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Non-dispersive infrared (NDIR) sensor for real-time nitrate monitoring in wastewater treatment

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ABSTRACT

Nitrate is a frequent water pollutant that results from human activities such as fertilizer over-application and agricultural runoff and improper disposal of human and animals waste. Excess levels of nitrate in watersheds can trigger harmful algal blooms (HABs) and biodiversity loss with consequences that affect the economy and pose a threat to human health. Municipal drinking water and wastewater treatment plants are therefore required to control nitrogen levels to ensure the safety of drinking water and the proper discharge of effluent.
Nitrate exhibits distinct absorption bands in the infrared spectral range. While infrared radiation is strongly attenuated in water, implementation of fiber optic evanescent wave spectroscopy (FEWS) enables monitoring of water contaminants in real-time with high sensitivity. This work outlines the development of a non-dispersive infrared (NDIR) detector for the real-time monitoring of nitrate, nitrite and ammonia concentrations targeting implementation at municipal wastewater treatment plants (WWTPs) and onsite wastewater treatment systems (OWTS).

Keywords: Non-dispersive infrared, fiber optic evanescent wave spectroscopy, wastewater, nitrogen analysis

1. INTRODUCTION

1.1 Analytical instrumentation in residential wastewater treatment

Rapid population growth strains available water resources. Residential and industrial wastewater treatment industry is under constant pressure to come up with efficient methods to handle large quantities of wastewater and to ensure its effective treatment before discharge and/or reuse. While certain technological details of raw sewage treatment may differ from plant to plant, the underlining water treatment principles are universal. Effective sewage treatment combines physical, chemical, and biological processes to remove pathogenic microorganisms and toxic wastes; to reduce organic contents; and to remove inorganic nutrients (nitrogen and phosphorous) that can cause eutrophication – the growth of algae that is toxic to humans and harmful to the environment. In recent years, automation of the wastewater treatment through real-time process monitoring has been a key trend in residential and industrial wastewater treatment which is reflected in a growing need for real-time analytical equipment. In this manuscript, we present our recent efforts to develop real-time sensor for detection of nitrate, nitrite and ammonia that is expected to replace grab-sample analysis at WWTPs and enable enhanced levels of process control during the biological treatment of sewage.

1.2 Nitrogen monitoring: WWTP process automation and optimization

Nitrogen in water and wastewater can be found in forms of ammonia, nitrite, nitrate and organic nitrogen. In raw wastewater, removal of ammonia is performed through nitrfication process that is driven by biological organisms that convert ammonia to nitrite, and ultimately to nitrate. This process is followed by the denitrification that converts nitrate into nitrogen gas, which is then released into the atmosphere (Figure 1 (a)). Both processes are facilitated in typical bio-reactors at WWTPs though different types of microorganisms specific to each process.

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Nitrification process requires aeration. Aeration is commonly achieved by means of industrial pumps and blowers that move large volumes of air to bubblers along the bottom of the basin. Powering the aeration equipment consumes anywhere between 50% and 75% of the total energy consumption for large and small plants, respectively [1]. Figure 1 (b) illustrates the energy consumption breakdown for an average wastewater treatment facility [1]. Optimization of the aeration process through implementation of a feedback control based on real-time monitoring of nitrogen levels could reduce power consumption by 10% to 30% [1,2,3].

