Influence of sulfite on radiolytic conversion of nitrate and nitrite in dilute aqueous solutions

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Nitrate and nitrite ions are reduced in deaerated diluted aqueous solutions in the presence of sulfite under the action of electron beam.

The removal of inorganic nitrogen compounds (nitrates, nitrites and ammonium ions) from wastewater is an important environmental problem. Such compounds are always present in industrial and municipal wastewater. Their high stability and solubility cause considerable difficulties for their removal by conventional methods of wastewater treatment. However, the environmental standards in many countries require that their residual concentrations in wastewaters were no higher than 10–40 ppm.

It is well known[1,2] that various pollutants can be removed from wastewater by electron-beam treatment. At the same time, the radiolytic decomposition of nitrogen-containing compounds in wastewater is inadequately studied. This work is devoted to the electron-beam removal of nitrates and nitrites at their simultaneous presence in aqueous solutions.

As a rule, the simultaneous presence of nitrates, nitrites and ammonium is characteristic of municipal wastewater after anaerobic biological treatment. In this study, the main attention was paid to the radiolytic conversion of nitrates and nitrites, because their removal causes maximum difficulty in practice. The removal of ammonium ions (in the form of ammonia) is connected with smaller difficulties, because its effective blowing off as a typical stage of aerobic biological treatment is available.

Model solutions were prepared using HNO_3, KNO_3, $NaNO_2$, NH_4OH and Na_2SO_3 of 'extra pure' grade. The optical measurements were carried out on Cary 1E and Specord M-40 spectrophotometers. The analysis for nitrate, nitrite and total nitrogen was performed by standard techniques.[3,4] For the selective determination of nitrites, the Griss reagent and the formation of $K_3[Co(NO_2)_6]$[4] were used.

An ELV-4 electron accelerator (1 MeV electron beam at a nominal beam power of 40 kW) was applied. The beam current was varied within the range 2–40 mA. The solutions were deaerated by bubbling pure nitrogen for 30–45 min or heating at 60–70 °C for 40 min. The solutions were moved through an electron beam as continuous jets with a flow rate of 3 m s^{-1} using a device described in ref. 5. For the removal of volatile nitrogen compounds, the irradiated solutions were kept in a thermostat at 50 °C for 40 min before the analysis. Computer simulation with the use of kinetic data[6–8] and an algorithm[9] was applied to explain the basic radiolysis stages.

On the basis of published data,[10] we can suggest that the removal of nitrate and nitrite from aerated aqueous solutions by electron-beam treatment does not occur at all or proceeds to a very low degree.

The reason for high radiation stability of the test system is an opposite action of oxidising and reducing products of water radiolysis. The main processes causing the removal of nitrate are the reactions with hydrated electrons e^-_{aq} and H atoms:

$$NO_3^- + e^-_{aq} \rightarrow NO_3^{2-} \qquad k = 9.7\times10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \qquad (1)$$
$$NO_3^- + H \rightarrow HNO_3^- \qquad k = 1.4\times10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \qquad (2)$$

OH radicals play an insignificant role in nitrate degradation. Radical anions formed in reactions (1) and (2) cause partial conversion of NO_3^- into NO_2^-:

$$NO_3^{2-} + H_2O \rightarrow NO_2 + 2OH^- \qquad k = 1.0\times10^3 \text{ s}^{-1} \qquad (3)$$
$$HNO_3^- \rightarrow NO_2^{\cdot} + OH^- \qquad k = 2.3\times10^2 \text{ s}^{-1} \qquad (4)$$
$$2NO_2^{\cdot} \rightarrow N_2O_4 \qquad k = 7.6\times10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \qquad (5)$$
$$N_2O_4 + H_2O \rightarrow NO_3^- + NO_2^- + 2H^+ \qquad k = 1.0\times10^3 \text{ s}^{-1} \qquad (6)$$

