

Photocatalytic Oxidation of Nitrite in Water to Nitrate

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ABSTRACT

It is found that the nitrite in water is converted into nitrate by irradiation in the presence of oxygen and titanium dioxide which acts as a catalyst. As nitrate is a less hazardous contaminant, this method might be worth investigating further for the treatment of water.

INTRODUCTION

It is well known that nitrite in water could lead to the formation of *N*-nitroso compounds by its interaction with body fluids, foodstuffs or other organic materials susceptible to nitrosation (Austin, 1960; Bogovski & Walker, 1974; Keefer & Roller, 1973). At very low dose levels *N*-nitrosoamines are found to induce cancer in experimental animals (Lijinsky & Epstein, 1970; Magee & Barnes, 1967). There is also indirect evidence to suspect that nitrosoamines cause cancer in man (Cook, 1971; Hawksworth *et al.*, 1974). Drinking water in some localities is contaminated with nitrite as a result of heavy use of nitrogenous fertiliser or leaching from sewage (Hawksworth *et al.*, 1974). The bacterial action on fertiliser or organic matter generates nitrites. Consequently, the development of methods for removal of nitrites from drinking water is extremely important.

Recently, the photochemical methods for decontamination of water have received a great deal of attention (Ahmed & Ollis, 1984; Matthews, 1986;

Oliver *et al.*, 1987). It has been found that organic matter and agrochemical contaminants in water can be completely mineralised by irradiation with sunlight in the presence of semiconductor photocatalysts, such as TiO_2 (Barbeni *et al.*, 1984; Matthews, 1986). We have found that nitrite in water can be converted to less hazardous nitrate by the same method. When an aerated aqueous solution of nitrite containing TiO_2 is irradiated, the nitrite is rapidly oxidised to the nitrate.

EXPERIMENTAL

The photocatalyst generally used in water decontamination studies is titanium dioxide. The suitability of this material depends on its complete inertness, its insolubility in water, and its efficient catalytic activity. In all experiments, Aldrich 99.9% TiO_2 was used without further purification. As the catalytic activity depends on the particle size, the particle size distribution was determined with a particle size counter (Horiba Capa 700). The average particle size was found to be $0.65 \mu\text{m}$ and the size distribution is presented in Fig. 1. Water used in all experiments was double distilled. Potassium nitrite was used as the nitrite source and the initial NO_2^- concentration in most experiments was 10^{-4}M . Nitrite was determined by the azo dye method (Canney *et al.*, 1974).

The photolysis experiments were carried out in a double-walled photochemical reactor (Applied Photophysics) thermostatted by circulating

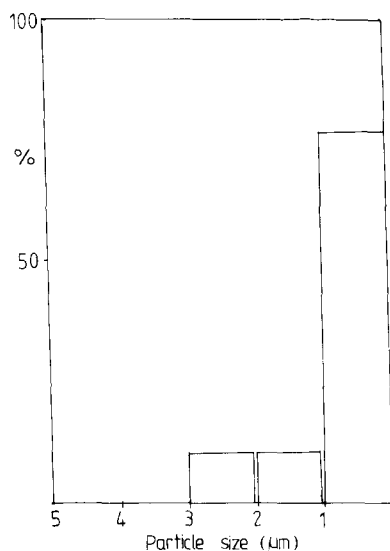


Fig. 1. Size distribution of titanium dioxide particles.

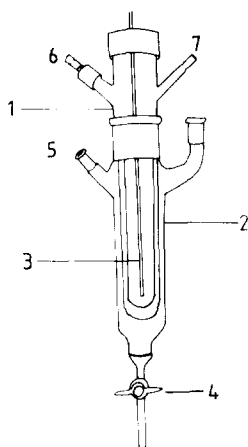


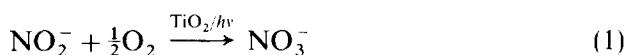
Fig. 2. Photochemical reactor: (1) quartz immersion well, (2) reaction flask, (3) mercury lamp, (4) gas inlet, (5) gas outlet, (6) water in, (7) water out.

water. The light source was a 450-W medium-pressure mercury lamp mounted at the central axis of the reactor (Fig. 2). Purified air, passed successively through wash bottles containing chromic acid, NaOH and water (to remove organic matter, nitric oxides and the spray), was bubbled through the solution at a rate of 550 ml min^{-1} . The temperature of the reaction mixture was varied by changing the temperature of the circulating water. At different intervals during the process of photolysis, aliquots of solution were drawn from the reactor, TiO_2 was removed by centrifuging and the solution estimated for NO_2^- by the azo dye method.