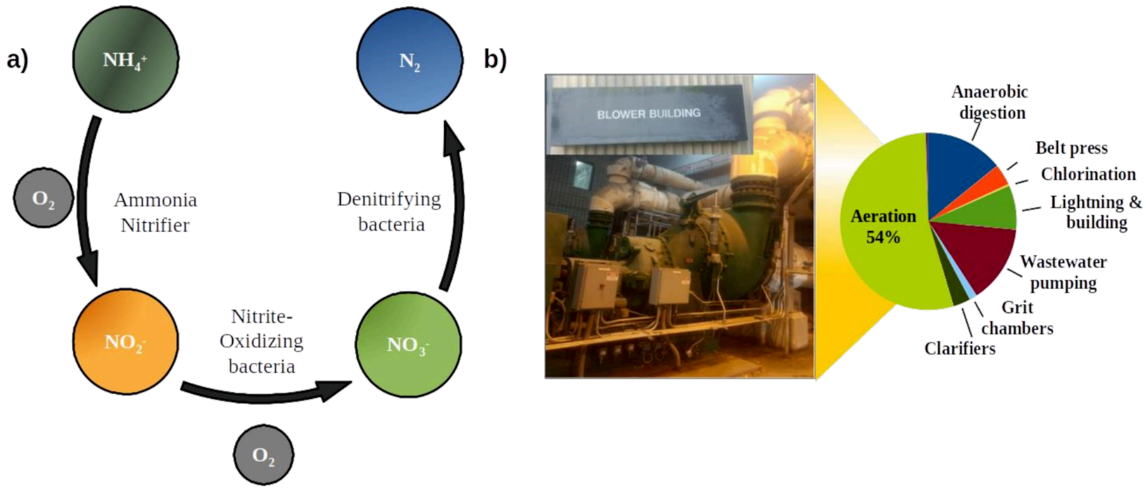

Figure 1: a) Nitrification / denitrification process reaction path. b) Energy consumption in wastewater treatment facilities from Ref. [1]. A blower building image is provided for visualization of aeration equipment.

Additional value that real-time nitrogen monitors provide is the ability to timely detect and address nitrification problems that can result in a buildup of toxic concentration of nitrite. Further nitrification may be inhibited if a reduction in dissolved oxygen concentration is detected.

However, due to the lack of reliable real-time monitors, many WWTPs rely on "grab-sampling", sending the collected wastewater samples to laboratories for analysis. Emerging ion-selective electrode (ISE) technology allows real-time measurements of nitrate and ammonia, but this technique is prone to ionic interferences and requires frequent calibration and maintenance [4]. Other techniques include nitrate monitoring using optical UV technology [5,6] or monitoring of ammonia using colorimetric tools that require reagents [7].

Max-IR Labs develops a unique nitrogen sensor that aims to replace grab-sample practices with real-time monitoring enabling closed-loop feedback control and reducing the risk of costly out-of-control events which can affect the overall operation of the WWTPs and result in a release of contaminated effluent into the environment. Although infrared technology is not one of the traditionally implemented techniques in water analytics, the recent technology advances in infrared components due to the ongoing support by the defense sector make possible a range of new commercial as well as defense-related high-value, innovative solutions.

In the following sections we discuss the sensitivity and specificity of this technique when applied to sensing of nitrate, nitrite and ammonia in water. The final section presents data from the Max-IR Labs non-dispersive instrumentation, implementing quantum cascade laser (QCL) as a source of infrared radiation.

1.3 Monitoring of contaminants in water using IR absorption technology

IR technology had been reported as a potential candidate for measurement of nitrate in soil by Linker et al [8]. This work aims to transfer IR technology from lab to field in a form of a non-dispersive infrared (NDIR) stand-alone instrument for implementation in wastewater treatment. Non-dispersive IR instrumentation is widely implemented in gas analysis and is available in various forms, from simple cells where gas concentration is measured by monitoring IR absorption within a volume of analyzed gas [9], to advanced quartz-enhanced photoacoustic spectroscopy (QEPAS) technologies [10].

However, implementation of infrared technology for monitoring of contaminants in aqueous environment is very challenging due to strong absorption of infrared radiation in water.

