Research Papers

Improvement of Cleanability of Stainless Steels with Various Surface Chemical Composition by Gaseous Ozone

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The effect of gaseous ozone on the cleanability of 316 L stainless steel was studied using its nonporous particles pretreated with heat-drying at 150°C, heating at 400°C, and immersion in 10% nitric acid. Bovine serum albumin (BSA) was used as the model fouling material. Dried, heated, and HNO₃-treated particles showed largely different surface chemical composition and the surface charge density (σ_{app}). Treatment of the above pretreated particles with 0.2% gaseous ozone resulted in decreases in the positive σ_{app} values of the particles, with only slight variations in their surface chemical composition. The saturation amounts of BSA adsorbed (Γ_{sat}) on dried particles decreased significantly ($P < 0.05$) after ozone treatment, whereas those on heated and HNO₃-treated particles were not changed. These phenomena were correlated with the degree of a decrease in the positive σ_{app} of the particles after ozone treatment. In continuous cleaning in a plug-flow column fed by a 0.1 M NaOH solution, it was indicated that the rate and efficiency of BSA desorption from all the particles increased as a result of ozone treatment. Kinetic analysis showed that significantly smaller proportions of a slower-desorbing BSA molecule and significantly higher values of first-order desorption rate constants were obtained for the ozone-modified particles than for their non-ozone-modified particles ($P < 0.05$). It was indicated that the cleanability of stainless steel particles could be improved by gaseous ozone treatment irrespective of the surface chemical composition of the original particles.

Keywords : Cleanability of Stainless Steel, Surface Chemical Composition, Gaseous Ozone, Surface Charge Density, Binding Strength

1. Introduction

The austenitic stainless steels are widely used as construction materials for process plants in the food and pharmaceutical industries^{1)~3)}. These alloys fulfill many requirements for food and pharmaceutical machinery, e. g., inert surface to the product, high corrosion resistance to detergents and antimicrobial chemicals, nontoxicity, and mechanical stability. To keep sanitary conditions of process plant, organic residues derived from products and living microorganisms on equipment surfaces should be removed at the end of each set of processing operation by routine cleaning and sterilizing operations. The product-contact surface of stainless steel is commonly treated by mechanical polishing and electropolishing to obtain smooth surfaces or by chemical passivation to improve the corrosion resistance^{4)~6)}. Although the passive film on stainless steel is damaged to some extent by chemicals such as chlorine during a long-term operation, the passive film spontaneously renews itself in the presence of oxygen and water, where characteristics of the passive film depends on passivation conditions^{7),8)}. The surface chemical composition of stainless steel is by far an important factor affecting the degree of fouling and the cleanability compared with its bulk chemical composition since adsorption and desorption behaviors of fouling mate-

rials are physicochemical features at solid-liquid interfaces.

Ozone is a powerful oxidizing agent and it is attractive as alternative cleaning and sterilizing agents to chlorine^{9),10)}. Previously, we demonstrated that the surface charge property of 316 L stainless steel particles could be changed after their exposure to gaseous ozone at low concentrations of 0.05 to 1.0% (v/v) with little changes in surface chemical composition¹¹⁾. It was also found that ozone-modified stainless steel particles showed a relatively lower affinity for protein adsorption compared with non-ozone-modified particles¹¹⁾. These findings suggested that oxidizing power of gaseous ozone was useful for the improvement of cleanability of stainless steel surface. The question then arises as to whether the cleanability of stainless steel is improved by gaseous ozone irrespective of the surface chemical composition of original stainless steels. However, a quantitative analysis of the effect of gaseous ozone treatment on the cleanability of stainless steel, and the influence of the surface characteristics on ozone modification have not so far been fully investigated.

