

Short Communication

Reduction of Nitrate by Iron(II)

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The reduction of nitrate, whether microbiological or chemical, is an important step in the nitrogen cycle.^{4,7,9} Some papers^{2,3} deal with the chemical reduction of nitrate by iron(II) catalyzed by Ag^+ or Cu^{2+} , and other papers^{4,9} deal with the reduction of nitrite by iron(II), but no quantitative information has been published relative to the uncatalyzed rate of reduction of nitrate. Unpublished results by Lind⁸ indicate a disappearance of nitrate ions of approximately 40% at 10 °C in 60

days. These experiments were carried out in stagnant solutions of various iron(II) compounds in buffer solutions at pH=6 or 8.

The present preliminary study was carried out to investigate the uncatalyzed rate of reduction of nitrate by iron(II) at 75 °C.

Experimental. The reaction was carried out in a 500 ml multifunnel glass flask fitted with inlet for nitrogen, outlet for nitrogen through a reflux condenser, thermometer and a septum membrane for sampling by hypodermic syringe. The reaction vessel was immersed in a water reservoir maintained at 75 ± 1 °C.

250–300 ml of a solution of known composition was placed in the reaction vessel in the cold water reservoir, which was heated to the reaction temperature within approximately 30 min. A stream of nitrogen of approximately 3 l/h secured a slight positive pressure and stirring of the liquid. Samples were taken at intervals with a hypodermic syringe.

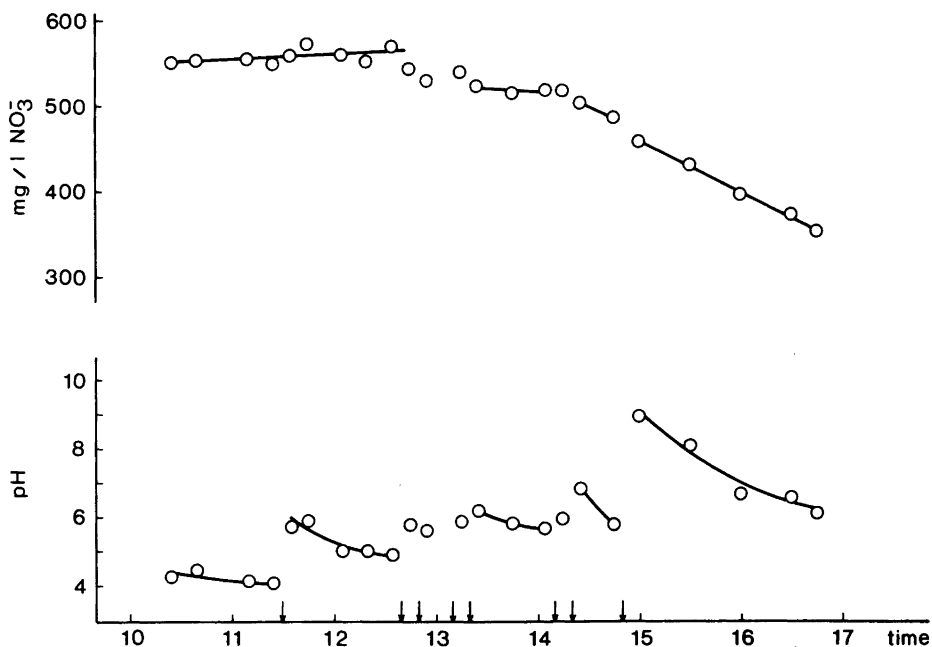


Fig. 1. pH and nitrate content versus time. An arrow indicates addition of NaOH-solution.

pH was adjusted by injections of dilute sodium hydroxide solution.

Reagents. The solution was prepared from boiled ion exchanged water, potassium nitrate (Pharmacocea Danica), and iron(II) sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (*zur Analyse*, Merck)). The nitrogen had a guaranteed maximum content of 1 ppm oxygen.

Measurement of pH. The pH of the samples was measured at room temperature by a standard Radiometer glass electrode.

Measurement of nitrate.* Nitrate was measured by flow injection analysis using a nitrate-ion selective electrode.^{5,10} Before measuring the sample was diluted 10 times with 0.01 M borax buffer solution⁵ and filtered if necessary.

Results and discussion. Preliminary runs showed no discernible reaction in two days at pH=3.8 (measured at 20 °C), but a certain reaction after adjustment of pH to 5.75. During reaction pH decreased, and the reaction stopped.

Fig. 1 shows the results from the main run. The solution contained 0.4209 g KNO_3 and 5.3225 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 500 ml H_2O corresponding to 516 mg/l NO_3^- . The analysis of the fresh solution showed 535 mg/l and the first sample from the reaction vessel showed 550 ml/l. Some water is lost from the solution by evaporation and collects partly as droplets in the (insulated) top of the vessel and in the reflux condenser. pH, originally at 4.0, was gradually raised, and the reaction started at pH=6.0 approximately. The pH referred to is the pH measured in a sample cooled down to room temperature. The pH readings were drifting towards higher values, already at pH=6.0, and increasingly at increasing pH. The readings obtained were the final ones.

Fig. 2 shows the rate of reaction as percent disappearance of NO_3^- per hour versus pH during the corresponding period. The maximum rate of reaction is at around pH=8.

It appears from Fig. 1 that pH decreases during the reduction of NO_3^- , and that the rate of reaction is very low below pH=6 approximately. Precipitation of iron(II) hydroxide also starts at pH=6 approximately.

Reduction of NO_3^- by $\text{Fe}(\text{OH})_2$ to NO_2^- will not change the pH of the solution, and reduction to NO_2 , NO , N_2O , N_2 or NH_3 will correspond to an increase of pH. In these experiments, however, a drop of pH was observed. Also Buresh and

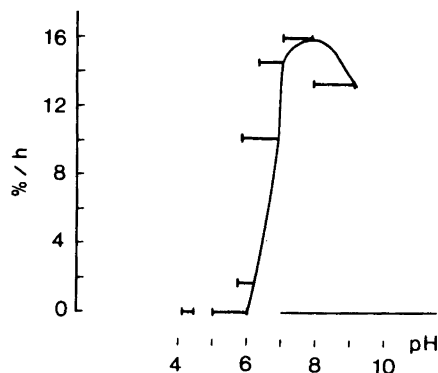


Fig. 2. Rate of disappearance of nitrate versus pH.

Moraghan³ observed a decrease of pH and ascribed this to slow hydroxide precipitation. The slow approach to equilibrium of the precipitation of iron(II) hydroxide is frequently reported in the literature.^{1,6} Buresh and Moraghan³ assume the reducing agent to be $\text{Fe}(\text{OH})_2$ rather than Fe^{2+} .

Another explanation of the drop of pH during the reduction is that the reducing agent is a colloidal $(\text{Fe}(\text{OH})_2)_m \cdot n\text{H}^+$, which is rather more positively charged than the product $(\text{Fe}(\text{OH})_3)_q \cdot r\text{H}^+$. The decline of the rate of reduction at pH above 8 would also be explained by assuming the reducing agent to be a positively charged colloid, $(\text{Fe}(\text{OH})_2)_m \cdot n\text{H}^+$.

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