However, the final conversion of nitrate into nitrite is mainly suppressed by back oxidation by OH radicals. Firstly, OH radicals react rapidly with the formed nitrite:

$$NO_2^- + OH \rightarrow NO_2^{\cdot} + OH^- \qquad k = 1.0\times10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \qquad (7)$$

Secondly, reaction (8) is possible:

$$NO_2^{\cdot} + OH \rightarrow HNO_3 \qquad k = 1.0\times10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \qquad (8)$$

The additional pathway for the back formation of nitrate is the reaction of nitrite with hydrogen peroxide in an acidic medium:

$$NO_2^- + H_2O_2 \rightarrow NO_3^- + H_2O \qquad k = 4.0 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \qquad (9)$$

Hence, the high reactivity of OH radicals towards NO_2 and nitrite ions in a combination with their low reactivity towards nitrate ions is the main obstacle for radiolytic degradation of nitrate.

In the case of nitrite, H atom and e^-_{aq} reduce nitrite:

$$NO_2^- + e^-_{aq} \rightarrow NO_2^{2-} \qquad k = 4.2\times10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \qquad (10)$$
$$NO_2^{2-} + H_2O \rightarrow NO + 2OH^- \qquad k = 1.0\times10^3 \text{ s}^{-1} \qquad (11)$$
$$NO_2^- + H \rightarrow NO + OH^- \qquad k = 7.1\times10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \qquad (12)$$

Note that reactions (7)–(9) can occur in the presence of nitrite.

Nitrogen oxide NO formed in reactions (11) and (12) seems to be the most stable among nitrogen oxides in deaerated solutions.[11] At the same time, the accumulation of NO in irradiated aqueous solutions is inhibited by its fast reactions with OH radicals and nitrogen dioxide with conversion into nitrite:

$$NO + OH \rightarrow HNO_2 \qquad k = 2.0\times10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \qquad (13)$$
$$NO_2^{\cdot} + NO \rightarrow N_2O_3 \qquad k = 1.1\times10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \qquad (14)$$
$$N_2O_3 + H_2O \rightarrow 2NO_2^- + 2H^+ \qquad k = 5.3\times10^2 \text{ s}^{-1} \qquad (15)$$

At high doses, reactions (16) and (17) are possible in nitrate solutions:

$$NO_2 + e^-_{aq} \rightarrow NO_2^- \qquad k = 1.0\times10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \qquad (16)$$
$$NO_2 + H \rightarrow H^+ + NO_2^- \qquad k = 1.0\times10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \qquad (17)$$

They not only promote the accumulation of NO but also interfere with the reformation of nitrate ions.

In aerated solutions, oxygen can participate in the reactions

$$NO_3^{2-} + O_2 \rightarrow NO_3^- + O_2^- \qquad k = 2.0\times10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} \qquad (18)$$
$$NO_2^{2-} + O_2 \rightarrow NO_2^- + O_2^- \qquad (19)$$

and transform H atoms and e^-_{aq} into oxidising species (H_2O_2, HO_2 and O_2^-).

Because of this, we can conclude that the removal of nitrogen compounds upon irradiation of aerated NO_2^- or NO_3^- solutions is almost impossible. Thus, upon irradiation of a 10^{-4} mol dm^{-3} aqueous nitrate solution, its concentration remained unchanged even at a dose of 10 kGy. In turn, the radiolysis of an aqueous nitrite solution is accompanied by the effective conversion into nitrate, and the total removal of compounds is over 4% at doses up to 10 kGy.

