BIOLOGICAL DEGRADATION AND CHEMICAL OXIDATION CHARACTERISTICS OF COKE-OVEN WASTEWATER

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Abstract. Biological and chemical oxidation characteristics of two kinds of coke-oven wastewaters, A and B, discharged from a conventional batch coke-oven and a newly developed continuous coke-oven, respectively, were studied for selecting effective treatment processes of the wastewaters. Pollutants contained in Wastewater-A could be removed by biological process with a sufficient effluent quality, while those which existed in Wastewater-B could not be satisfactorily removed. Microbial community structure investigation using the respiratory quinone profile clarified that *Pseudomonas putida* (dominant quinone: ubiquinone-9) was a dominant species in the biological treatment system. The refractory organic pollutants, existed in Wastewater-B, were mineralized more effectively by Fenton's reagent than by ozone. A wastewater treatment process, in which Fenton's oxidation is followed by a biological treatment, was proposed for the treatment of Wastewater-B based on the experimental results.

Keywords: biological removability, coke-oven wastewater, Fenton's oxidation, quinone profile, treatability evaluation

1. Introduction

Industrial wastewaters, containing various refractory organic pollutants, are often discharged into the water environment without appropriate treatments. In order to remove refractory organic pollutants effectively from industrial wastewaters, the optimal treatment process with high quality effluent and low operating cost must be selected and moreover appropriate operation of the wastewater treatment process is required.

Major components of coke-oven wastewaters are condensate of coke-oven gases, which contain many refractory compounds in high concentration such as phenol, thiocyanate, sulfide, cyanide, ammonia and so on. Furthermore, various compounds such as fluorene, pyrene, acenaphthene, phenanthrene and flouranthrene, can also be found in wastewaters (Littleton *et al*., 1992). Particularly, phenolic compounds can easily migrate within different aqueous environments and contaminate groundwater because of their high solubility in water (Chang *et al*., 1995).

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TABLE I

Characteristics of coke-oven wastewaters used in the experiments

Characteristics		Wastewater-A[a]	Wastewater-B[b]
pH		9.8	9.5
COD_{Cr}	(mg L^{-1})	5150	19800
BOD	(mg L^{-1})	1670	5390
DOC	(mg L^{-1})	1920	6860
NH_4^+-N	(mg L^{-1})	3150	3430
NO_3^--N	(mg L^{-1})	20	240
BOD/COD_{Cr}		0.32	0.27
BOD/DOC		0.87	0.79
COD_{Cr}/DOC		2.70	2.90

[a] A: Wastewater discharged from a conventional batch coke-oven.
[b] B: Wastewater discharged from a newly developed continuous coke-oven wastewater.

The principal method used for the treatment of coke-oven wastewater is a conventional activated sludge process, but its effluent quality is insufficient to meet the stringent effluent standard in many cases (Suschka *et al.*, 1994). There is an urgent need for improving effluent quality to protect the healthy water environment. It was found recently that refractory organic pollutants could become biodegradable instead of mineralization after appropriate chemical oxidation (Bowers *et al.*, 1989; Medley *et al.*, 1983; Lee and Carberry, 1994).

The purpose of the present research was to optimize the treatment processes for different kinds of coke-oven wastewaters based on treatability evaluation of the wastewaters. The wastewaters discharged from a conventional coke-oven (batch operation) and a newly developed coke-oven (continuous operation) were used as the model wastewaters. The change in bacterial population in the course of acclimation of the microbes inhabiting a lab-scale biological treatment system was clarified using respiratory quinone profile. And thus the microbial population change in the treatment process was correlated with the performance of wastewater treatment.

Furthermore, the chemical oxidation characteristics of the residual refractory organic pollutants in the biological treatment effluents of the coke-oven wastewaters were evaluated from the viewpoint of improvement in biodegradability and the mineralization by chemical oxidation (Fenton oxidation and ozonation). Based upon the investigations mentioned above, an effective treatment process for coke-oven wastewaters was suggested.

