November, 1982] © 1982 The Chemical Society of Japan NOTES Bull. Chem. Soc. Jpn., 55, 3677—3678 (1982) 3677

An Effective Process for Treatment of Malodor in Exhaust Gas by Hypochlorite

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(Received January 12, 1982)

Synopsis. Pilot-plant studies were carried out to find out the optimum conditions for hypochlorite-oxidation treatment of malodorous multi-components in exhaust gas from night soil treatment plants. A two-step process was proved to be the most effective: a part of malodorous components are absorbed and oxidized in the first packed-tower into which a pH 7 aqueous solution of sodium hypochlorite slowly introduced and then unreacted components are oxidized in the second tower with a pH 11 solution.

There have been known several methods for treatment of malodor in exhaust gas from night soil or sewage treatment plants, such as adsorption by activated carbon,[1)] catalytic oxidation,[2)] and wet scrubbing systems using absorptive solutions with oxidizing agents and/or alkaline solution, and water.[3)]

The authors have described in the earlier papers[4—8)] the wet scrubbing systems using packed towers through which hypochlorite or hydrogen peroxide solutions were allowed to pass and have clarified the relationship between oxidation conditions of malodorous sulfide components and the decrease of COD (chemical oxygen demand) of effluent water. We have defined the conditions (pH of absorptive solution, it's NaOCl concentration, superficial gas velocity, *etc.*) for absorptive oxidation of hydrogen sulfide[4,5)] and coexistent malodorous components in exhaust gas such as ammonia, trimethylamine, methanethiol, dimethyl sulfide, dimethyl disulfide, trace acetaldehyde and styrene.[6—8)] In the above studies, the effectiveness of scrubbing systems was assessed in terms of the overall mass transfer coefficient K_Ga.[9)]

In this paper, the optimum conditions for effective NaOCl oxidation of mixed systems of malodorous multi-components are investigated with actual exhaust gas, using a pilot-plant.

Experimental

Equipment. Polyvinyl chloride towers of diameter 100 cm, packed with Takiron Trical P 175 packings, were used for absorptive oxidation.

Chemical Analysis. Carbon dioxide and chlorine were determined by the detector tube method and the orthotolidine method, respectively. Hydrogen sulfide, methanethiol, dimethyl sulfide, dimethyl disulfide, trimethylamine, styrene and acetaldehyde were determined by the gas chromatography,[10,11)] and ammonia was determined by the spectrophotometry.[10)]

Procedure. Sample gas was introduced into the packed tower from the bottom by a blower and the absorptive solution was sprayed onto the packings at the top of the tower, so as to make gas and solution contact in countercurrent fashion. The gas was sampled at the inlet and outlet of the tower and analyzed.

Results and Discussion

Figure 1, prepared by rearranging the data in the earlier papers,[4,6—8)] shows the relationship between the pH values of NaOCl solutions and the K_Ga values of malodorous gas components under the conditions that they are oxidized separately with 1.2×10^{-2} mol/l NaOCl solution at the superficial gas velocity of 1.7 m/s and the liquid/gas ratio of 2 l/m^3. As shown there, the K_Ga values for NH_3, $(CH_3)_3N$, CH_3SCH_3, CH_3SSCH_3, CH_3CHO, and $C_6H_5CH{=}CH_2$ are the largest, respectively at pH 6, while those for CH_3SH and H_2S are the largest at pH 11, respectively. Since the removal rate rises with the increase of the K_Ga value, it can be estimated that the most effective oxidation would result at pH 6 and 11 for an actual exhaust gas which contains those components in a mixed state. Then, an experimental study to verify the estimation was carried out with actual mixed systems of those components in exhaust gas from a night soil treatment plant, which contains H_2S, CH_3SH, CH_3SCH_3, CH_3SSCH_3, NH_3, $(CH_3)_3N$, $C_6H_5CH{=}CH_2$, CH_3CHO in 39, 0.05, 1.74, 0.0089, 18.6, 0.32, <0.01, <0.05 ppm, respectively, using two packed towers (60 cm and 180 cm height) arranged in parallel. The exhaust gas was

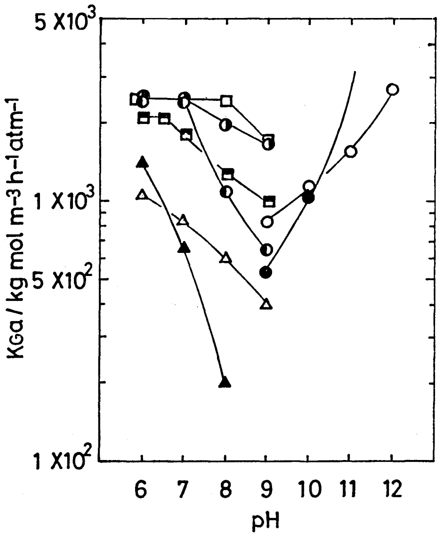

Fig. 1. Effect of pH on K_G a of malodorous components.
Superficial gas velocity: 1.7 m/s, liquid/gas ratio: 2 l/m^3, NaOCl: 1.2×10^{-2} mol/l, packed height: 60 cm (180 cm for H_2S), tower diameter: 8 cm (40 cm for H_2S), □: NH_3 (10 ppm), ⬒: $(CH_3)_3N$ (5 ppm), ○: CH_3SH (5 ppm), ◑: CH_3SCH_3 (5 ppm), ●: H_2S (60 ppm), ◐: CH_3SSCH_3 (5 ppm), △: CH_3CHO (1 ppm), ▲: $C_6H_5CH{=}CH_2$ (1 ppm).

oxidized both with pH 6 NaOCl solution (in the 60 cm tower) and with the pH 11 solution, separately in parallel. The NaOCl concentration, superficial gas velocity and liquid/gas ratio were set to be the same as described above. The K_Ga values of NH_3, $(CH_3)_3N$, and CH_3SCH_3 were determined to be 2550, 2100, 2600 (kg mol/m^3 h atm), respectively, when oxidized with pH 6 solution and that of H_2S to be 2500 with pH 11 solution. These values almost agree with those in the earlier papers[4,6,7] (determined for each component, separately). Therefore, the estimation was verified and the pH values, 6 and 11 were proved to be effective for oxidation of actual malodorous gas in mixed multicomponent systems. However, since so much chlorine releases (about 10 ppm) from the absorptive solution at pH 6 that the NaOCl concentration can't be controlled, it is preferable for the actual operation to set the pH at 7 and 11, respectively; at this pH chlorine release can be suppressed to less than 3 ppm.