The aim of this study is to quantitatively investigate the effect of gaseous ozone treatment on the cleanability of stainless steels with various surface properties. To focus discussion on physicochemical features, we used nonporous stainless steel particles

fouled with bovine serum albumin (BSA) as the model fouling experiment. Samples of stainless steel particles that have largely different surface chemical composition were prepared by pretreatments with heat-drying, heating, and chemical passivation in HNO_3 . The cleaning experiment was conducted in a plug-flow column fed by a 0.1 M NaOH solution, where the hydrodynamic forces are very low. This system is well suited for investigating the effect of physicochemical binding. The curve of BSA desorption was kinetically analyzed as a function of time. The cleanabilities of non-ozone-modified and ozone-modified pretreated particles were compared by evaluating the kinetic constants for BSA desorption.

2. Experimental

2. 1 Materials and chemicals

Nonporous 316 L stainless steel particles were obtained from The Nilaco Corp. (Tokyo). Before use, stainless steel particles were washed in acetone followed by in ethanol with sonication, and then dried at 150°C for 4 h (non-surface-treated particles). The specific surface area of non-surface-treated particles, as determined by BET method, was 0.40 m²/g (mean diameter : 8 μm). Crystalline BSA (Lot M 9 B 4259) was purchased from Nacalai Tesque Inc. (Kyoto) and used as received.

2. 2 Surface pretreatment and ozone treatment

To prepare samples of stainless steel particles with various surface chemical composition, a 20 g-aliquot of stainless steel particles was (i) dried at 150°C for 4 h, (ii) heated at 400°C for 4 h under an atmosphere, or (iii) immersed in 200 ml of 10% HNO_3 at 60°C for 1 h.

Gaseous ozone of 0.2% (v/v) was generated from pure oxygen (99.999%, v/v) by a silent discharge ozonizer as described previously¹¹. A 20-g aliquot of the above surface-pretreated stainless steel particles was placed in a cylindrical glass column (28 mm diameter × 220 mm length), and then 0.2% gaseous ozone was passed through the glass column at a flow rate of 1.0 dm³/min for 1 h.

2. 3 Adsorption experiments

To examine the saturation amount of BSA adsorbed (Γ_{sat}) on stainless steel particles, adsorption experiment was conducted in a 0.025 dm³ glass vial at 40°C and at the pzc_{app} of BSA (pH 5.0) for 2 h, using a BSA solution of 5 g/dm³ in the presence of 10⁻³ M KNO_3 as described previously¹¹. The Γ_{sat} was determined as the sum of the amount of BSA removed and that of BSA still remaining on the particles after treatment with 0.1 M NaOH solution as described previously¹¹.

To prepare BSA-fouled stainless steel particles, 0.025 dm³ of BSA solution and 5 g of stainless steel particles were put into a 0.125 dm³ glass vial, which was then reciprocally shaken (140 oscillations per minute) for 2 h. To unify the initial amount of BSA adsorbed (Γ_0) on each of the pretreated particles with or without ozone treatment, initial concentration of BSA solution was controlled based on the adsorp-

tion isotherm. After being shaken for 2 h, BSA-stainless steel suspension was transferred into 0.05 dm³ of centrifugation tube, and BSA-fouled particles were collected by centrifugation (2,300 × g for 1 min). The BSA-fouled particles collected were washed 5 times with 0.025 dm³ of deionized water by centrifugation (2,300 × g for 1 min). The thus obtained BSA-fouled particles were dried at 40 °C for 16 h and stored in a desiccator before use in the cleaning experiment.

When BSA-fouled stainless steel particles were immersed in 10⁻³ M KNO_3 solution at 40°C for 2 h, no desorption of BSA occurred, indicating that the adsorption of BSA on the surface-treated stainless steel particles was irreversible.