The nitrite concentration was found to decrease rapidly with time. The increase in the nitrate concentration was detected by the cadmium reduction method (Canney *et al.*, 1974).

RESULTS AND DISCUSSION

The decrease in the NO_2^- concentration with the progress of photolysis is presented in Fig. 3. It is seen that the rate of the reaction increases with the increase of pH. The reaction rate was also found to depend on the quantity of catalyst used (Fig. 4). The overall reaction occurring can be written as



Thus, if the O_2 concentration remains constant (i.e. when the purging is rapid), nitrite concentration will decrease with time according to

$$[\text{NO}_2^-] = [\text{NO}_2^-]_0 e^{-kt} \quad (2)$$

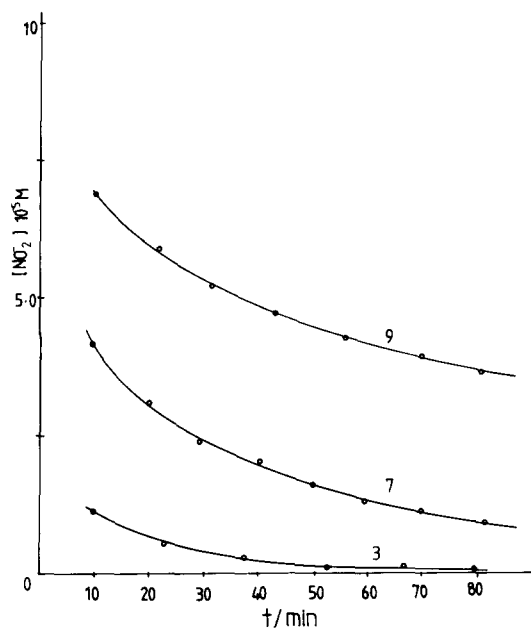


Fig. 3. Plot of NO_3^- concentration versus time. The numbers indicated near each curve are the pH values. (TiO_2 concentration = 0.3 g litre^{-1} , temperature = 25°C .)

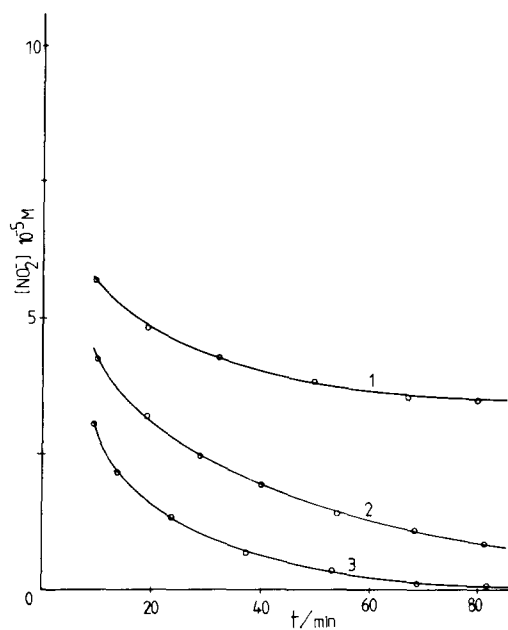


Fig. 4. Plot of NO_2^- concentration versus time at different concentrations of the catalyst: (1) $0.15 \text{ g litre}^{-1}$, (2) $0.30 \text{ g litre}^{-1}$, (3) $0.60 \text{ g litre}^{-1}$. (pH = 7, temperature = 25°C .)

