

Study on Property of Gel-embedded Nitrobacteria Carrier and Its Application in Treating Urban Sewage

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Abstract: The diffusion behavior□mechanical performance□activation and biological property of gel-embedded nitrobacteria carrier LQ-1 were measured, and its application in the treatment of urban sewage was studied by pilot experiment. The results show that the interpenetrating holing-through structure (about 5μm) is formed in the immobilized nitrifying bacteria carrier. When the compression rate is 85% □the compressive stress reaches 0.49 MPa. More than 95% of the diffusion process can be completed in 10 minutes. The optimal activation time of immobilized carrier is 13d under suitable temperature, and a higher biological activity can be achieved after activation at low temperature (<10°C). Reducing the microbial content, the property of carrier above can still be obtained. The activation time of gel-embedded nitrobacteria carrier in pilot experiment is no more than 11d, and the system can achieve qualified operation at low sludge concentration. The effluent concentration of NH₃-N is below 1 mg/L with removal rate more than 99% by using the activated carrier under conditions as temperature 13~15°C, influent loading 72.5 m³/d (1.45 times of design value), adding ratio of carrier 12%, Do about 5 mg/L, which reveal that carrier is conducive to the upgrading and reconstruction of municipal wastewater treatment plant.

Introduction

Scarcity of water resources and deterioration of water environment have now become the bottleneck of the sustainable development of society. With the wastewater discharge standard increased gradually in the 12th five-year period, most of municipal sewage treatment plants have to upgrade and reconstruct. Statistics showed that only 6% of the municipal sewage treatment plants can meet the first grade A standards of Urban Sewage Disposal Plant Contamination Integrated Discharge Standard of China (GB 18918-2002). One of the most important reasons for this situation is the low NH₃-N removal efficiency in winter.

Immobilized microorganism technology, which provides a simple, economical and efficient solution for the problem above, attracted widely attention in recent years. Immobilized microorganism represents a kind of technology that locates the free microbes or enzymes into a limited apace and keeps their reusable activity through specific chemical or physical methods, so that the concentration, purity, efficiency and stability of microorganism in bioreactor can be

increased. When it was used in the treatment of wastewater, it can realize the separation of sludge retention time (SRT) and hydraulic retention time (HRT) in the reactor, in which the efficient and stable removal of COD, NH₃-N and TP could be reached without expanding the volume of reactor. Therefore, immobilized microorganism technology is considered as a kind of efficient, energy-saving, easily-operated and promising technology for wastewater treatment. Generally, immobilized microorganism technology has four forms such as adsorption method, bonding method, cross linking method and embedding method. Among them, the embedding method has been researched and used widely for its better comprehensive performance [1-3]. Nevertheless, as the mechanical property, chemical stability and manufacturing cost of embedding carrier are still unsolved, most researches still stayed in the laboratory stage and the large-scale production and engineering application hadn't be achieved.

The comprehensive structural analysis and performance investigation of LQ-1, a kind of gel-embedding nitrobacterium carrier prepared by Sound Group co., LTD, were studied in this paper. Furthermore, LQ-1 was used to treat municipal sewage in the A/O activated sludge system, in which the starting and operating conditions of LQ-1 in low temperature were tested, so that to provide the technology reference and engineering experience for enhancing the removal efficiency of NH₃-N by activated sludge system in urban sewage treatment plant under the condition of low temperature.

Materials and methods

Nitrobacterium carrier LQ-1: made in laboratory, Synthesis process was shown in figure 1 and synthesis method followed the references [4-5].

Biological performance testing device: reactor with effective volume 2L was made in laboratory using PVC material.

Super fine screen: rotating filter net with aperture 200 meshes was self-prepared.

Pilot bioreactor: reactor with volume of 3.6m×1.45m×2.9m (effective height 2.4m) was prepared using carbon steel material, it was divided to anoxic zone and aerobic zone with effective volume of 4.4m³ and 8.8 m³, respectively, and the design influent loading was 50m³/d.