2. Materials and Methods

2.1. Wastewater samples

Two kinds of coke-oven wastewaters, namely A and B, discharged from two coking plants were used. Wastewaters-A and -B were discharged from a conventional coke-oven (batch type) and a newly developed coke-oven (continuous type), respectively. Characteristics of the two kinds of coke-oven wastewaters in terms of COD_{Cr}, BOD and dissolved organic carbon (DOC) are summarized in Table I. It can be seen that values of COD_{Cr}, BOD and DOC of Wastewater-B were 3 times higher than those of Wastewater-A. Values of the BOD/COD_{Cr} and BOD/DOC ratios of Wastewater-A were 0.32 and 0.87, respectively, and those of Wastewater-B, were 0.27 and 0.79, respectively. This indicated that the biodegradability of Wastewater-B is more poor than Wastewater-A.

2.2. Biological treatment experiments

Biological treatment tests were carried out using a laboratory scale submerged aerobic biofilter with continuous operation. Main part of the apparatus was a transparent polyvinyl chloride (PVC) column (inner diameter: 10 cm, height: 30 cm, effective volume: 1.9 L). Ceramic balls with a diameter of 8–10 mm were used as the packing medium to provide solid surface for microbial attachment. The biofilter was inoculated with supernatant of activated sludge taken from a sewage plant, and then fed with artificial wastewater composed mainly of glucose and peptone (1:1, w/w) to cultivate the microbial film on the surface of the packing medium. After the microbial concentration in the apparatus reaching up to about 800 mg L^{-1}, the feeding of the artificial wastewater was stopped and the coke-oven wastewater was continuously fed into the biofilter at a given flow rate. The coke-oven wastewaters were preliminary treated by air stripping to remove ammonia before feeding to the biofilter. The biofilter was aerated to maintain DO concentration higher than 3 mg L^{-1}. The temperature was controlled at 20±1 °C. Other conditions of the biological treatment tests are shown in Table II.

2.3. Ozonation experiments

Ozonation test was carried out, using a batch operation apparatus consisting of a glass column (65 mm in diameter and 220 mm in height). Ozone gas (ozone concentration: about 7 mg L^{-1}) was fed into the column from the bottom at a flow rate of 0.3 L min^{-1}. Ozone concentration in the exhaust gas of the reactor was monitored spectrophotometrically by using the relationship between ozone concentration (C_{O_3}) and the absorbent at 245 nm (A_{254}) for 50 mm cell ($C_{O_3} = 3.09 \times A_{254}$). The ozone consumption was calculated from the concentration difference between the inlet and the outlet.

TABLE II
Operating conditions of the biological treatment experiments

Experimental runs	A-1	A-2	B-1	B-2
Wastewater	A	A	B	B
Influent DOC (mg L^{-1})	400	1000	1400	3000
Dilution ratio of raw wastewater	5	2	5	2
Hydraulic retention time (h)	24	24	70	70
DOC loading (kg m^{-3} hr^{-1})	0.5	1.0	0.5	1.0
BOD loading (kg m^{-3} hr^{-1})	0.7	1.3	0.3	0.7

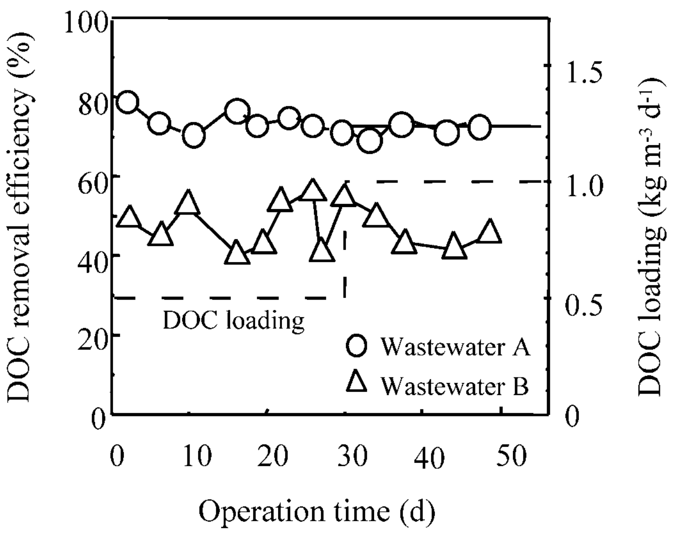

Figure 1. DOC removal efficiencies of coke-oven wastewaters in the biological process.

