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Evaluation of flocculation performance of polysaccharide-protamine complex flocculant by flocculation model

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Abstract

Flocculation experiments were conducted with three kinds of polysaccharide-protamine complex flocculants. Alginate, κ-carrageenan, and pectin were used as typical polysaccharides. The polysaccharides have carboxyl and sulfate groups, and it can be considered that the polysaccharides could bind basic protein, such as protamine, at around the neutral pH (pH 6.5-7.5). The relative absorbance was used as an index of the flocculation efficiency. Influences of the mass ratio (polysaccharide/protamine) and dosage of the complex flocculants on the flocculation efficiency were investigated. Judging from the results, the optimum mass ratio of polysaccharide and protamine was found as 0.4 for alginate and 1.0 for κ-carrageenan and pectin. The previously proposed flocculation model was applied to the data successfully and the proportional constant, stoichiometric coefficients, and the equilibrium adsorption constant regarding as forming flocs were determined by fitting to the data and using a least square method. Judging from the model parameters, the total number of acidic groups, and the molecular weight of each polysaccharide, the alginate-protamine complex could be the most effective flocculant.

Keywords: flocculation; complex flocculant; alginate; κ-carrageenan; pectin; protamine

1. Introduction

The flocculation of suspended solids has been used to improve solid-liquid separation in mineral processing operations, wastewater treatment, and so on. The usages of conventional chemically synthesized flocculants and alum are not desirable because of their high environmental impacts. From these reasons, in the last two decades, the development of environmentally friendly biodegradable flocculants have been studied and reported, i.e., chitin or chitosan [1-3], methylated proteins [4-6], extracellular polymers produced by bacteria [7-9], chemically modified natural polymer or polysaccharide [10-17], starch-based flocculant [18], cellulose-based flocculant [19-21], alginate-based flocculant [22-24], and so on. Among them, polysaccharides have also frequently been employed as bio-flocculants. Polysaccharides used as bio-flocculant were mainly alginate, chitosan, cellulose, starch, pullulan, xanthan, and pectin [25,26].

Recently the studies on the utilization of pectin [26-30] and κ-carrageenan [31-34] as flocculants have been reported. Pectin is easily found in most fruits and κ-carrageenan is found in most red algae, which are distributed worldwide. The major component of pectin is a polymer of α-D-galacturonic acid, and the carboxyl groups of the α-D-galacturonic acid are either free or esterified with methyl group [27]. On the other hand, The structure of κ-carrageenan is made up of α(1-4)-D-galactose-4-sulphate and β(1-3)-3,6-anhydro-D-galactose [35]. Judging from their structures, both pectin and κ-carrageenan have an anionic group as sulfate and carboxyl groups, respectively.

Recently we reported a new type of bioflocculant, which is consisted of an alginate-protamine complex [36]. This approach allowed that a single substance alone does not have flocculation ability, but by mixing two substances to form a complex, flocculation ability can appear. Alginate and protamine are mainly included in brown algae and salmon milt as nucleoprotein, however, not all brown algae and salmon milt are globally used as food or industrial raw materials. From viewpoint of the utilization of bio-resources, our approach of complex flocculant can be regarded as one of the ways to increase the added value of bio-resources. It is necessary to verify whether this complex flocculant can achieve an effective flocculation effect even in combination with other polysaccharides besides alginate. It is also necessary to verify whether the optimal conditions for flocculation performance can be determined by our flocculation model using various types of flocculants.

In this study, we used three polysaccharides, alginate, κ-carrageenan, and pectin to form a complex flocculant mixing with protamine. Pulverized quartz sand powder was chosen as model solid particles. The flocculation experiments were conducted and the influence of the mass ratio of polysaccharide and protamine and the dosage of the complex flocculants were investigated to compare their flocculation efficiency. In addition, the flocculation model proposed previously [37] was applied to evaluate their flocculation efficiency.

2. Experimental

2.1. Materials

Protamine sulfate from salmon, *κ*-carrageenan, and quartz sand were purchased from Wako Pure Chemical Industry (Japan). Sodium alginate and pectin were purchased from Kanto Chemical Co. Inc. (Japan). Hydrochloric acid and sodium hydroxide (analytical grade) were used for pH adjustment. These reagents were used without further purification.