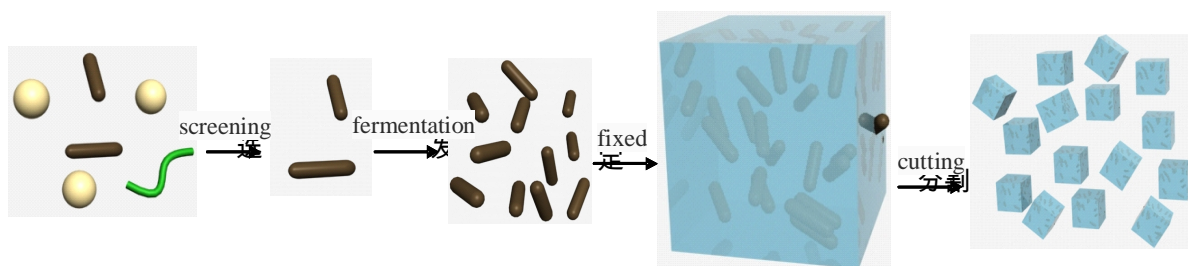


Fig.1. Synthesis process of nitrobacterium carrier LQ-1

Mechanical Property Test. Compression strength: cylindrical carrier were tested in the universal material testing machine with method followed GB/T 8813-2008.

Compression ratio: compression ratio (relative deformation, %) = $(H_0 - H_1) / H_0$, where H_0 and H_1 means the uncompressed thickness and compressed thickness, respectively.

Chloride ion diffusion experiment: a certain volume of carrier was put into solution of sodium chloride with certain concentration. Diffusion finished as the concentration of chloride ion reached equilibrium.

Scanning Electron Microscope: model of the instrument was FEI Quanta200ESEM, Peltier refrigeration, tested at 2°C, 500 Pa and 30 kV acceleration voltage [6].

Biological property test. Parallel tests of sequential batch experiment were carried out in a reactor with effective volume of 2L in which a percentage of embedding carrier and $\text{NH}_3\text{-N}$ wastewater prepared in laboratory or domestic wastewater were added. DO was kept between 2 and 6 mg/L. Activation performance under different temperatures was tested and then the activated carrier were transferred to different ambient temperatures to test its ability of removing $\text{NH}_3\text{-N}$.

Pilot experiment. The main treatment process of the experiment was shown in Fig.2. The wastewater from primary sedimentation tank was pumped into the super fine screen (a rotating filter net) to catch impurities with size over 2mm such as particle, floats, hair and fiber. Then the effluent was pumped into the anoxic zone where TN was removed by denitrifying bacteria. The mixture flowed to aerobic zones where COD and $\text{NH}_3\text{-N}$ were removed. The effluent from aerobic zones flowed to secondary sedimentation tank to separate sludge with water of the mixed liquor. Supernatant solution was discharged. Part of sludge at the bottom of secondary sedimentation tank flowed back and excess sludge was discharged.

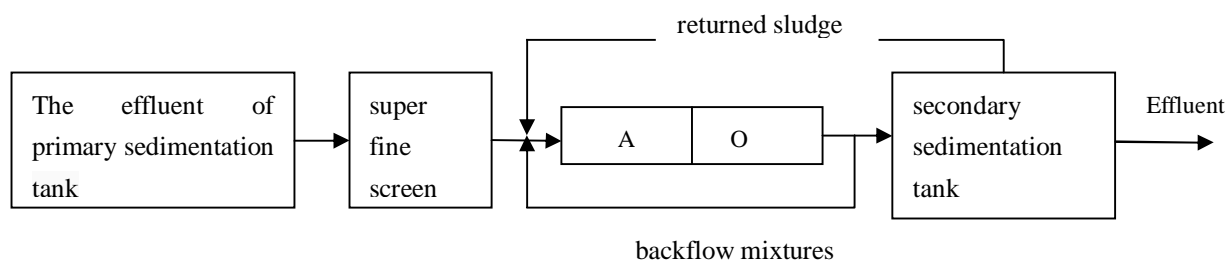


Fig.2 Technical flow process diagram

Results and Discussion

LQ-1 is a kind of cube-like water gel with side length of 3mm, milky white or light gray, translucent, highly elastic, with density as 1.02 g/cm^3 .

Physical property. The diffusion behavior, compression strength and micro pore structure were tested for they are the most critical parameters on effect and performance of carrier in the engineering application.