2.4. Fenton oxidation experiments

Oxidation experiments, using Fenton's reagent, were carried out in 500 mL beakers containing 200 mL of wastewater. The pH of the wastewater was adjusted to about 3, and then $FeSO_4$ and 35% H_2O_2 were added to the wastewater and the mixture was stirred for 1 hr. Then the pH of the wastewater was adjusted to 7 for the precipitation of ferric and ferrous ions. Dissolved organic carbon (DOC), BOD and the biodegradability in term of BOD/DOC ratio of the supernatant were measured.

2.5. Analytical methods

Total organic carbon (TOC) and DOC were determined using a TOC analyzer (Model TOC-500, Shimadzu, Japan). DOC was determined using the filtrated sample

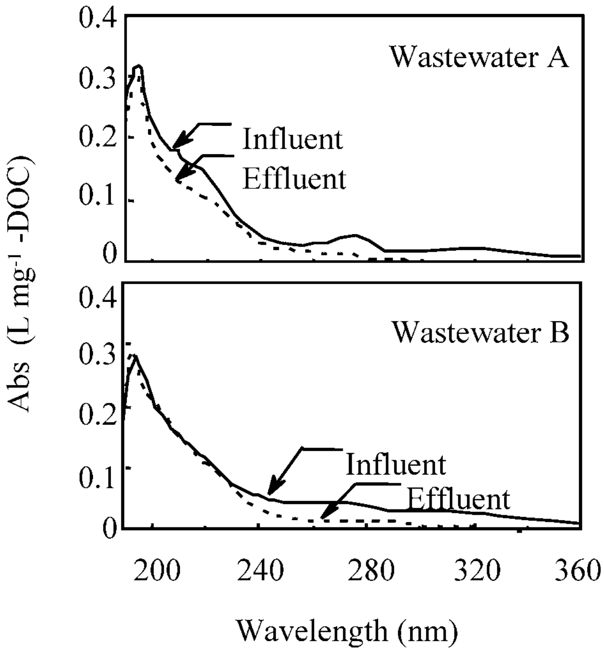

Figure 2. Comparisons of UV absorption spectra between before and after biological treatment of coke-oven wastewaters.

through membrane filter with pore size of 0.45 μm. BOD was determined with a BOD tester (Taiyo-Kaken, Japan). COD_{Cr} (COD, hereafter) was determined according to the *Standard Methods* (APHA, 1992).

3. Results and Discussion

3.1. Biological treatment characteristics

Fractional removals of DOC for both Wastewaters-A and -B in the laboratory scale biofilter are shown in Figure 1. The DOC removal efficiency of Wastewater-A was stablized at 70–75% regardless of the increase in DOC loading, while BOD removal was as high as 95% (data not shown). DOC removal efficiency of Wastewater-B was 40–60%, when the DOC volumetric loading was 0.5–1.0 kg-C m^{-3} d^{-1}, while the fractional BOD removal (data not shown) was as high as 90%, regardless of DOC volumetric loading. This fact indicated that some less biodegradable, i.e., refractory, organic matters remained in the effluent of the biological treatment process (Zang *et al.*, 1998).

Changes in UV absorption spectra of both wastewaters, after the biological treatments compared with that of the original raw wastewater, are shown in Figure 2. Aromatic compounds such as phenols could be completely removed by

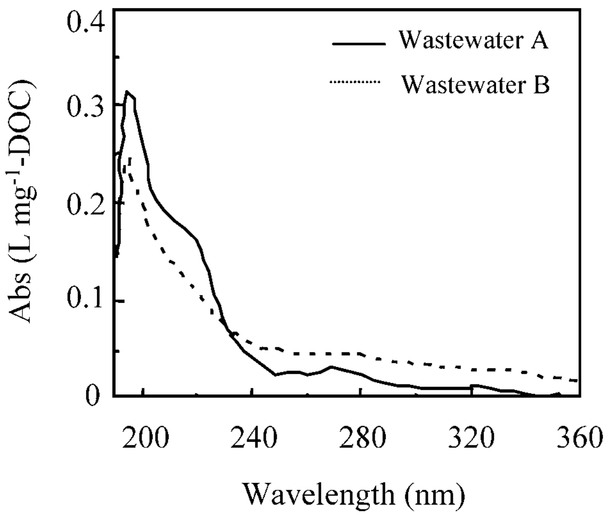

Figure 3. UV absorption spectra of organic pollutants removed by biological treatment.

the biofilter, since the specific peaks of phenol compounds at 210 and 270 nm (Silverstein *et al.*, 1982) of the influent wastewater disappeared after the biological treatment. UV absorption spectra of the organic pollutants in Wastewaters-A and -B, removed by the biological process, are shown in Figure 3. The spectra were obtained from the difference between the spectrum of influent and that of the effluent for A and B, respectively. The DOC removed by the biological process showed the typical spectra of phenolic compounds. These results do not show the specific information on the removed organic materials, but they are very powerful in identifying the characteristics of the pollutants (Urano, 1981).