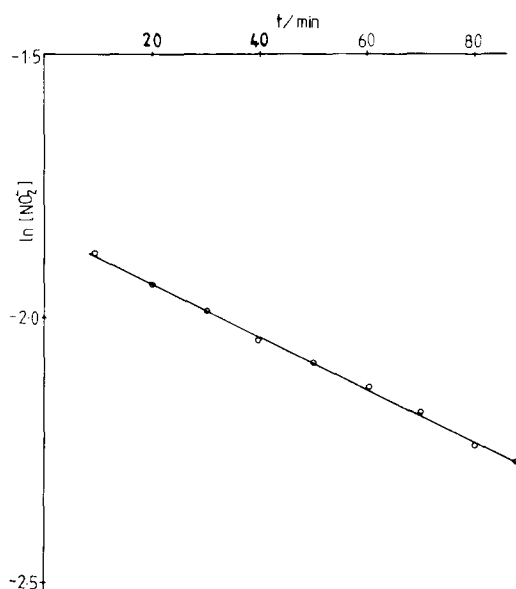


Fig. 5. A plot of $\ln [\text{NO}_2^-]$ versus time. (pH = 7, temperature = 25°C, TiO_2 concentration = 0.3 g litre⁻¹.)

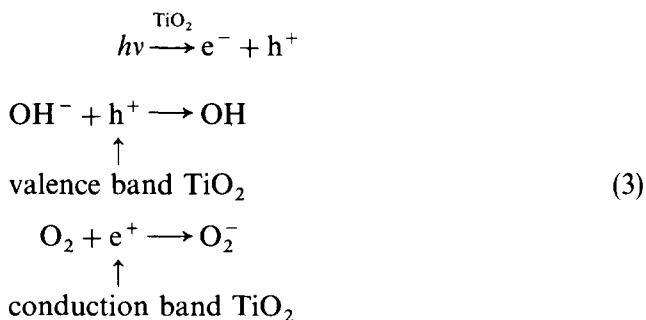
where k is the rate constant. The plot of $\ln [\text{NO}_2^-]$ against time was found to fit into a straight line (Fig. 5), and the values of the rate constants at different concentrations of the catalyst and different pHs are given in the Table 1.

The initial step in the photo-oxidation process of this reaction is believed to be the formation of free hydroxyl radicals generated by transfer of positive charges from the valence band of the semiconductor to OH^- ions, with concomitant transfer of conduction band electrons to molecular oxygen (Matthews, 1986). The photons absorbed by the semiconductor

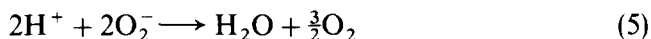
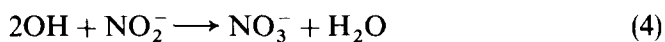
TABLE 1
The Values of the Rate Constant at Different pHs
and Concentrations (C) of the Catalyst

$K \text{ min}^{-1}$	pH	$C \text{ g litre}^{-1}$
0.0013	7	0.15
0.0045	7	0.30
0.0083	7	0.60
0.0083	3.2	0.30
0.0014	9.2	0.30

particles create the necessary electron-hole pairs, i.e.



The hydroxyl free radicals oxidise nitrite to nitrate while electrons from O_2^- are donated to H^+ ions, i.e.



The reaction step (4) explains our observation that an increase of pH favours the oxidation of nitrite to nitrate.

CONCLUSION

The above experiment clearly demonstrates that nitrite in water can be converted into less hazardous nitrate by a simple photochemical method using sunlight. However, as the percentage of UV light that sensitises TiO_2 (i.e. wavelength $\sim 370\text{ nm}$) is smaller in sunlight than from a UV lamp, irradiation for a longer interval of time would be necessary. In a separate experiment we have noted that a nitrite concentration of 10^{-4} M can be converted to nitrate by exposure to sunlight (intensity $\sim 750\text{ W m}^{-2}$) for $\sim 6\text{ h}$ (TiO_2 concentration $= 0.3\text{ g litre}^{-1}$). Eventually methods will have to be developed for the removal of nitrate from water. The above photochemical method might be worth investigating further as the first step in a process for the removal of nitrite and nitrate from drinking water.

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