics of the reactions of Fe²⁺(EDTA) with NO and oxygen and physical properties, were taken from the results described in the previous chapters of this thesis. As such, all results described in this thesis are integrated in the absorber model. The height of the packed tower reactor to obtain 90% removal efficiency has been determined as a function of the process conditions. Based on the modelling results, a remarkable improvement in absorber performance is expected when operating the reactor at low temperatures. In this situation, the height of the column to achieve high efficiencies and the rate of the oxidation reaction are reduced considerably. As a result, the rate of EDTA degradation, which has shown to be coupled to the rate of oxidation, is expected to be
reduced as well. At certain process conditions, desorption of NO may occur, indicating that over design of the absorber unit may lead to reduced column performance.