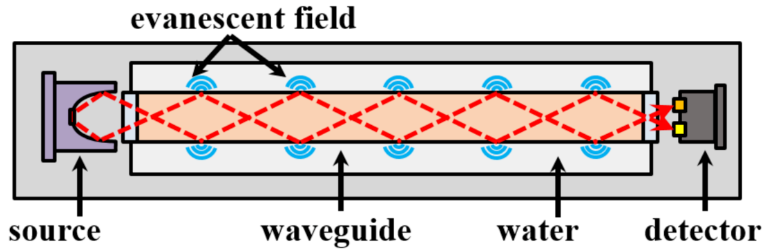

Figure 2 Schematic drawing of the cell based on FEWS principles, where the radiation is transmitted through an optical waveguide and the detection performed by means of the evanescent field.

To overcome this challenge, Max-IR Labs sensor utilizes infrared waveguides for radiation transfer from source to detector. This technique is known as fiber-optic evanescent wave spectroscopy (FEWS) [11], where the interaction between the radiation in the optical waveguide and the surrounding liquid is through the evanescent waves, as shown in Figure 2. Optical fibers from silver-halide ($AgCl_xBr_{1-x}$) material [12] were implemented as FEWS elements. Application of this technique for monitoring of nitrogen compounds in water is discussed in the following sections.

2.2 Nitrite, ammonia and nitrate in water: spectral analysis

Figure 3 presents IR data obtained from nitrate, nitrite and ammonia of concentration of 200ppm, recorded at single-bounce attenuated total reflection (ATR) Nicolet™ is50 FTIR spectrometer equipped the DTGS detector. The data clearly shows absorption peaks due to all of the nitrogen species of interest. There is a clear separation between the three nitrogen species, which is a strong advantage for implementation in the real-time wastewater analysis. Infrared absorption due to ammonia has the lowest intensity. However, as will be shown in the following sections, adjustment of the experimental parameters allow detection of ammonia beyond 1ppm limit.

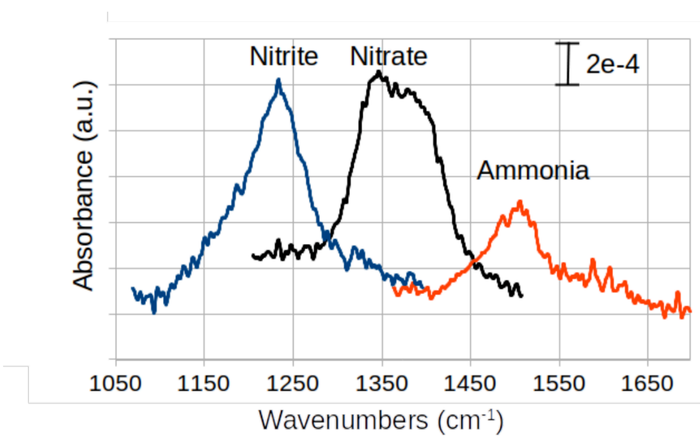

Figure 3: IR absorption of 200ppm nitrite, nitrate and ammonia in water. Data obtained in a single-bounce ATR experiment.

2.2.1. Calibration curves

Dilute concentrations of nitrate solution with varying concentration were measured in the FEWS cell (presented in Figure 2) using FTIR spectrometer. The area of the nitrate absorption band as a function of concentration is presented in Figure 4 (a), while absorbance spectra are presented in Figure 4 (b).