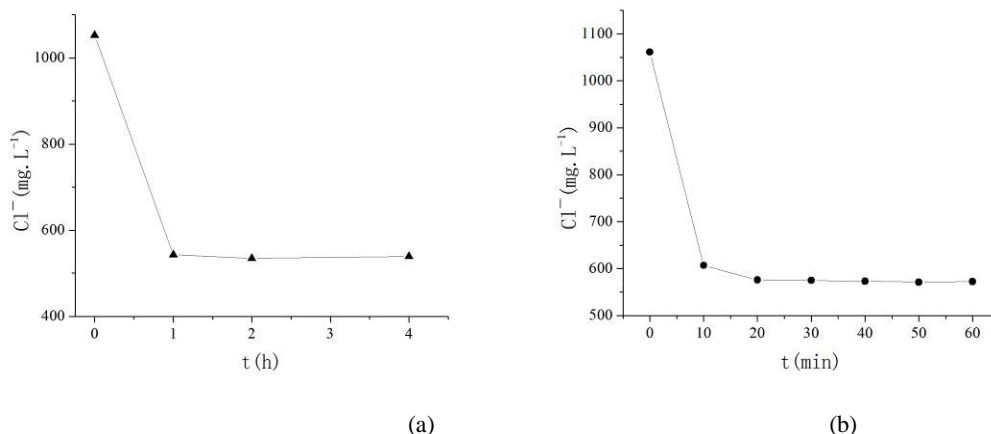


Fig. 3 Cl⁻ diffusion experiment (a- diffusion at 4h □ b- diffusion at 1h)

Diffusion behavior. Diffusion behavior was tested by detecting the concentration of Cl⁻ periodically, after put carrier into NaCl aqueous solution, till to the equilibrium of Cl⁻. Changes on the concentration of Cl⁻ were shown in Fig. 3. From Fig. 3(a), it was found that diffusion was likely to be completed within 1h. When the sampling interval was shorten to 10min, the diffusion

proceeded above 95% in 10 min and finished in 20 min, which was shown in Fig. 3(b). Good diffusion behavior of carrier is benefit to the reaction of substrate and nutrients in the wastewater. Each carrier contains abundant tiny grids, where microbes stayed inside, while NH_4^+ , NO_3^- , H_2O and microbial decomposition could pass in or out freely. Lots of interpenetrating holing-through structure inside carrier also revealed its good diffusion effect.

Mechanical property. Carrier with smaller modulus could be broken when collided with the wall or in the course of transportation, so modulus and deformation should be considered comprehensively and the compression ratio was the most useful and direct parameter. Results of compression experiment showed that carrier kept still intact when it was compressed from 3.5 cm to 5 mm. The compression strength was 0.26 and 0.48 MPa when the compression ratio was 80% and 85%, respectively, which revealed that carrier had good mechanical property and was very suitable for application at strong aeration environment.

Microstructure characterization. As microbial carrier has hydrogel structure with high moisture content, it is difficult to get real sample morphology through conventional scanning electron microscopy (SEM) which could cause collapse deformation of structure. The microstructure of carrier was detected by environmental scanning electron microscopy (ESEM) with conditions similar to the natural state of hydrogel as 2°C , 500 Pa, and accelerating voltage 30 kV. It was shown in Fig.4 that neither water droplets nor dehydration distortion were observed under the conditions. Distribution and morphology of holes in gel could be seen clearly by observed the compared structure and controlled structure of LQ-1 after bacteria proliferation. Porous state was found in the carrier with hole size $3\sim 10\mu\text{m}$ that evenly distributed. With the proliferation of nitrifying bacteria, the hole size had no significant change while a large number of irregular microbial communities were formed, which showed that the internal pore structure of carrier was conducive to the transfer of substrate and nutrient and attached-growth of microbial cells inside the carrier.

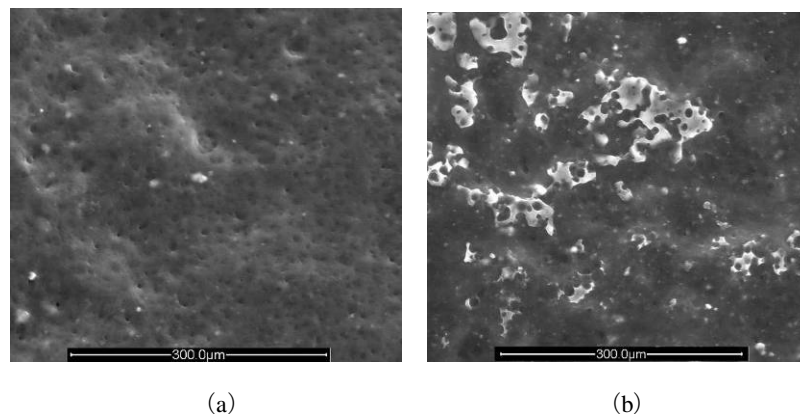


Fig.4. Internal structure of LQ-1
(a- compared structure; b- after nitrobacterium proliferation)

