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EFFECT OF OZONE ON YELLOW SUBSTANCES ACCUMULATED IN A RECYCLING SYSTEM FOR FISH CULTURE

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ABSTRACT: Yellow substances accumulating in fish culture recycling systems are highly resistent to biological oxidation. By-pass ozonization was applied to oxidize these substances, which include long-chained molecules, such as melanoids, which mainly consists of amino acids and reduced sugars. Their absorption maximum was determined at 315 nm. In a small experimental recycling system (8.2 m^3 volume; 45 kg fish load), short term ozonation (2-8 hrs) resulted in an effective color removal.

INTRODUCTION

During recent years interest in utilization of ozone in water recycling systems has increased considerably. Although ozone application for drinking-water sterilization has been put into practice for more than half a century in many countries (FRISON, 1950; BERGER, 1958; CAMPBELL, 1963; CHERVINSKY and TRAHTMAN, 1972), ozone treatment of waste water with high organic loads has been tried in only a few cases (GARDINER and MONTGOMERY, 1968; BAUCH and BURCHARD, 1970; BEAR, 1970; HUTCHINSON *et al.*, 1975). Some results of these investigations indicate that rapid oxidation of nitrite can be achieved quantitatively and many organic substances not easily digested by biological filters can be degredated to a considerable extent. Among these, yellow substances are those which will accumulate rapidly in almost all recycling systems.

Aquaculturists tend to reject ozone as a means of water treatment in fish-culture systems because of its wellknown high toxicity (HUBBS, 1930). However, ozonation is a standard treatment technique utilized by aquarium hobbyists (SANDER, 1970). SCHLESNER (1973) has shown that ozonation of water containing high organic loads does not result in complete sterilization, but still allows sufficient bacterial growth for efficient biological filtration. During recent years, ozone has been successfully applied in sea water recycling systems (ROSENTHAL and SANDER, 1975, SANDER and ROSENTHAL, 1975; ROSENTHAL and WESTERNHAGEN, 1976). Fish-culture recycling systems using activated sludge as a biological filter showed a tremendous accumulation of yellow substances. As known from the literature, ozonation is one method for color removal in waste water (NEBEL et al., 1975). In many waterworks humus color reduction of up to 58 % has been attained with an ozone dose of 3.2 mg O_3/l (SAMDAL, 1966, GJESSING, 1976). For practical reasons it was considered to be of interest to investigate the effect of ozone on yellow substances accumulated in a fish culture recycling system.

MATERIAL AND METHODS

Experimental ozonation was performed in a freshwater recycling system in which a large amount ofyellow substances had already accumulated. The system had a total volume of 8.2 m^3. The capacity of the fish tanks amounts to o.9 m^3, which is equivalent to 11 % of the total water volume. The biological filter system consists of an activated sludge unit (2.2 m^3), a settling tank of 1.2 m^3 and two denitrification units (1.2 m^3 each). The system has been operating on a steady-state basis for several months prior to the