Next, to make the oxidation process more effective, a two-step oxidation was planned to be tried using two packed towers arranged in series, whereby malodorous components are oxidized in the first tower with pH 7 NaOCl solution and next in the second with the pH 11 solution. Then, another experimental study was carried out with exhaust gas from a night soil treatment plant, which contains H_2S, CH_3SH, CH_3SCH_3, CH_3SSCH_3, NH_3, $(CH_3)_3N$, $C_6H_5CH=CH_2$, CH_3CHO in 40, 0.08, 1.97, 0.024, 18.8, 0.024, <0.01, <0.05 ppm, respectively. The gas was introduced into the first tower (60 cm height), where part of H_2S and the other components except CH_3SH were absorbed and oxidized, next into the second (180 cm height), where the remaining H_2S and CH_3SH were oxidized. The NaOCl concentration, superficial gas velocity and liquid/gas ratio were set to be the same as described above. In the effluent gas from the second tower, 0.002 ppm of H_2S and 0.05 ppm of NH_3 were detected and the other malodorous components were reduced to the concentrations below their determinable limit. The treated gas was almost odorless. Therefore, it can be concluded that malodor is removed almost completely by the two-step process under the conditions described above. In the practical operation, however, it is preferable to set the pH around at 10 rather than 11 in the second tower, in the case where much CO_2 gas (1500—3000 ppm) coexists, as in the case of aeration tanks or sludge storage tanks in sewage treatment plants, in order to prevent troubles of carbonate-scaling.

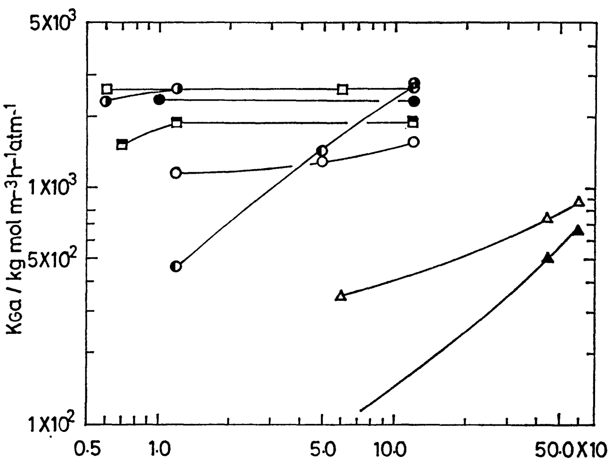

Fig. 2. Effect of mole ratio on K_Ga of malodorous components.
Superficial gas velocity: 1.7 m/s, liquid/gas ratio: 2 l/m^3, packed height: 60 cm (180 cm for H_2S), tower diameter: 8 cm (40 cm for H_2S), pH 11 for H_2S and CH_3SH, pH 7 for the others, □: NH_3 (5—10 ppm), ⬒: $(CH_3)_3N$ (1—5 ppm), ○: CH_3SH (5 ppm), ◑: CH_3SCH_3 (5 ppm), ●: H_2S (10—100 ppm), ◐: CH_3SSCH_3 (5 ppm), △: CH_3CHO (0.1—1.0 ppm), ▲: $C_6H_5CH=CH_2$ (0.1—1.0 ppm).

Figure 2, prepared by rearranging the data in the earlier papers,[4,6–8] shows the relationship between the NaOCl concentration and K_Ga. Malodorous components are classified roughly into two groups: namely, one to be oxidized almost completely at the mole ratio (hypochlorite/malodorous components) of 12 (or larger) and another to be oxidized at the ratio of larger than 120. CH_3SH, CH_3SSCH_3, CH_3CHO, and $C_6H_5CH=CH_2$ belong to the latter. But their contents in actual exhaust gas are negligible small (less than 5 ppm), compared with H_2S, NH_3, $(CH_3)_3N$, and CH_3SCH_3 in the former group. Accordingly, it is adequate that the NaOCl concentration was determined to be 1.2×10^{-2} mol/l on the basis of the mole ratio 12.

This process is applicable to the treatment of malodorous exhaust gas from sewage treatment plants and kraft pulp mills.

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9) For a system in which gas mixtures are lean and the absorptive reaction is irreversible, the overall mass transfer coefficient K_Ga is given by the following equation:[3)]

$$K_Ga = G_m/Ph \ln y_1/y_2, \qquad (1)$$

where

K_Ga = overall mass transfer coefficient (kg mol/m^3 h atm),
G_m = superficial mole velocity of gas (kg mol/m^2 h),
h = packed height (m),
P = total pressure (atm),
y_1, y_2 = concentration of gas at the inlet and outlet of the packed tower (mole fraction).

10) Announcement No. 9, "Method for Determination of Malodorous Materials," issued by the Environmental Protection Agency, Japan, May 1972.

11) Announcement No.47, "Revised Method for Determination of Malodorous Materials," issued by the Environmental Protection Agency, Japan, Sept. 1976.