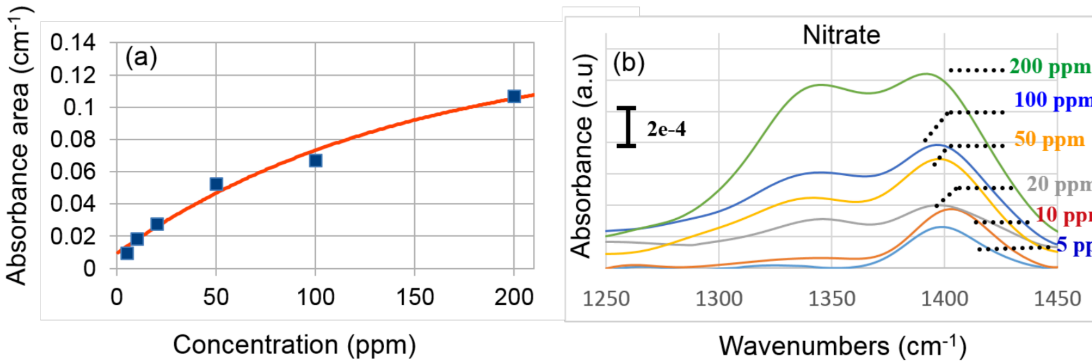

Figure 4: Nitrate calibration curves. (a). Absorbance area as a function of concentration; (b)Absorbance spectra. All data collected in FEWS mode utilizing multiple internal reflections.

Notably, at higher concentrations, nitrate absorption peak presents a broad, double-peak spectrum with maxima at 1340cm^{-1} and 1390cm^{-1}. As the concentration decreases, the intensity of the peak at 1340cm^{-1} decreases in relation to the peak at 1390 cm^{-1}. For this reason, we focused our NDIR efforts in the spectral range between 1390cm^{-1} to 1410cm^{-1}.
Calibration curves obtained for ammonia in FEWS configuration are presented in Fig. 5. The maximum of the peak due to ammonia absorption is at 1450cm^{-1}. Absorption peaks down to concentration of 1ppm can be clearly observed. Improvement of SNR by implementation of QCL sources is presently explored by our group with the aim to achieve detection of ammonia down to concentration of 0.1ppm.

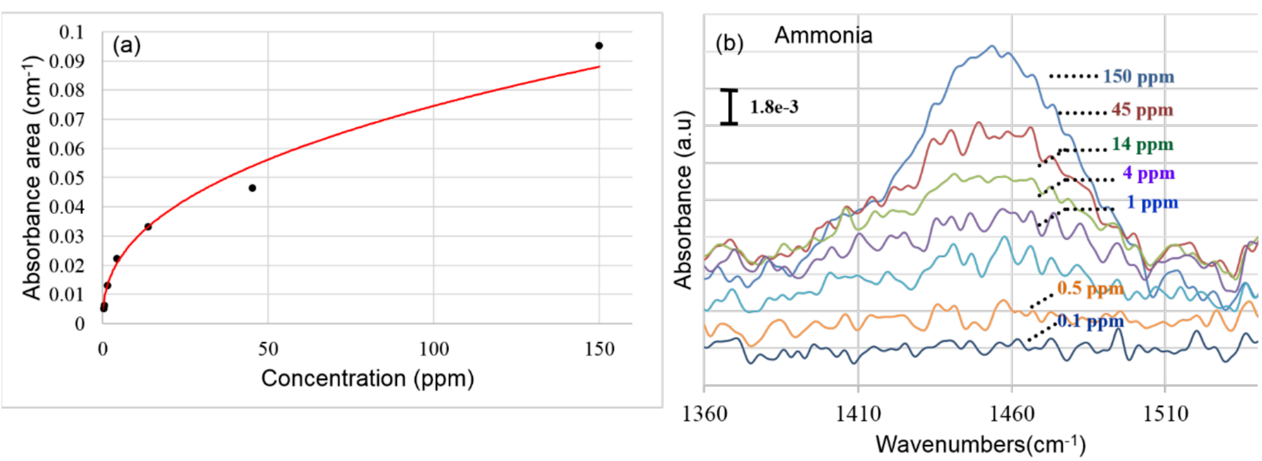

Figure 5: Ammonia calibration curves. (a). Absorbance area as a function of concentration; (b) Absorbance spectra. All data recorded in FEWS mode utilizing multiple internal reflections.

Fig. 6 presents data obtained from nitrite solutions in water. The maximum of the absorbance peak is at 1230cm^{-1}. Here, the data was recorded in single-bounce ATR mode, where the absorption peak can be clearly observed down to concentration of 5ppm. Implementation of the FEWS method in combination with QCL source are presently explored by our team for monitoring of nitrite levels with concentration below 1ppm.