The microbes inhabiting the biofilter can be characterized by the analysis of respiratory quinone profile (Collins and Jones, 1981; Fujie *et al.*, 1994; Hu *et al.*, 1996, 1999a, b; Lim *et al.*, 1997). Quinone is the electron transport constituent in the bacterial respiratory chain, and exists in almost all bacteria. The mole fraction of quinone species, i.e., quinone profile, in a mixed culture of bacteria, can be used as an index of the change in bacterial population, because each bacterium usually has a coherent dominant quinone. A large difference between the quinone profiles of the biofilter treating coke-oven Wastewaters-A (QP-A) and -B (QP-B), and that of the activated sludge in the municipal plant (QP-AS), were observed. As shown in Figure 4, the dominant quinone specie of QP-A and QP-B was ubiquinone-9 (UQ-9), while that of QP-AS were ubiquinone-8 (UQ-8) and menaquinone-9(H_2) (MK-9(H_2)). These results showed that the microbes having UQ-9 as a dominant quinone, such as *Pseudomonas putida*, could contribute to the biodegradation of phenolic compounds contained in the coke-oven wastewaters (Krieg *et al.*, 1984; Whiteley and Bailey, 2000).

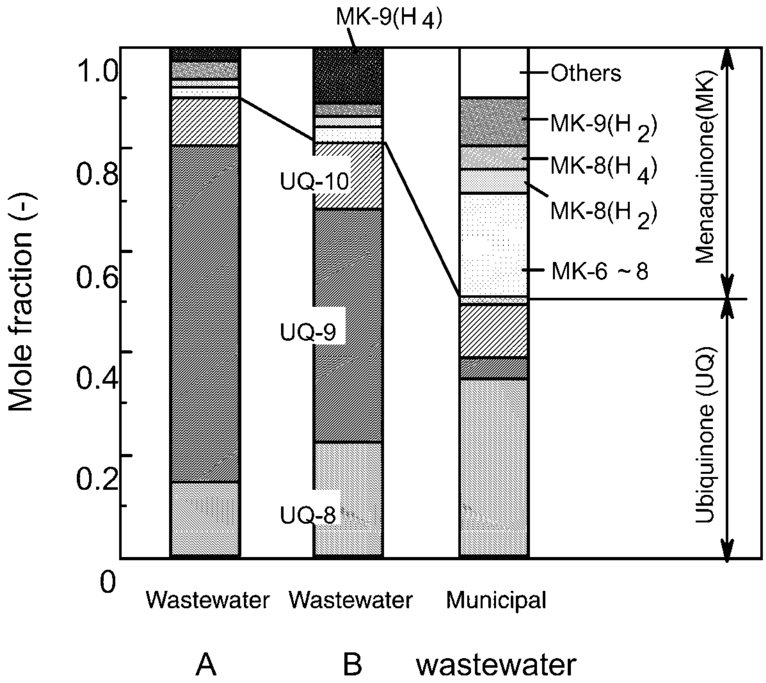

Figure 4. Quinone profiles of the microbes inhabiting microbial film of biofilter treating the Wastewaters-A and -B, respectively, in comparison with that of activated sludge in municipal plant.