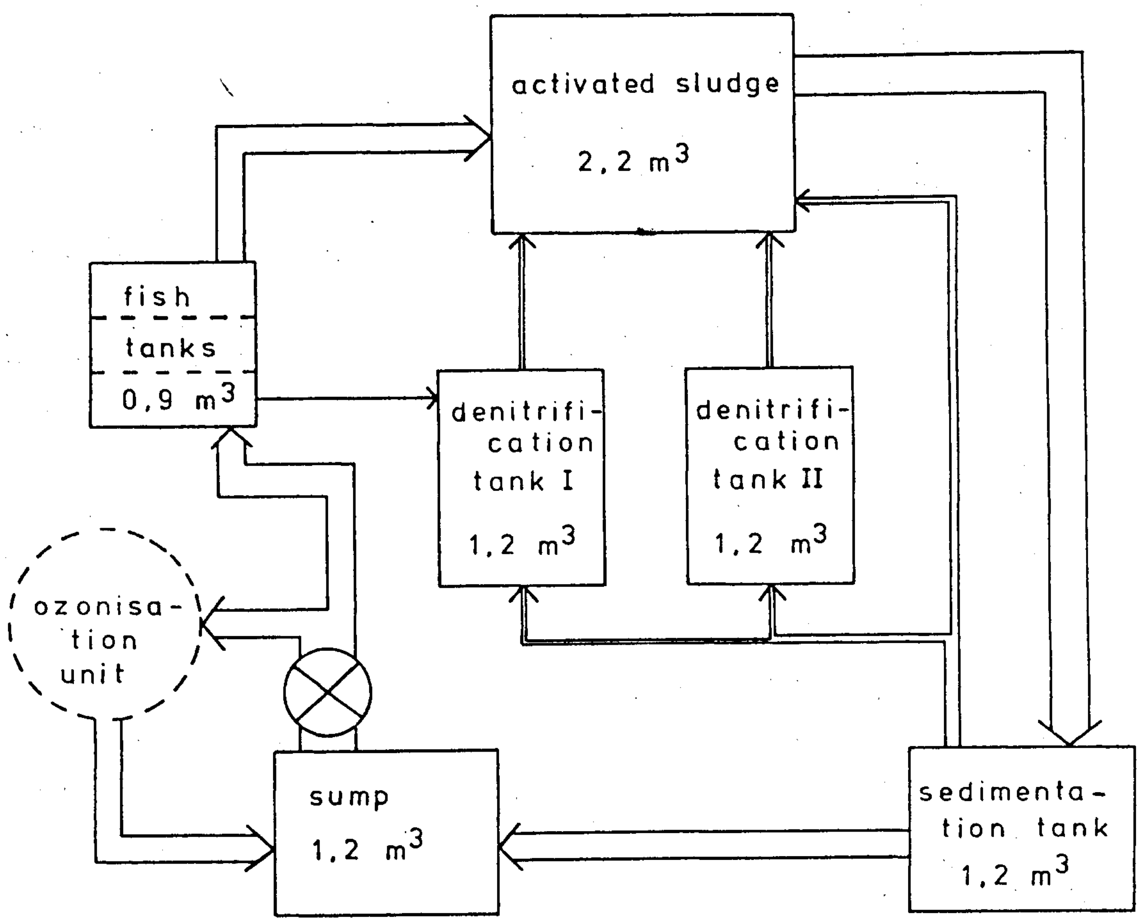

Fig. 1: General design of the fish-culture recycling system using biological filtration and by-pass ozonation. The width of the arrows indicate relativ water flow rates.

beginning of the ozonation experiment. During the ozonation experiment the denitrification unit was not operating. Fig. 1 depicts the general layout of the recycling unit. During the experimental period of 30 days the total fish load averaged about 45 kg wet weight of common carp (Cyprinus carpio L.). Therefore, thefish-water ratio in the fish tank and in the total system accounted for 1:20 and 1:180, respectively.

Ozone was added to the system in two different operational strategies. During the first part of the experimental period ozone was introduced to the system in a by-pass to the biological filter at a rate of 10 g/h for only an 8 hour period, beginning in the morning hours, immediately after the first feeding of the fish. The system then was allowed to readjust itself to conditions prior to ozone application for one week (biological filtration only). Then, ozonation was repeated. In a second series of ozonation trials ozone was applied for a 1-2 hour period per day, in order to reach steady-state conditions. At the end of the experimental period (day 28) the denitrification unit had been restarted by continuous addition of sugar solution.

For measuring the yellowish color, water samples were filtered through 0.22 micron membrane filter in order to remove turbidity. The absorbance of the samples was measured at 315 nm (Perkin-Elmer spectrophotometer Type 124, Wolfram-lamp), using destilled water as a blank.

Chemical analysis of the following parameters has been carried out on a daily basis except for weekends: NO_2^-, NO_3^-, NH_4^+, and pH.