Biological property

Activation performance and removal effect of carrier at different temperature

Temperature is one of the most important factor for nitrification and the most appropriate temperature is $20\sim 30^\circ\text{C}$ ^[7]. When temperature decline to 15°C , nitrification become slowly and stop completely

below 5°C. Shuang Zhang et al. studied the treatment of sewage at normal and low temperature by gel-embedded nitrobacteria carrier, and the results showed that carrier kept higher removal rate of NH₃-N at low temperature after activation and enhancement [3]. Influence of temperature at 25°C and 14°C on the removal of NH₃-N by carrier was studied. Two parallel systems were used with adding ratio as 12% and similar other conditions except for temperature. Intermittent experiment was adopted to determine the degradation of NH₃-N by detected its concentration after 24h. It was shown in Fig.5 (a) that the removal of NH₃-N enhanced with the increase of reaction time at 25°C and achieved balance after 13d, while it had no changes at 14°C all the time. Therefore, appropriate temperature should be ensured to obtain good activation performance of carrier.

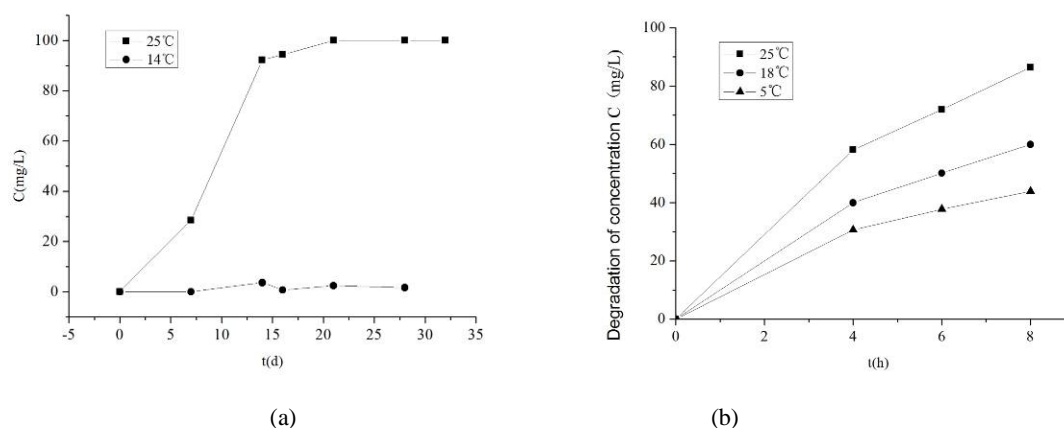


Fig.5. Influence of temperature on activation performance and removal effect of NH₃-N (a - the activation performance; b - removal of NH₃-N)

Influence of temperature on the removal of NH₃-N by carrier activated was studied by using the artificial wastewater containing NH₃-N. From Fig. 5(b), it could be observed that the removal of NH₃-N enhanced with the increase of time at different temperatures, while the removal amount were proportional to the temperature. Nitrobacteria embedded in the carrier maintain higher biological activity even at temperature below 5°C, which suggested that method of embedding could enhance the reproductive capacity and removal ability of nitrobacteria at low temperature.

Influence of microbial content on the activation performance of carrier

The activation performance and production cost of carrier largely depend on microbial content embedded. Two kinds of carrier with different microbial content named No.1 and No.2 (No.1 was twice No.2) were chosen as the object, and the degradation of NH₃-N in 8h exceeded to 50 mg/L was considered as the criterion of activation success. Intermittent experiment of activation was studied with adding ratio of carrier and initial concentration of NH₃-N as 12% and 100mg/L, respectively. Fig.6 showed that the activation time of No.1 and No.2 was about 11 days and 12 days, which suggested that appropriate reduction of microbial content in carrier had almost no effect on the activation performance when the quality of bacteria could be guaranteed.