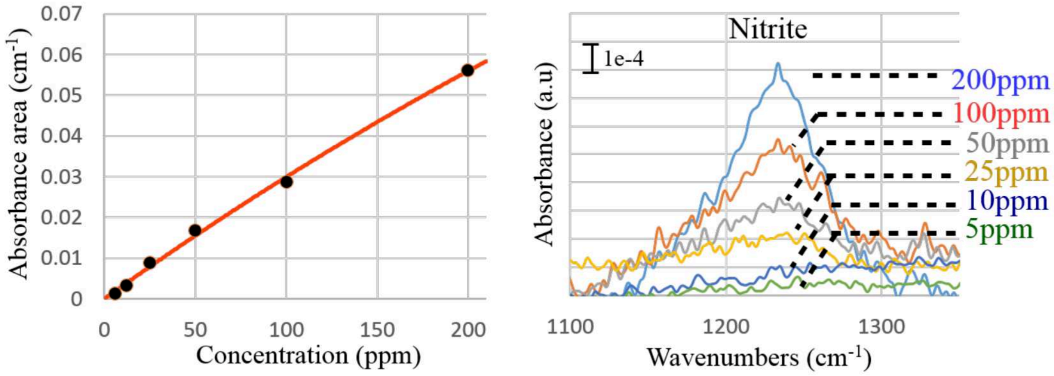

Figure 6: Nitrite calibration curves. (a). Absorbance area as a function of concentration; (b) Absorbance spectra. All data recorded using single-bounce ATR conditions.

2.3 NDIR sensing of nitrate in water

Calibration curves from nitrate, nitrite and ammonia allowed estimation of the maximum absorption peak for further engineering of the QCL-based NDIR system, which is discussed in this section.

Figure 7 presents Max-IR Labs preliminary data obtained from nitrate solutions with varying concentration in NDIR mode. For implementation in onsite septic systems, the nitrate concentration of interest is in the range between 5ppm to 60ppm. Experimental data presented in Figure 7 was obtained during sequential increase of nitrate in the water flowing through the FEWS cell. Initial nitrate concentration was 25ppm. The nitrate concentration was then varied to 35ppm and then to 45ppm, each time resulting is a clear step-form signal response. Increase in the nitrate concentration led to a stronger absorption of the radiation by the nitrate species in the water, resulting in a drop in the observed signal. It can be seen that the optical response is instantaneous, with the integration time/data collection time interval of 1sec.

Future upgrades are aimed on incorporation of nitrite and ammonia monitoring capabilities and increase of the sensitivity that could enable to monitor nitrogen species down to 0.1ppm concentration levels. Field experiments are scheduled at wastewater treatment setting in the near future.

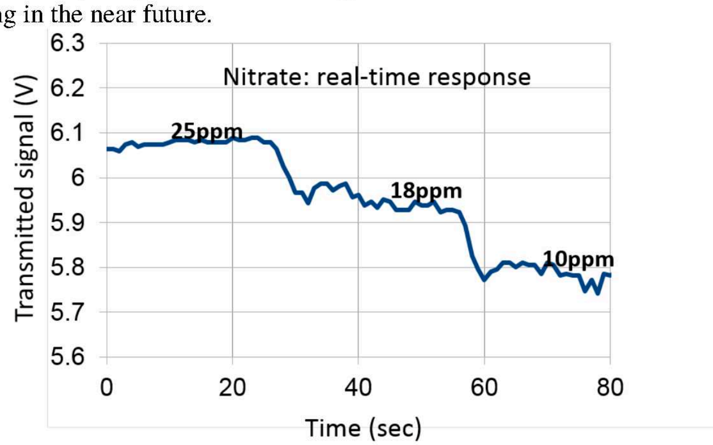

Figure 7 Real-time response of NDIR system to varying nitrate concentration.

2. ACKNOWLEDGEMENTS

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