RESULTS

Figure 2 demonstrates the absorption spectrum observed in filtered water of the recycling system, indicating a peak at 315 nm. This observation shows clearly that these yellow substances do not consist mainly of aquatic humus, which can be measured according to GJESSING,(1976) at an absorbance of 430 nm against a platinum cobalt standard, although humus itself has no absorption maximum in the visible wavelength range. For the purpose of this study it has been assumed that the height of the observed peak is related to the concentration of these color-causing substances, which have not yet been identified. According to BEER-LAMBERTs-law, the light

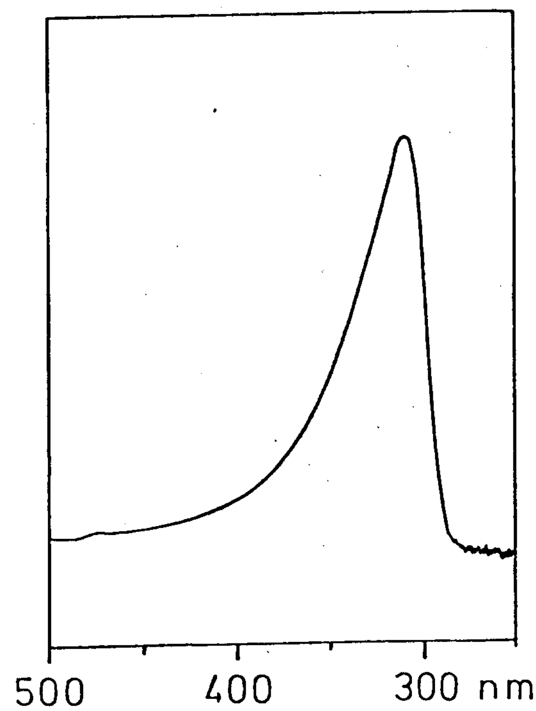

Fig. 2: Typical shape of the extinction curve of a filtered water sample (absorbance maximum at 315 nm)

absorption is proportional to the number of molecules of absorbing material through which light passes.

As can be seen from figure 3, by-pass ozonation over an 8 hour period results in a continuos decrease of the observed peaks, indicating a rapid oxidation of the color causing substances. Regardless of the initial concentration of yellow substances, the differences in the peaks of absorbance between the inlet and outlet of the ozonation unit are almost the same. Nevertheless, a slight increase in the efficiency of color removal with decreasing initial concentration of the yellow substances has been obtained, when calculating the percentage reduction of the absorbance for each 8 hour ozonation period seperately. These data are listed in Table 1.