2. 4 Cleaning experiment

The cleaning experiment was conducted at 40°C in a plug-flow column fed by a 0.1 M NaOH solution as described previously¹². A 1-g portion of the dried BSA-fouled stainless steel particles were packed into stainless steel column (4 mm φ × 50 mm), which was then installed vertically in a column oven. Rinse solution (10⁻³ M KNO_3 , pH 5.2) and the NaOH solution were fed from the bottom of the column at a flow rate of 2.5 × 10⁻⁴ dm³/min (space time : 2.0 min) for 120 min, respectively. The particles were then withdrawn from the column and the amount of BSA remaining on the particles was determined. The amount of residual BSA on the particles at any time was calculated from the amount of BSA desorbed and that of BSA remaining on the particles¹³. The desorption curve was obtained by plotting the logarithm of the amount of residual BSA against cleaning time (see below).

2. 5 Kinetic analysis

To analyze the nonlinear curve of BSA desorption, the concept that two first-order reactions occur independently and simultaneously during the cleaning process was used¹⁴ :

$$\ln \Gamma = \ln \{ \exp(\ln \Gamma_0^f - k^f t) + \exp(\ln \Gamma_0^s - k^s t) \} \quad \cdots (1)$$

where Γ , Γ_0^f , and Γ_0^s are the amount of adsorbed BSA at any given time t , and the amounts of a faster-desorbing BSA (BSA^f), and a slower-desorbing BSA (BSA^s) at zero time, respectively ; k^f and k^s are the desorption rate constants of BSA^f and BSA^s , respectively. The k^f and k^s values reflect the rates of BSA desorption in the initial and later stages of cleaning, respectively. Γ_0^s includes the amount of BSA remaining on the particles after 120-min cleaning (Γ_r). The kinetic constants were calculated by a data-fitting procedure based on a nonlinear least-squares regression method¹⁴.

2. 6 Analytical procedures

The BSA concentration was measured by the dye-binding method as described previously¹⁴. The apparent surface charge density (σ_{app}) of stainless steel particles were determined by potentiometric titration as described previously¹¹. The chemical composition of the outermost surfaces of stainless steel particles was determined by X-ray photoelectron spectroscopy (JPS-9200 ; JEOL Ltd., Tokyo) using a

monochromatized AlK α radiation at 300 W (12 kV). For the analysis, stainless steel particles were molded into a plate (13 mm diameter $\times$ 1 mm thickness) by compression (40 MPa, 2 min).

2. 7 Statistical analysis

All experiments of adsorption and cleaning were replicated three times for each of the samples. The Γ_{sat} , Γ_0 , Γ_r , and kinetic constants of eq. 1 were represented as the mean value $\pm$ standard deviation (SD). Significant differences in the mean values were determined with t test at the level of $P < 0.05$.

3. Results

3. 1 Characterization of surface-pretreated stainless steel particles

Table 1 shows the atomic composition of main metal components of the outermost surfaces of the dried, treated, and HNO $_3$ -treated stainless steel particles before and after 0.2% ozone treatment. Large differences were observed in the surface atomic composition depending on pretreatment method. Compared with the atomic composition of non-surface-treated particles, heat-drying at 150°C exerted no influence on the surface chemical composition, whereas pretreatments with heating at 400°C and 10%

HNO $_3$ resulted in the enrichment of iron and chromium in their surfaces, respectively. On the other hand, as a result of ozone treatment, no significant variations in the surface chemical composition were found in all the pretreated particles.

Figure 1 shows the σ_{app} curves of non-surface treated, dried, heated, and HNO $_3$ -treated stainless steel particles as a function of pH before and after 0.2% ozone treatment. The pzc_{app} of non-surface-treated particles was found to be 9.8 (Fig. 1A). Pretreatments with heat-drying at 150°C, heating at 400°C, and 10% HNO $_3$ resulted in the shifts in the $\text{pzc}'_{\text{sapp}}$ to 9.0, 7.3, and 6.0, respectively (Figs. 1B, 1C, and 1D). The σ_{app} curves of heated and HNO $_3$ -treated particles were characterized by low absolute values of positive and negative σ_{app} over the pH range of 4 to 10 compared with the curves of dried particles. In all cases of the pretreated particles, the σ_{app} curves were shifted to the acidic side after conducting ozone treatment. As a consequence, the $\text{pzc}'_{\text{sapp}}$ of ozone-treated particles were situated at points corresponding to more acidic pH values than the $\text{pzc}'_{\text{sapp}}$ of non-ozone-treated particles. The degrees of the shift in the pzc_{app} and of decrease in the absolute values of σ_{app} were more pronounced on dried particles (Fig. 1B). On the other hand, only a little change in the σ_{app} curve of HNO $_3$ -treated particles was observed (Fig. 1D).