3.2. Degradation by ozonation

Effluent of the biological treatment was ozonated to characterize the chemical oxidation characteristics of the pollutants. Changes in the organic removal efficiency and biodegradability of both wastewaters by ozonation are shown in Figure 5 as a function of the molar ratio of utilized ozone, i.e., the amount of ozone dissolved into the wastewater, to the initial value of DOC (O_3/DOC). The fractional DOC removal of both wastewaters was similar and their values were less than 15%. The residual organics in the effluent of the biological treatment may not be effectively mineralized by ozonation. Fractional removal of COD in Wastewater-A by ozonation was similar with that of Wastewater-B when O_3/DOC was 0.2, but the fractional removal of COD in Wastewater-A increased noticeably when O_3/DOC increased to 0.3. Both of BOD/DOC and BOD/COD ratios decreased in the ozonation of Wastewater-A, while the BOD/DOC of Wastewater-B did not change. The experimental results showed that the ozonation would not be suitable for mineralizing less-biodegradable organic pollutants contained in the wastewaters used here.

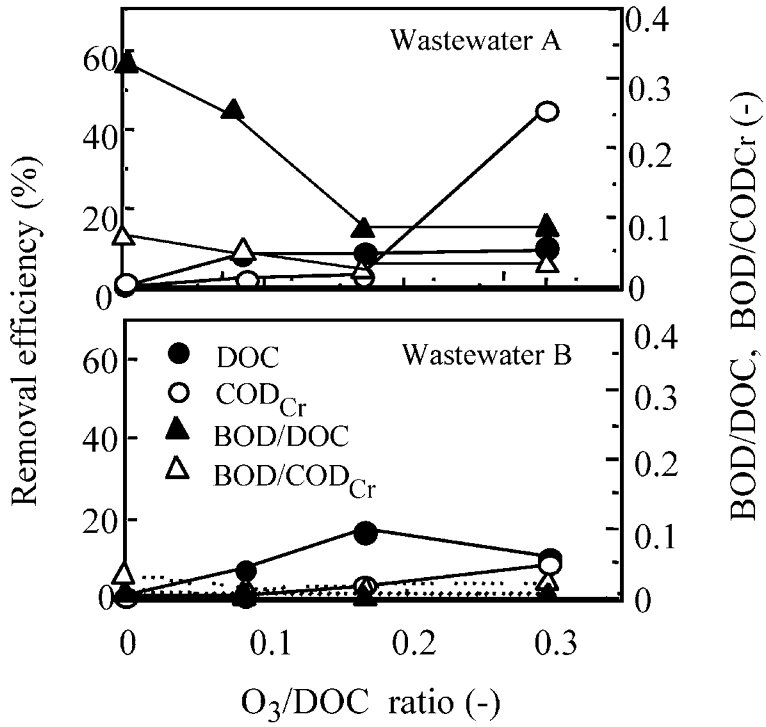

Figure 5. Removals of DOC, COD and changes in the biodegradability of the organic pollutants contained in the biological treatment effluent by the ozonation.

3.3. Fenton oxidation characteristics

Removal efficiencies of DOC and COD by the Fenton's oxidation of the biological treatment effluent are shown in Figure 6. H_2O_2 dosage in term of molar ratio of H_2O_2/DOC ranged from 0.1 to 5 in the experiments. DOC and COD removal efficiencies increased with the increase in H_2O_2/DOC and removal efficiencies reached up to around 70% at H_2O_2/DOC = 5 in both wastewaters. BOD/DOC and BOD/COD of the wastewaters after Fenton's oxidation decreased considerably at H_2O_2/DOC = 0.2. Changes in the refractory and the biodegradable organic carbons in the wastewaters during the Fenton's oxidation are shown in Figure 7. The biodegradable organic carbon was calculated from the DOC removal observed in the five-days BOD test (Lim *et al.*, 1997). The refractory organic carbon in both wastewaters reduced with the increase in H_2O_2 dosage. These results demonstrated that the residual refractory organic matters in the effluent of biological treatment could be ultimately mineralized to CO_2, while the improvement of biodegradability could not be expected. Wastewater-B discharged from the newly developed continuous coke-oven could be effectively treated with a biological process followed by Fenton's oxidation.