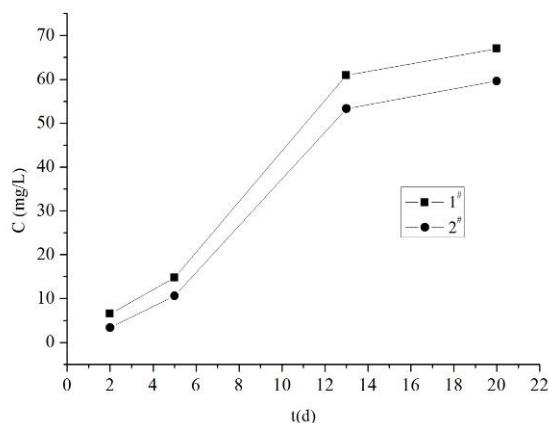


Fig.6. Influence of microbial content on the activation performance of carrier

Study on pilot experiment

Startup of pilot experiment

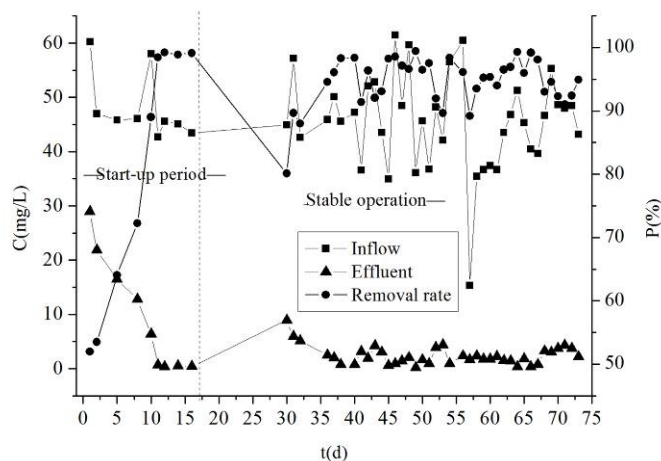


Fig.7. Removal efficiency of NH₃-N during start-up and stable period

The effluent of primary settling tank in a sewage treatment plant was used as wastewater of pilot experiment with conditions as sludge concentration 1500 mg/L, adding ratio of carrier 5.5%, and influent loading 25 m³/d (half of the design value). Fig.7 showed that the influent concentration of NH₃-N kept between 40 and 60 mg/L, while the effluent of which was above 10 mg/L at the first few days of running. It was mainly because that carrier added into the reactor was not activated and might release some nitrogenous substances. With time increased, the concentration of NH₃-N reduced gradually and reached to 6.36 mg/L after 10 days, which was already approached the level of emission standard 5 mg/L, and the removal rate was over 90%. At the 11th day, the effluent concentration of NH₃-N had been completely stable below 1 mg/L and the removal rate reached nearly 100%. The result suggested that activation time of carrier required only 11 d, similar to that of intermittent operation in laboratory.

The adding ratio of carrier in the aerobic zone of reactor increased to 7.95% at the 29th day, when the sludge concentration and influent loading gradually increased to about 1750 mg/L and 50 m³/d. Temperature of the wastewater maintained above 20°C during the whole period. The influent concentration of NH₃-N was mostly kept between 36 and 62 mg/L except for some rainy days. The average effluent concentration and removal rate of NH₃-N was stable at 2.04 mg/L and 95% between

35 and 74 days. The results also indicated that carrier was benefit to reach discharge standard for effluent concentration of $\text{NH}_3\text{-N}$ even at lower sludge concentration, which could reduce the amount of excess sludge.

Operation at low temperature

Pilot experiment on the removal effect of $\text{NH}_3\text{-N}$ by carrier was conducted in winter with conditions as temperature between 13 and 15°C, sludge concentration about 3000mg/L, adding ratio of carrier 12%, Do about 5mg/L, initial influent loading 50 m³/d and increased gradually. As shown in Fig.8, the influent concentration of $\text{NH}_3\text{-N}$ kept between 40 and 50 mg/L with small fluctuation in the experimental period. The effluent concentration of $\text{NH}_3\text{-N}$ was not stable and exceeded the drainage standard at the first few days in the lower water temperature, which was mainly because that nitrification system couldn't adapt to the adverse effects of lower water temperature immediately. With the running time increased, the effluent concentration of $\text{NH}_3\text{-N}$ decreased gradually and kept steadily below 1 mg/L with removal rate about 99% after 10 days as the nitrobacterium in carrier proliferated rapidly and the biological activity of system was recovered. The results showed that carrier activated could realize quick start and stable and high efficient operation at low temperature without affected by external environment.