3. 2 Adsorption of BSA

Experiments were designed to assess the effect of ozone treatment of the surface-pretreated stainless steel particles on BSA adsorption. To minimize the effects of electrostatic interaction between BSA molecules on their adsorption, BSA adsorption was conducted at the pzc_{app} of BSA, i. e., pH 5.0, where all the particles were positively charged. Table 2 shows the saturation amounts of BSA adsorbed (Γ_{sat}) on, and σ_{app} values at pH 5.0 of dried, heated, and HNO $_3$ -treated particles with and without 0.2% ozone treatment. Compared with the Γ_{sat} (2.82 mg/m 2) on dried particles, a larger Γ_{sat} of 3.78 mg/m 2 was obtained on heated particles, whereas an extremely low Γ_{sat} of 1.64 mg/m 2 was observed on 10% HNO $_3$ -treated particles. No correlation was found between Γ_{sat} and σ_{app} values

Table 1 Atomic composition of the surface-pretreated stainless steel particles before and after 0.2 vol % gaseous ozone treatment.

Stainless steel	Component (atom %)			
	Fe	Cr	Ni	O
Non-surface-treated	6.7	6.5	ND ^a	78.0
Pretreatment				
Dried (150°C)	7.0	6.5	ND	77.6
Heated (400°C)	12.0	3.2	ND	75.1
10% HNO $_3$ -treated	5.2	10.8	ND	75.7
Pretreatment + 0.2% ozone				
Dried (150°C)	6.7	6.3	ND	77.9
Heated (400°C)	10.1	2.6	ND	76.5
10% HNO $_3$ -treated	5.8	10.1	ND	75.4

^a ND : not detected.
Gaseous ozone (0.2 vol %) treatment was conducted at room temperature for 60 min.

Fig. 1 σ_{app} curves of non-surface-treated and pretreated stainless steel particles as a function of pH before and after 0.2% ozone treatment. (A) Non-surface-treated particles. (B) Dried particles at 150°C. (C) Heated particles at 400°C. (D) 10% HNO $_3$ -treated particles. Potentiometric titration was conducted in 10 $^{-1}$ M KNO $_3$ solution. Symbols : $\circ$, before ozone treatment ; $\bullet$, after ozone treatment.

at pH 5.0 of non-ozone-modified pretreated particles. After conducting ozone treatment, the Γ_{sat} on dried particles decreased significantly ($P < 0.05$), whereas Γ_{sat} values on heated and HNO_3 -treated particles were the almost same as those on their particles before ozone treatment. The σ_{app} value of dried particles at pH 5.0 decreased from $+0.60$ to $+0.15 \text{ C/m}^2$ by ozone treatment. This change was relatively large compared with those observed for heated particles (from $+0.28$ to $+0.18 \text{ C/m}^2$) and HNO_3 -treated particles (constant at $+0.06 \text{ C/m}^2$).