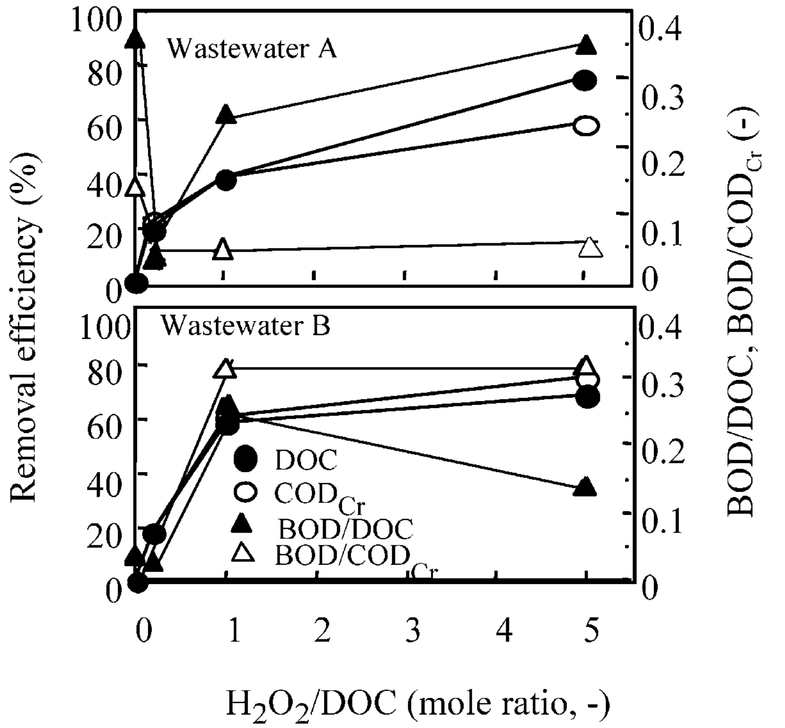

Figure 6. Removals of DOC, COD and changes in the biodegradability of organic pollutants contained in the biological treatment effluent by Fenton's oxidation.

4. Conclusions and Summary

Biological removal and chemical oxidation characteristics of two kinds of coke-oven wastewaters discharged from a conventional batch coke-oven and a newly developed continuous coke-oven were investigated respectively for the development of effective treatment processes of those wastewaters. Following conclusions were obtained.

(1) The wastewater from the conventional batch coke-oven can be treated by the biological process to give a satisfactory effluent, while the wastewater from the newly developed continuous coke-oven can not.

(2) *Pseudomonas putida*, dominant quinone of which is ubiquinone-9, was considered to be the dominant specie of the microbes contributing to the biological degradation of pollutants contained in the coke-oven wastewaters.

(3) The refractory organic pollutants contained in coke-oven wastewaters can be effectively mineralized, using Fenton's reagent, but not by ozone.

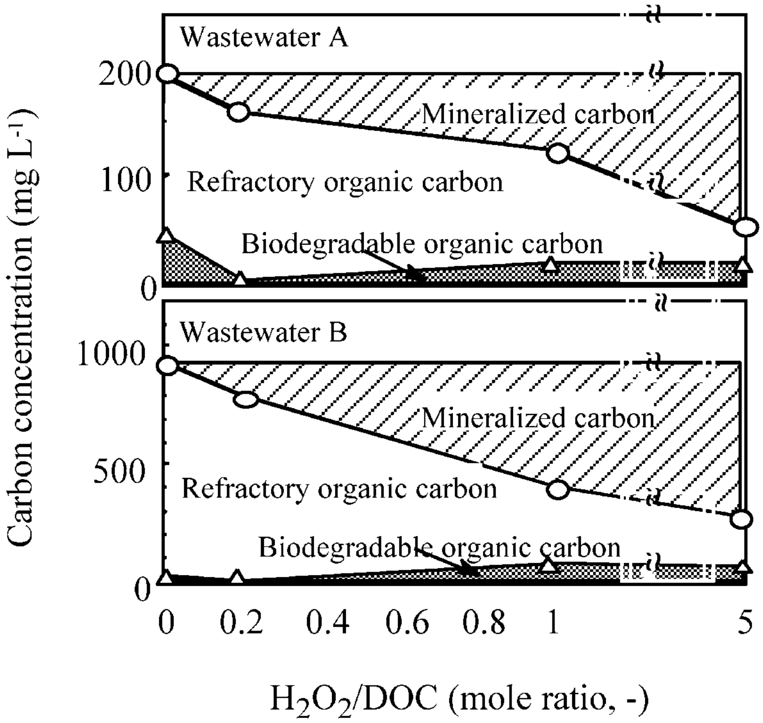

Figure 7. Transformation of the residual organic carbon in the effluent of biological treatment by Fenton's oxidation.

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