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A green procedure using ozone for Cleaning-in-Place in the beverage industry

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HIGHLIGHTS

- Efficiency of typical cleanings was improved by changing the gasket material.
- Ozone dramatically improved cleaning efficiency comparing to typical cleaning.
- Combination of silicone gasket and ozone resulted in the most effective cleaning.

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ABSTRACT

Cleaning-in-Place (CIP) in the beverage industry is typically carried out in production lines with alkaline and acidic solutions with detergents. This cleaning not only produces alkaline and acidic wastewater with detergents but also takes significant time. One of the important targets for CIP is adsorbed odorous compounds on gaskets, hence, we have tried to establish a rapid and green CIP process to remove traces of such compounds, especially *d*-limonene, an odorous component of orange juice, using two approaches; an ozone cleaning method and a change of gasket material from ethylene propylene diene monomer (EPDM) rubber to silicone rubber. By changing the gasket material from EPDM rubber to silicone rubber, the removability of *d*-limonene by typical alkaline and acidic cleanings with detergents was improved. However, complete removal of 4 mg g^{-1} of *d*-limonene on both EPDM and silicone gaskets could not be achieved even using a series of conventional cleaning procedures that included alkaline and acidic cleaning for 220 min. Ozone treatment dramatically improved the removability of *d*-limonene, removing 87% from the EPDM gasket at 60 min and 100% from the silicone gasket at 30 min. The combination of the silicone gasket and ozone treatment resulted in the most effective cleaning. The main removal mechanism for ozone treatment was confirmed to be oxidation by molecular ozone. Effectiveness of changing the gasket material from EPDM rubber to silicone rubber in reducing residual amounts of odorous compounds adsorbed on the gaskets was also confirmed for furfural and 4-vinylguaiacol.

1. Introduction

In recent years the beverage industry has seen a steady increase in non-mass and jobbing production as opposed to mass production. In this production style, typically one production line is used to produce multiple products. Water and time are required for the cleaning and disinfection of the production line and filling equipment to prevent cross-contamination before changing to a different product. Frequent automatic cleaning, termed Cleaning-in-Place (CIP), is, therefore, applied. CIP normally consists of cold or hot water flushing, alkaline cleaning with detergents, acidic cleaning with detergents and disinfection by chemical disinfectants such as sodium hypochlorite (Eide et al., 2003). Water flushing is conducted to remove residues in pipes. However, many deposits cannot be removed by water alone or removal takes too long. Therefore, cleaning chemicals based on acidic or alkaline solutions are used to modify the deposit into a removable form (Fryer and Asteriadou, 2009). Alkaline solutions can dissolve mainly fats and proteins whereas acidic solutions can remove minerals. The detergents in both alkaline and acidic solutions enhance the solubility of adsorbed organic compounds and facilitate their desorption.

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Minimization of the environmental impact of CIP is important. Cleaning with alkaline or acidic solution can generate large volumes of wastewater that may be of very high or low pH and have high COD due to both deposits and cleaning chemicals. However, use of cleaning chemicals is necessary to shorten the time for CIP.

Appropriate management of industrial wastewater involves not only in-plant control alternatives such as waste minimization, reuse, water use reduction but the application of end-of-pipe treatment (Oktay et al., 2007). Although a management strategy sometimes skips the first stage for the financial outlay, in-plant control applications have a potential to reduce total wastewater management cost by the reduction of pollutant loading to be treated (Erdogan et al., 2004). Innovative in-plant control technologies should be developed to minimize water use and chemicals for CIP.

One of the important targets and significant challenges for CIP is odor. Contamination by trace odours from previous products would degrade production quality. For example, lipophilic aroma compounds such as *d*-limonene and methyl butanoate from orange juice (Arena et al., 2006; Qiao et al., 2007), 1-hexanol from apple juice (Elss et al., 2006) and 4-vinylguaiacol from coffee (Mayer et al., 2000) can be adsorbed on pipe surfaces and especially on rubber of gaskets, and be resistant to cleaning.

The challenge for innovative and efficient CIP is to use ozone rather than cleaning chemicals and not to use alkaline and acidic solutions. Ozone is a powerful oxidant and is frequently used for the decomposition and removal of organic compounds, especially odorous compounds, in air and water (Lalezary et al., 1986; Glaze et al., 1990). Moreover, ozonized water has been used in the semiconductor process as a cleaning solution (Uemura et al., 2007). Therefore, ozone would be expected to have the ability to remove organic deposits such as trace odorous compounds remaining in pipes. Ozone has a great advantage compared to alkaline and acidic solutions with cleaning chemicals because portions of deposits can be degraded by ozone and ozone itself is also degraded to oxygen during treatment and does not remain in the wastewater. In contrast, with conventional treatment, degradation of deposits does not occur and thus the alkaline and acidic wastewaters with deposits and cleaning chemicals require further wastewater treatment.