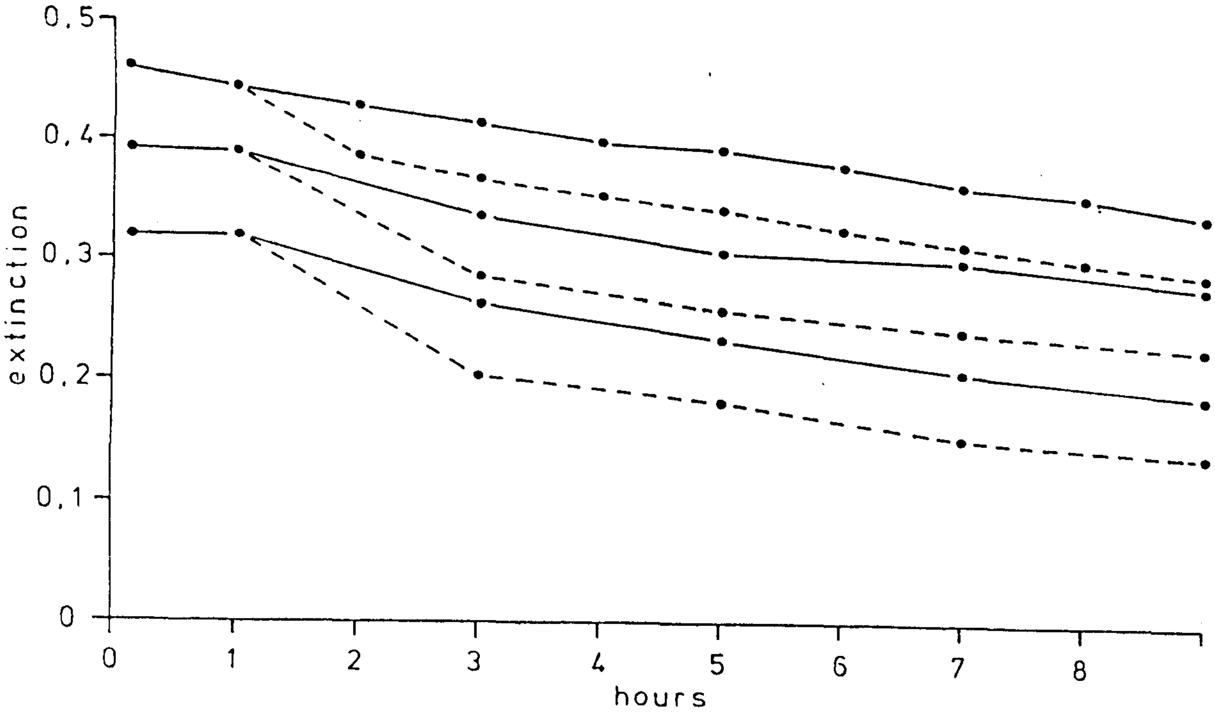

Fig. 3: Absorbance peaks (extinction) of filtered water taken at hourly intervals during ozonation at the inlet (solid line) and outlet (hatched line) of the ozonation unit

Table 1: Efficieny of color removal over an 8 hour ozonation period in relation to the initial concentration of yellow substances.

Trial	extinction at 315 nm		reduction of color
	prior to ozonation	after 8 h ozonation	(%/h)
A	0.46	0.34	3.2
B	0.39	0.28	3.5
C	0.32	0.19	5.1

The same trend had been observed more distinctly within one ozonation period of 8 hours, when