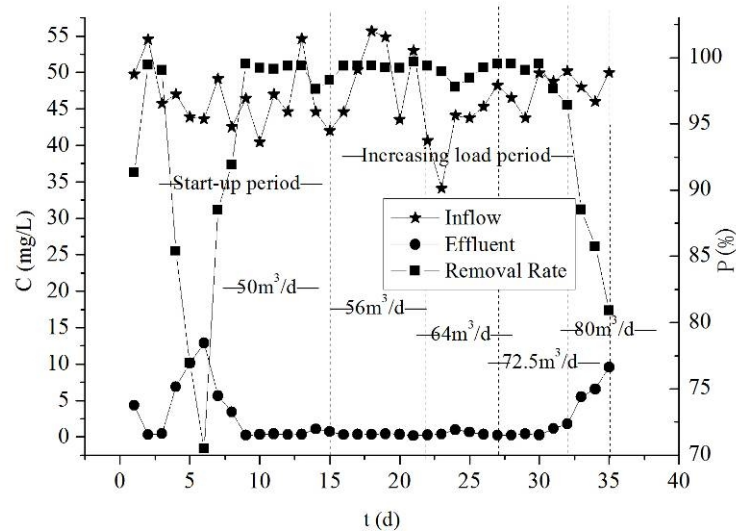


Fig.8. Removal efficiency of $\text{NH}_3\text{-N}$ at low temperature

The impact of influent loading on the experimental system was also studied at low temperature. It could be seen from Fig.8 that during the period when the influent loading increased from 50 to 56, 64, and 72.5 m³/d gradually, the influent concentration of $\text{NH}_3\text{-N}$ fluctuated from 30 to 55mg/L, while the effluent concentration kept steadily below 1mg/L with removal efficiency above 97%, which showed the good adaptability of hydraulic impact load of carrier. When the influent loading raised to 80 m³/d (1.6 times of design value), the effluent concentration of $\text{NH}_3\text{-N}$ enhanced rapidly and the removal rate decreased to 80%, which mean that influent loading had exceeded the capacity of biological treatment system. Under the condition of reach the drainage standard, the shortest HRT of aerobic tank was only 3h, far lower than the conventional process. The results showed that it was a very suitable method for the upgrading and reconstruction of municipal wastewater treatment plant

by added carrier into the biological treatment system.

Conclusions

(1) Sound Cube Microbial carrier LQ-1 has good diffusible ability which can ensure its effective mass transfer. Interpenetrating holing-through structure (about 5 μm) is evenly formed in the immobilized carries which is conducive to multiplication of nitrobacteria. When the compression rate is 85%, the compressive stress reaches 0.49 MPa.

(2) Temperature is an important factor affecting the activation of carrier. The activation of carrier can complete within 13 days under suitable temperature (above 20°C). The removal efficiency of $\text{NH}_3\text{-N}$ decreases with temperature decline, while the carrier can still remove 45mg/L of $\text{NH}_3\text{-N}$ in 8 hours under low temperature, which suggests that immobilized embedding technology is helpful for maintaining higher biological activity of nitrobacteria under low temperature. Under the premise that guarantees the activation of carries, the microbial content can be properly reduced to save production cost.

(3) Pilot experiment of immobilized carries shows that activation time of carrier is less than 11 days under suitable conditions. The removal efficiency of $\text{NH}_3\text{-N}$ reaches above 95% evenly 100% as the dosing ratio of carries is 10%.

(4) The removal efficiency of $\text{NH}_3\text{-N}$ by carrier keep stable and high-efficient under the conditions as temperature 13-15°C, sludge concentration 3000mg/L, DO above 5mg/L. The effluent concentration of $\text{NH}_3\text{-N}$ is mainly below 1mg/L which entirely reach the first grade A standards of GB18918-2002. Carrie is proved to be suitable for the upgrading and reconstruction of municipal wastewater treatment plant.

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