3. 3 Kinetic analysis of nonlinear curve of BSA desorption

In order to simplify the comparison of the cleanability, non-ozone-modified and ozone-modified particles with the almost same Γ_0 value as each other were prepared for each of the pretreated particles because the rate of BSA desorption depends on Γ_0 values^{(12),(14)}. Figure 2 compares curves of BSA desorption from non-ozone-modified and ozone-modified dried, heated, and HNO_3 -treated particles, during cleaning with 0.1 M NaOH solution. In all cases of pretreated particles, the rate of BSA desorption was higher in the initial stage of cleaning and gradually

decreased as the residual amount of BSA decreased toward the later stage of cleaning. Significant differences, however, were observed in the curves of non-ozone-modified and ozone-modified particles. Each of the ozone-modified particles apparently showed a higher rate of BSA desorption and a smaller amount of BSA remaining on the particles after 120-min cleaning (Γ_r) than their non-ozone-modified particles. The solid lines in Fig. 2 were derived from the computer analysis using eq. 1 based on a nonlinear regression method. For each nonlinear curve, a fairly good fit of eq. 1 to the experimental data was obtained (multiple coefficient : $R > 0.998$). The estimated constants of eq. 1 for each curve are summarized in Table 3. In all cases of the pretreatment particles, significantly smaller values of Γ_0^s and Γ_r were obtained on the ozone-modified particles ($P < 0.05$). This indicated that the proportion of Γ_0^s , i. e., slower-desorbing BSA^s, to the whole adsorbed BSA molecules on stainless steel particles decreased by surface modification with gaseous ozone. In the case of dried particles, the k^f and k^s values for ozone-modified particles were 1.9-fold and 1.2-fold higher than those for non-ozone-modified particles although there was no significant difference ($P < 0.05$) in the k^s . Both the k^f and k^s values for ozone-modified HNO_3 -treated particles were significantly higher than those for non-ozone-modified particles ($P < 0.05$). On the other hand, in the case of heated particles, only the k^s increased significantly ($P < 0.05$), whereas the k^f was hardly changed.

4. Discussion

The results showed that the cleanability of stainless steel particles with various surface chemical composition during cleaning with 0.1 M NaOH solution could be improved by the surface modification with gaseous ozone. Apparently, the cleanability of stainless steel particles depends both on the magnitude of forces of interaction between BSA and stainless steel surfaces, and on the susceptibility of their surfaces to the clean-

Table 2 Saturation amounts of BSA adsorbed on, and the σ_{app} values of surface-pretreated stainless steel particles at pH 5.0 before and after 0.2 vol % gaseous ozone treatment.

Stainless steel	Γ_{sat}^a	σ_{app}
	(mg/m ²)	(C/m ²)
Dried (150°C)	2.82 ± 0.10	0.60
Dried (150°C)+0.2% ozone	2.07 ± 0.12	0.15
Heated (400°C)	3.78 ± 0.10 A	0.28
Heated (400°C)+0.2% ozone	3.91 ± 0.21 A	0.18
10% HNO ₃ -treated	1.64 ± 0.06 B	0.06
10% HNO ₃ -treated+0.2% ozone	1.62 ± 0.02 B	0.06

^a Mean value ± SD of the triplicated experiments.
Mean values marked with the same letter represent data that are not significantly different ($P < 0.05$).
BSA adsorption was conducted at 40°C and at pH 5.0.

Fig. 2 Curves characterizing the desorption of BSA from non-ozone-modified and ozone-modified stainless steel particles during cleaning with 0.1 M NaOH solution. (A) Dried particles at 150°C. (B) Heated particles at 400°C. (C) 10% HNO_3 -treated particles. Cleaning experiment was carried out at 40°C in a stainless steel column by feeding the NaOH solution at space time of 2.0 min. Symbols : ○, non-ozone-modified particles ; ●, ozone-modified particles.