measuring the absorbance between inlet and outlet of the ozonation unit in hourly intervals (Fig. 4). The increased efficiency of color removal (Table 1; Fig. 4) with decreasing initial concentration of yellow substances is not unexpected. By always applying the same amount of ozone per volume water treated (4.7 mg/l), a larger portion of the remaining amount of yellow substances can be oxidized during each cycle.

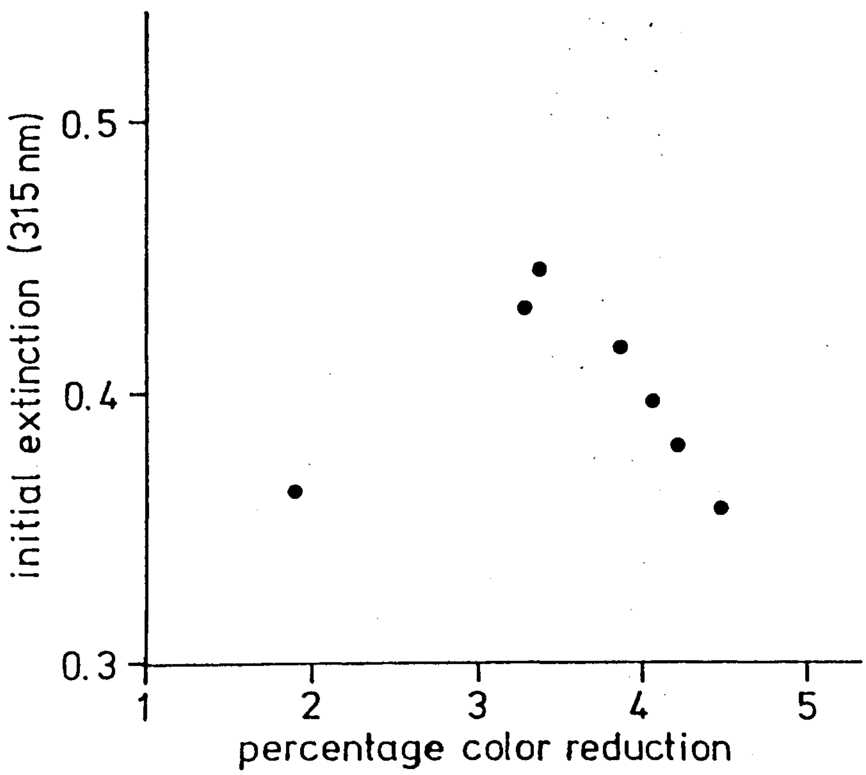

Fig. 4: Percentage color removal during 1 hour ozonation in relation to initial concentration of yellow substances.