It is obvious that, for an increase in the efficiency of removal of nitrate and nitrite, it is necessary to use scavengers (S) of OH radicals under deaerated conditions. It is important that the scavenger should have a low reactivity towards reducing products

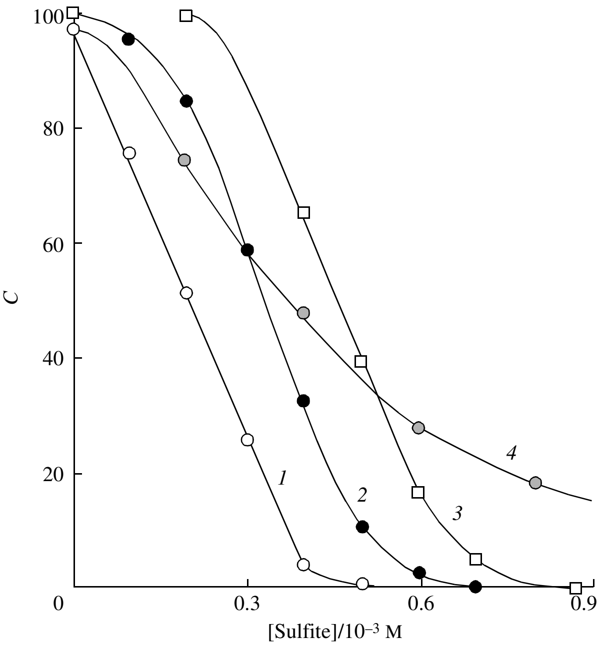

Figure 1 Influence of sulfite concentration on residual nitrate and nitrite content (*C* is the sum of ions, %) in irradiated aqueous solutions with initial concentration: (*1*) 10^{-4} mol dm^{-3} nitrite; (*2*) 5×10^{-5} mol dm^{-3} nitrite and 5×10^{-5} mol dm^{-3} nitrate; (*3*) 10^{-4} mol dm^{-3} nitrate; (*4*) 2×10^{-4} mol dm^{-3} nitrite (dose, 1.5 kGy; pH 7).

of water radiolysis. On the other hand, taking into account the high rate constant of reaction (7), the value $k(\mathrm{OH} + \mathrm{S})\times[\mathrm{S}]$ should be higher at least by a factor of 2–3 than the value $k(\mathrm{OH} + \mathrm{NO_2^-})\times[\mathrm{NO_2^-}]$. Because of this, the sulfite ion can be used as the most suitable scavenger of OH radicals. The final product of its radiolytic conversions is the non-hazardous sulfate ion. The rate constant for reaction of OH radicals with sulfite is high, 1.5×10^9 dm^3 mol^{-1} s^{-1} (near diffusion limit). At the same time, sulfite has a low reactivity towards reducing products of water radiolysis. An additional advantage of sulfite is its high reactivity towards nitrogen dioxide NO_2 ($k = 3.5\times10^7$ dm^3 mol^{-1} s^{-1}).

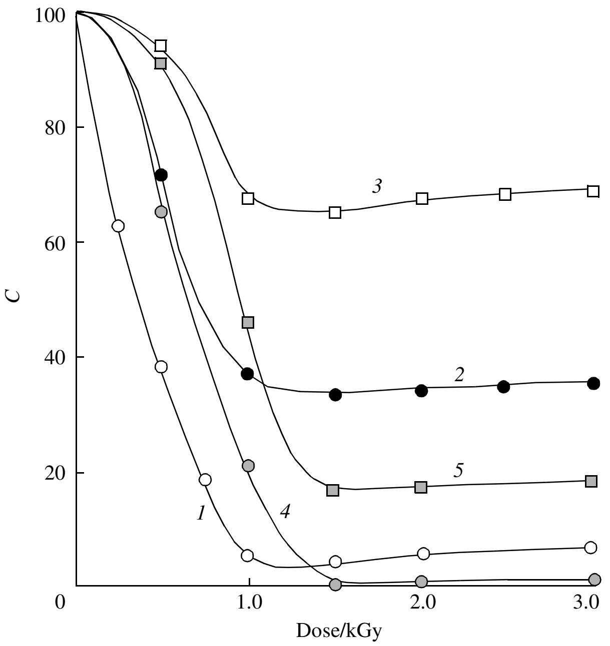

Figure 2 Influence of dose on residual nitrate and nitrite content (*C* is the sum of ions, %) at pH 7 in the presence of (*1*)–(*3*) 4×10^{-4} mol dm^{-3} and (*4*), (*5*) 6×10^{-4} mol dm^{-3} sulfite in aqueous solutions with initial concentration: (*1*) 10^{-4} mol dm^{-3} nitrite; (*2*), (*4*) 5×10^{-5} mol dm^{-3} nitrite and 5×10^{-5} mol dm^{-3} nitrate; (*3*), (*5*) 10^{-4} mol dm^{-3} nitrate.