Table 3 Kinetic constants^a of eq. 1 derived from data-fitting procedure and measurement values^a of Γ_0 and Γ_r

Stainless steel	Γ_0	Γ_r	Γ_0^f	Γ_0^s	k^f	k^s
	(mg/m ²)		(mg/m ²)		(min ⁻¹)	
Dried (150°C)	2.06 ± 0.05 A	0.41 ± 0.02	1.21 ± 0.04 A'	0.84 ± 0.01	0.062 ± 0.001	0.0064 ± 0.0001 A''
Dried (150°C) + 0.2% ozone	2.07 ± 0.11 A	0.28 ± 0.01	1.41 ± 0.14 A'	0.67 ± 0.09	0.12 ± 0.01	0.0077 ± 0.0012 A''
Heated (400°C)	3.27 ± 0.09 B	0.68 ± 0.06	1.84 ± 0.16	1.43 ± 0.08	0.16 ± 0.02 B'	0.0065 ± 0.0006
Heated (400°C) + 0.2% ozone	3.33 ± 0.02 B	0.47 ± 0.02	2.22 ± 0.02	1.11 ± 0.04	0.16 ± 0.02 B'	0.0078 ± 0.0001
10% HNO ₃ -treated	1.62 ± 0.05 C	0.59 ± 0.02	0.89 ± 0.07 C'	0.73 ± 0.06	0.053 ± 0.004	0.0019 ± 0.0005
10% HNO ₃ -treated + 0.2% ozone	1.62 ± 0.02 C	0.37 ± 0.01	1.00 ± 0.05 C'	0.62 ± 0.03	0.082 ± 0.005	0.0046 ± 0.0006

^a Mean value ± SD of the triplicated experiments.
Mean values marked with the same letter represent data that are not significantly different ($P < 0.05$).
Cleaning was conducted in a plug-flow column at 40°C by feeding 0.1 M NaOH.

ing action of the NaOH solution.

The Γ_{sat} values on dried, heated, HNO₃-treated stainless steel particles ranged between 1.6 and 3.8 mg/m². Norde and Giacomelli¹⁵⁾ calculated the maximum amount of BSA adsorbed of ca. 4 mg/m² for a closely packed monolayer on solid surfaces by assuming that the BSA molecule can be approximated by an equilateral triangle with a side of ~8 nm and a depth of ~3 nm. The Γ_{sat} values obtained in this study was less than this calculated value. In addition, BSA was adsorbed onto all of the particles in an irreversible fashion. These findings suggest that BSA molecules (BSA^f plus BSA^s) are directly adsorbed on the particles within a monolayer coverage.

Ozone treatment changed the σ_{app} curve of dried particles considerably, but not the surface chemical composition. The Γ_{sat} on ozone-modified dried particles was significantly less than that on their non-ozone-modified particles. These results were in good agreement with our previous studies^{11),16)}. The facts that the shift in the pzc_{app} to the acidic side and decrease in the positive values of σ_{app} occurred by ozone treatment were due to the removal of surface OH groups, especially the base OH groups (M-OH₂⁺), by oxidative action of gaseous ozone^{11),17)}. The base OH groups, i. e., the surface OH groups singly coordinated to the metal ion, act as the adsorption site for carboxyl groups on organic acids¹⁸⁾. BSA is also adsorbed on positively charged stainless steel surfaces (M-OH₂⁺) through varying numbers of carboxyl groups on the molecule¹⁹⁾. Therefore, the decrease in Γ_{sat} on the dried particles could be interpreted as arising from the decrease in the positive σ_{app} of stainless steel particles at pH 5.0. The Γ_{sat} values on ozone-modified, heated, and HNO₃-treated particles were the almost same as those on their non-ozone-modified particles, respectively. According to the above discussion, this was probably due to that ozone treatment of heated and HNO₃-treated particles resulted in only slight changes in their surface chemical

composition and the σ_{app} values. On the other hand, the Γ_{sat} , expressed as mass, was not always correlated with the magnitude of the forces of interaction between BSA and stainless steel surfaces. Kinetic analysis of curves of BSA desorption showed that significantly smaller proportions of Γ_0^s (including Γ_r) to Γ_0 , and significantly higher values of at least either k^f or k^s were obtained for all the ozone-modified particles ($P < 0.05$) when compared at the same Γ_0 values as those on the non-ozone-treated particles (Table 3). These findings indicated that the binding strength of BSA on the ozone-modified particles was smaller than that on their non-ozone-modified particles, even if there was no significant difference in the Γ_{sat} values. It is reasonable that the binding strength of BSA depends on the number of attached carboxyl groups on BSA²⁰⁾. A small σ_{app} value of ozone-modified particles allow a conformation of BSA with less interaction points and hence weak interactions with BSA. These BSA molecules are more rapidly desorbed by cleaning with the NaOH solution. Thus, controlling the σ_{app} value of stainless steel particles was found to be one of important factors improving their cleanability.