Fig. 5 indicates the overall changes in color removal and pH reduction. Immediately after each ozonation trial the concentration of yellow substances increased drastically at the outlet of the ozonation unit, due to the rapid dilution of the treated water with the total of the system. Accumulation rates of these

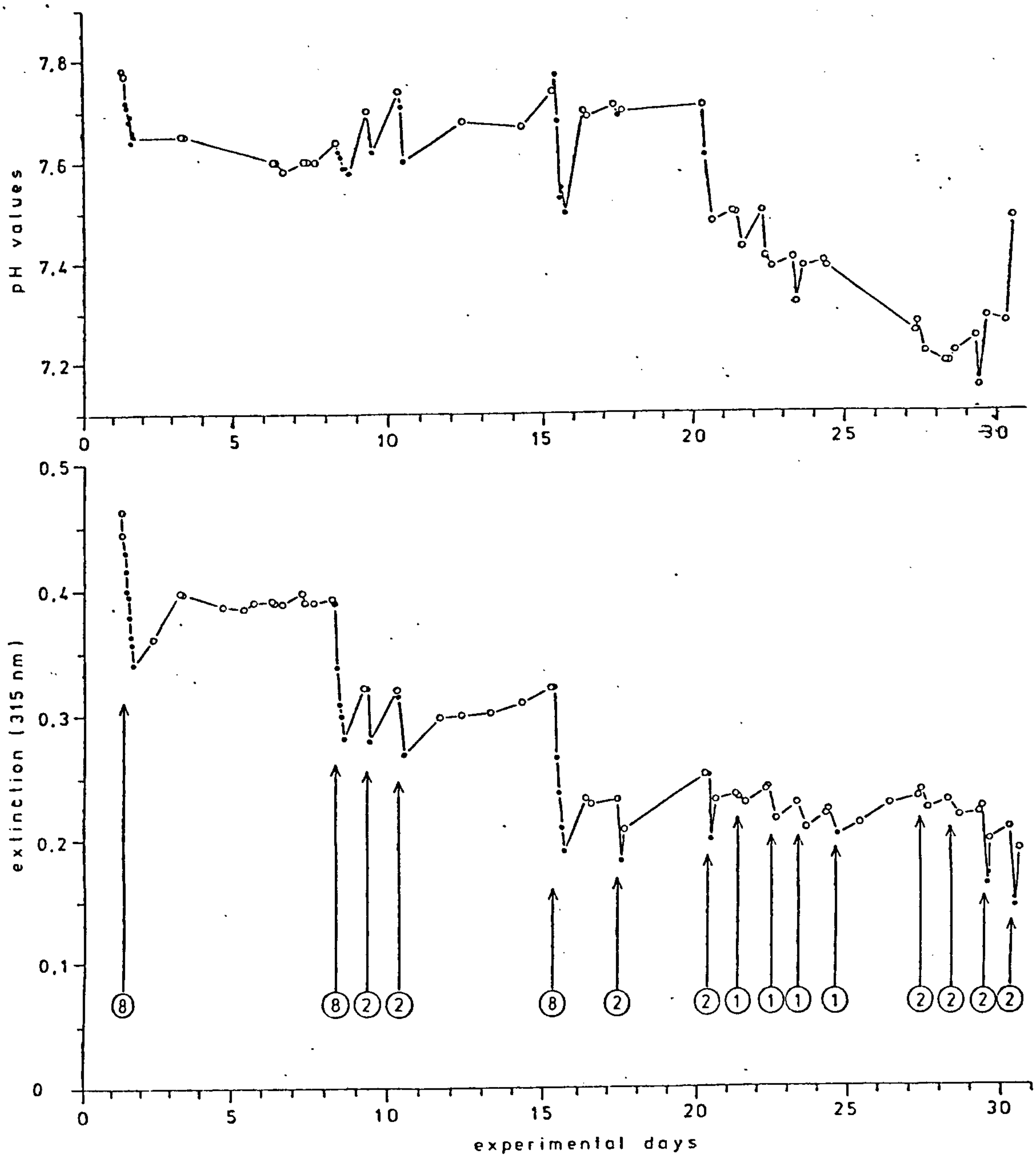

Fig. 5: Effect of by-pass ozonation on the concentration of yellow substances and pH-values of a fish-culture recycling system. Open circles: data represent the daily average of samples at times without ozonation. Solid circles: data obtained from samples taken during ozonation. Encircled numbers indicate hours of ozonation. Absorbance is given in arbitrary units.

substances are slow. During the period between the first two ozone treatments (day 2-8), the extinction peaks observed rose from 0.341 to 0.393, which is equivalent to an increase of 2 % per day. The total amount of yellow substances added daily via feeds to the system remained the same, but a higher accumulation rate occurs, because the total content has been substantially reduced due to ozonation. Therefore between the second and third ozonation period (day 11-15) daily acccumulation rates reached about 4 %.

Compared to the concentration of yellow subatances prior to the first ozonation treatment, the three suceeding 8 hour ozonation periods restulted in a total reduction of the extinction peaks by at first 26 %, then 28.5 % and finally 40.8 % (Fig. 5). When ozone was applied in shorter intervals for shorter periods (1-4 hrs) the extinction values were kept down to about 40-50 % of the initial values.

Nitrogen compunds in solution, such as NO_3^--N, NO_2^--N and NH_4^+-N, did not change significantly during the experimental period, except for an initial slight decrease in ammonia and nitrite after the first ozonation period (Fig. 6). From earlier experimental data anddfrom the literature it is well known that these values vary considerably during the day under standard operational procedures (see also PAGE and ANDREWS, 1974). The steady increase of the nitrate concentration in the system has to be attributed to the fact that we did not operate the denitrification unit between day 2 and 28. The general reduction in pH values during the same period might be related in part to this increase in nitrate, but also partly caused by ozonation.