Figure 1 shows that the presence of sulfite in irradiated solution prevents the system from back radiolytic reactions. The presence of about 5×10^{-4} mol dm^{-3} sulfite provides virtually complete removal of nitrogen-containing compounds at a dose of 1.5 kGy from 10^{-4} mol dm^{-3} (curve *1*) and an about twofold decrease in concentrations of these compounds in a 10^{-4} mol dm^{-3} nitrate solution (curve *3*). The analysis testifies that, under these conditions, the residual compound in nitrate solution (curve *3*) is mainly represented by nitrite (about 86%). The increase in sulfite concentration up to $(8–9)\times10^{-4}$ mol dm^{-3} provides virtually complete removal of nitrogen compounds from all the test solutions at an initial concentration of 10^{-4} mol dm^{-3}. The same amount of sulfite causes 80% removal of the compounds from a 2×10^{-4} mol dm^{-3} nitrite solution (curve *4*).

Figure 1 also shows that the initial presence of nitrate in irradiated solution (curves *2* and *3*) causes a lower sensitivity of the system upon increasing sulfite content. At a low concentration of sulfite [below $(1–2)\times10^{-3}$ mol dm^{-3}], the radiolytic removal of nitrate from solution is virtually absent. However, in the case of nitrite solutions, a noticeable removal of these compounds is observed even at a low sulfite concentration.

As follows from Figure 2, the maximum effect of sulfite additives is observed at comparatively low doses (1–2 kGy). At higher doses, the effect decreases. It is caused by an insufficient amount of the additive. Thus, at a 6×10^{-4} mol dm^{-3} sulfite concentration, the growth of dose from 0.5 to 1.5 kGy results in the effective removal of nitrogen compounds from a 10^{-4} mol dm^{-3} nitrate solution ($G = 0.7$ ion per 100 eV) up to the residual content ~17% (curve *5*). However, at doses over 1.5 kGy the removal of the compounds is not observed. Other way, a slow growth of the residual concentration of nitrogen compounds with dose takes place. A decrease in the sulfite concentration to 4×10^{-4} mol dm^{-3} results in that a limiting degree of nitrate degradation considerably decreases. At a dose of 1.2 kGy, the degree of removal is not lower than 65%. A similar situation is also observed in 10^{-4} mol dm^{-3} nitrate–nitrite solutions. It is obvious that the change in the dose dependence is caused by a deficit of OH scavengers. However, under experimental conditions, an increase in the dose was reached by changing the dose rate, and this fact could have an effect on the observed dose dependence.

The experimental results can be satisfactorily described by computer simulation of a set of the above reactions. Both experimental and calculated data show that, for the removal of comparatively small amounts of nitrogen compounds (~20 ppm of nitrate and nitrite) high doses and high concentrations of added sulfite are required. It is very difficult to say definitely to which compounds nitrate and nitrite degrade upon electron-beam treatment. It is not excluded that such compounds are N_2 and N_2O. These compounds were detected as radiolysis products of aqueous nitrate–acetate solutions.[12]

Therefore, the radiolytic degradation of nitrate and nitrite in aqueous solutions can be carried out in the presence of effective scavengers of OH radicals. A maximum effect was observed when the $k(\mathrm{OH} + \mathrm{S})\times[\mathrm{S}]$ value was higher than $k(\mathrm{OH} + \mathrm{NO_2^-})\times[\mathrm{NO_2^-}]$ value by a factor of 2–3. The most suitable scavenger is sulfite. Anaerobic conditions are preferable for the radiolytic degradation of nitrate and nitrite.

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