Besides the magnitude of the BSA-stainless steel interactions, another factor governing the cleanability is the electrostatic repulsive action of stainless steel surfaces against the adsorbed BSA molecule. It has been pointed out that the primary function of cleaning chemicals is to minimize the magnitude of attractive forces between soil and solid surface by adsorption of cleaning chemicals both on soil and on solid surface, and that preferential displacement is one of the principal cleaning mechanisms²¹⁾. The detergency of NaOH solution is due to the action of OH⁻ ions. High concentrations of OH⁻ ions enhance the degrees of solubility and dispersion of adsorbed BSA molecule in the NaOH solution. In addition, OH⁻ ions cause deprotonation (i. e., adsorption of OH⁻) of acid surface groups on stainless steel particles and BSA. As a

result, BSA and stainless steel surfaces are more negatively charged, creating the electrostatic repulsive forces between BSA and stainless steel surfaces. Large negative σ_{app} values of stainless steel particles at alkaline conditions are equivalent to the presence of large numbers of adsorption site for OH^- ions. Therefore, the surfaces showing large-negative charge are susceptible to the cleaning action of OH^- ions and they give greater repulsive forces toward BSA, thereby accelerating BSA desorption and reducing the Γ_r . In this study, ozone-modified dried and ozone-modified heated particles showed larger negative σ_{app} values at alkaline pH region than their non-ozone-modified particles except for the case of HNO_3 -treated particles (Fig. 1). The σ_{app} value could not be measured in 0.1 NaOH solution (pH 13) by potentiometric titration. Nevertheless, it was suggested that elevated repulsive forces on ozone-modified particles are responsible for a decrease in Γ_r and an increase in the k^s . It was noted that relatively larger Γ_r values were obtained on heated and HNO_3 -treated particles although Γ_{sat} values were different from each other. It has been reported that cleanability of 20% HNO_3 -treated 316 L stainless steel surfaces fouled with β -lactoglobulin during cleaning with 0.25 M NaOH solution were lower than non- HNO_3 -treated surfaces^{(22), (23)}. It is assumed that heated and HNO_3 -treated particles could not give great repulsive forces toward BSA because their particles were less negatively charged at alkaline pH region. In a practical cleaning, it is desirable to accelerate the rate of the later stage of cleaning (k^s), and reduce the amount of soils remaining on stainless steel surfaces (Γ_r). These requirements were fulfilled to some extent by surface modification of stainless steel particles by gaseous ozone.

In this paper, the point of the argument was focused on the comparison of the cleanabilities only of each of the pretreated particles before and after ozone treatment, but not among the pretreated particles. Studies on the influence of the enrichment of Fe or Cr in the passive film on stainless steel particles on the degree of fouling and cleanability are also in progress and will be reported elsewhere.

5. Conclusions

In this study, the cleanabilities of non-ozone-modified and ozone-modified stainless steel particles with various surface properties were compared by evaluating the kinetic constants for BSA desorption in a plug-flow column fed by a 0.1 M NaOH solution.

Kinetic analysis showed that the cleanability of stainless steel particles could be improved by gaseous ozone treatment irrespective of the surface chemical composition of the original particles. It was concluded that modification of the σ_{app} value by ozone could induce a reduction of the binding strength of BSA and an increase in electrostatic repulsion forces between BSA and stainless steel surfaces in the NaOH solution.

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