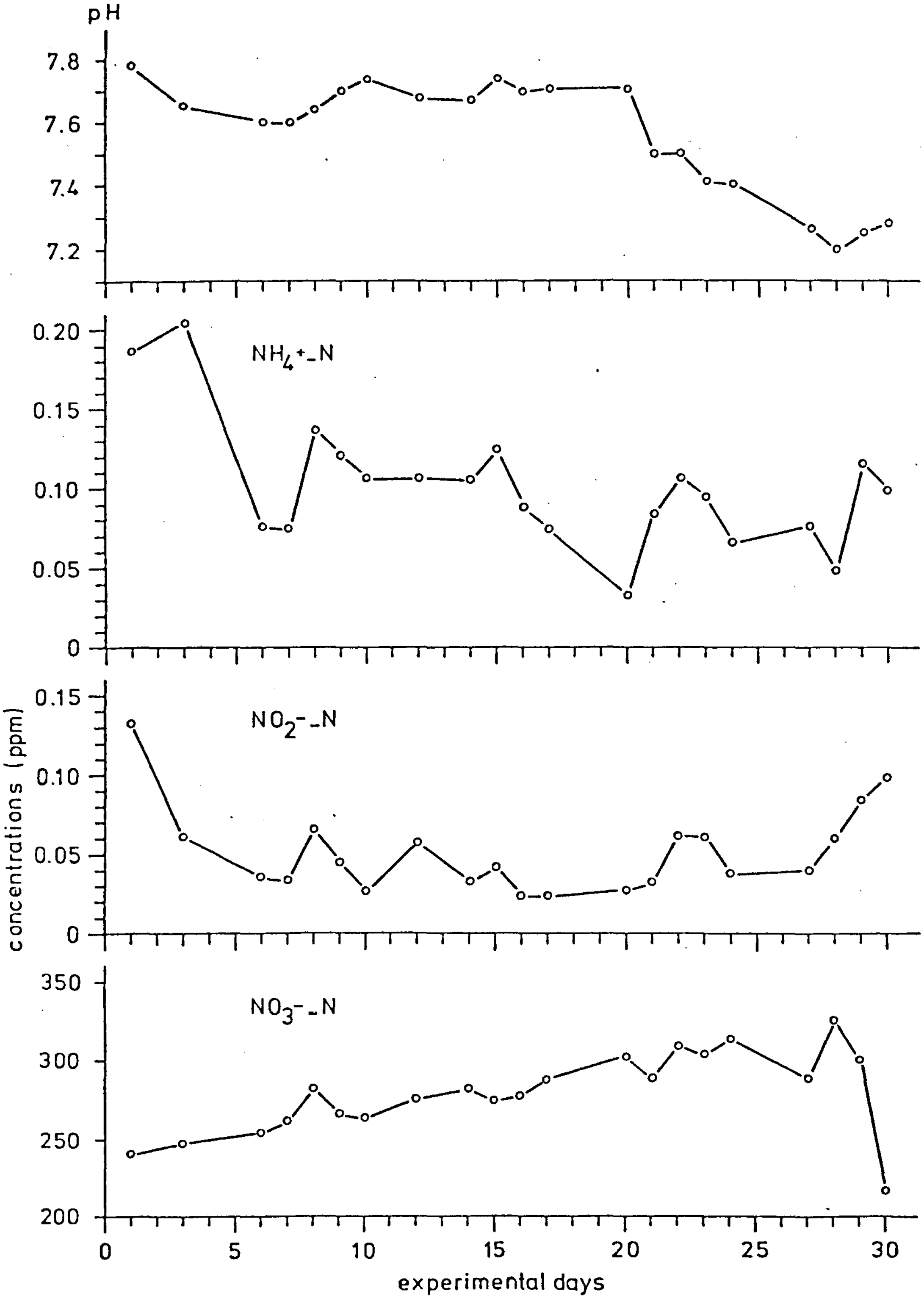

Fig. 6: Fluctuations of some nitrogen compunds and pH values in a fish-culture recycling system. Data obtained from samples taken during morning hours from the fish tank inlet, prior to feeding.

DISCUSSION

Yellow substances accumulated in aquaculture recycling systems have so far not been analysed. Although their optical properties are not identical to those of humic acids of natural waters, the resistance against bacterial degradation seems to be similar. Our experiments indicate that these substances originate from biological decomposition of feed pellets. The wave-lenght of maximum absorption of color is not always identical, but can vary within samples, depending on the kind of feed used. From the optical and chemical properties known so far, it is believed that these yellow substances include melanoids, that means long chained molecules, mainly consisting of amino acids and reduced sugars which are highly inert to biological filtration. They are oxidized efficiently only by strong oxidants, such as ozone.

The observed peaks at 315 nm are obtained from filtered samples. The filtration may have eliminated the influence of colored particles. The choice of method for determining color removal may not have been the best but was by far the simplest way. In practice it is difficult to measure with the same accuracy throughout any experiment. Short-term sample storage might have influenced the color, and, as most colored waters are only weakly buffered, changes in absorption maximum may also have been caused by slight pH changes.

The decrease in pH values during ozonation is not easy to explain. Other observations reported in the literature indicate that ozonation tends to shift the pH towards the neutral point (KIRK et al., 1972).

How much ozone is needed to keep the total amount of yellow substances down to appreciable low vaulues? From our data, an average accumulation rate of 4.2 % per day of the initial concentration has been calculated under present operational conditions (i.g. fish load, feeding level). At a flow rate of

1600 l/h through the ozonation tower, a reduction of yellow substances by 8.4 % was reached within 1 hour, when ozone was applied at a concentration of 4.7 mg/l. Thus, a total amount of about 3.8 g O_3, equivalent to a 30 minutes ozonation treatment, is necessary to destroy the daily production of color causing substances.

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