Gaskets in the production pipe lines must also be considered, since deposits can form on rubber surfaces. Rubber compounds used for pipe lines in the beverage industry are mainly ethylene-propylene-diene monomer (EPDM) rubbers, which have no unsaturated bonds in the main chain and are, therefore, resistant to ozone, thermal aging and weather (Rutherford et al., 2005). Moreover such rubbers have an economical advantage over other rubber compounds such as those based on chloroprene, acrylonitrile-butadiene/polyvinyl chloride, nitrile and silicone. Greene et al. (1994) found that among gasket materials used in fluid food processing, ozone treatment affected the tensile strength of EPDM and Viton, whereas the tensile strengths of polyethylene, silicone rubber and PTFE were not significantly affected; the authors concluded that the effects of ozone treatment on the physical properties of the gasket materials studied were minor even though slight effects were observed on EPDM and Viton. Polyethylene, silicone rubber and PTFE, are, therefore, considered to be strong candidates for gasket materials that would be amenable to ozone cleaning. However, to date, there have been no evaluations of gasket materials from the standpoint of cleaning.

In this study we sought to establish a rapid and green CIP process to remove trace odorous compounds from beverage products adsorbed on gasket rubber. Two removal approaches were tested; the application of an ozone cleaning method and changing of the gasket material from EPDM rubber (EPDM gasket) to silicone rubber (silicone gasket).

2. Materials and methods

2.1. Materials

The flavor of an orange consists of more than 200 compounds (Shaw, 1991) and limonene is the most abundant (Gomez-Ariza et al., 2004). Major constituents of apple juices and aromas were reported to be 1-hexanol, 1-butanol, *E*-2-hexenol, *E*-2-hexenal and butyl acetate, and 1-hexanl showed the highest concentration both in the juice and aroma (Elss et al., 2006). The major component of an apple juice concentrates was also reported to be furfural (Elss et al., 2006). 2-Furfurylthiol, 4-vinylguaiacol, several alkylpyrazines, furanones, acetaldehyde, propanal, methylpropanal and 2- and 3-methylbutanal had the greatest impact on the flavor of ground coffee (Czerny et al., 1999). Four odorous compounds, *d*-limonene from an orange, 1-hexanol and furfural from an apple and 4-vinylguaiacol from a coffee were used in this study and main physicochemical properties of these compounds are summarized in Table 1; they were purchased from Sigma Chemicals.

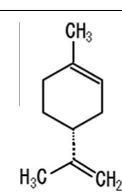
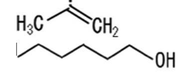
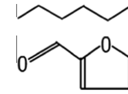
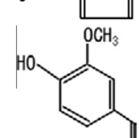
Prior to this research we investigated a beverage company to ascertain the CIP procedures and solutions in use. The alkaline cleaning solution for a conventional cleaning process contained 3% NaOH with detergents (Adeka Mate AC from Adeka Clean Aid) and the acidic cleaning solution contained 3% HCl with phosphate detergents (Adeka 3 from Adeka Clean Aid) and descaling agents (mixture of Pankereto from Hirata Kagaku and Alfa-RP from Futaba Kosan).

Gaskets of EPDM and silicone rubbers were purchased from Air Water Mach. The gasket diameters were 10.8 mm (inside) and 15.6 mm (outside) and the weight was 0.24 g.

2.2. Adsorption of odorous compound on gasket

A 300 mL-beaker with 250 mL of distilled water produced using a RFD240RA (Advantec) was prepared and a glass column (20 mm diameter) was inserted into the beaker. The top of the column was over the surface of the water and the bottom was set at the middle of the beaker. Then an odorous compound was added on the surface of the water inside the glass column. The odorous compound formed an oil layer on the surface of the water because of limiting solubility in water. To make the odorous compound saturated water, the water was stirred using a magnetic stirrer for 3 h. Then

Table 1
Physicochemical properties of odorous compounds used in this study.

Compound	Molecular structure	Molecular Mass ($g\ mol^{-1}$)	Water solubility ($g\ L^{-1}$)	Log P
d–limonene		136.2	0.014[a]	4.20
1–hexanol		102.2	5.9[b]	2.03
Furfural		96.1	83[b]	0.41
4–vinylguaiacol		150.2	0.93[a]	2.57[c]

[a] Water solubility at 25 °C.
[b] Water solubility at 20 °C.
[c] Predicted by using the ACD/Labs' ACD/PhysChem Suite.