2.2. Preparation of quartz powder suspension

The quartz powder and its suspension were prepared by the following procedure. The quartz sand was washed with distilled water and was dried at 60°C. Then, it was pulverized for 48 hr using a ceramic ball mill. The pulverized quartz powder was washed with distilled water repeatedly 2 times and was dried at 60°C for 48 hr. The size distribution was measured with a laser-scattering size distribution analyzer (LA-300 HORIBA, Ltd., Japan). The mean particle diameter of the quartz powder was 47.3 μm, and the standard deviation was 25.3 μm. The desired weight of powder was boiled with 1000 mL of distilled water in an Erlenmeyer flask to soak the particle surface thoroughly with water. A dilute HCl or NaOH solution was added to adjust the final pH of the suspension to pH 6.9-7.1. In this study, this suspension was used as a stock suspension for all the experiments. In most experiments, the concentration of the suspension was 3 g/L.

2.3. Clarification experiments

Quartz powder suspension (3 g/L, 100 mL) was poured into a 100 mL glass graduated cylinder. The solutions of protamine (2 mL) and polysaccharide (2 mL) were mixed and stirred vigorously for five seconds, and then the mixture was added immediately to the quartz powder suspension in a 100 mL glass graduated cylinder. In the case of single component experiments, 2 mL of protamine or polysaccharide was added to the quartz powder suspension. After the addition of protamine, polysaccharide, or their mixture, the suspension was stirred with a magnetic stirrer at 500 rpm. After 5 minutes, stirring was stopped and the suspension was left to stand for 1 minute. Then a 3.5 mL sample was sampled at a depth of 2 cm from the surface of the suspension. The absorbance of the sample was measured at 700 nm spectrophotometrically. The flocculation efficiency was evaluated with the relative absorbance, A/A_0, where A and A_0 represent the absorbance of the suspensions in the presence and the absence of flocculant, respectively. Most of the clarification experiments were repeated at least twice. All clarification experiments were conducted in the range of pH 6.95-7.05.

2.4. Flocculation model

In the flocculation model, a bridging flocculation process could be considered to be a binding reaction between the surface covered with flocculant on one particle and the bare surface of another particle.

$$m\mathrm{FS} + n\mathrm{S} \leftrightarrow \mathrm{F}_m\mathrm{S}_{m+n}\ ;\ K_\mathrm{b} \quad (1)$$

Where FS and S represent the surface covered by flocculant and the bare surface, and m and n represent the stoichiometric coefficients concerning FS and S. K_b is the equilibrium constant of the reaction expressed by Eq. (1). The detailed derivation would like to be referred to in the previous paper [37]. The flocculation efficiency, η, was defined by the following equation.

$$\eta = A_\mathrm{f}K_\mathrm{b}\theta_\mathrm{a}^{\ m}(1 - \theta_\mathrm{a})^n \quad (2)$$

$$\eta = 1 - A/A_0 \tag{3}$$

Where A_f and θ_a are the proportional constant and the fractional coverage of particle surface by flocculant. θ_a was defined as follows.

$$\theta_a = X/X_s = KC/(1 + KC) \tag{4}$$

Where C and K represent the equilibrium concentration and the equilibrium adsorption constant. X and X_s represent the adsorption density and the saturated adsorption density of complex flocculants. The mass balance of the complex flocculant gives the following relationship.

$$m_pX = (C_i - C)V \tag{5}$$

Where m_p and V represent the mass of particles in the suspension and the volume of suspension. C_i represents the initial concentration of complex flocculant in the suspension. From Eqs. (4) and (5), C is obtained as follows.

$$C = (1/2)(P + (P^2 + 4C_i/K)^{0.5}) \tag{6}$$

P in Eq. (6) is defined as:

$$P = C_i - (m/V)X_s - (1/K) \tag{7}$$

As described above, we assumed K is equal to K_p. The experimental flocculation efficiency

$(1 - A/A_0)$ was applied to Eq. (2), and, the model parameters, A_f, K_b, X_s, n, and m were determined by using Eqs. (3), (4), and (6), and a least-squares method.

3. Results and discussion

3.1. Verification of flocculation ability of polysaccharide-protamine complex flocculant

Typical results of the clarification experiments are shown in Fig. 1. The ordinate, A/A_0, is the relative absorbance, and the lower A/A_0 value means higher flocculation efficiency. Fig. 1a shows the influence of protamine dosage on the flocculation efficiency without polysaccharides. The value of A/A_0, decreased with an increase in the dosage of protamine and showed the minimum value (ca. 0.45) at ca. 1×10^{-3} g/L of protamine dosage in the system. In Fig. 1a, the maximum and minimum standard deviations were 2.46×10^{-2} and 1.06×10^{-3}, respectively.

At around the neutral pH (pH 6.5-7.5), protamine which is a basic protein has a positive charge, because the isoelectric point of protamine is about pH 12-13 [38], while quartz particle has a negative surface charge. Thus, protamine could flocculate the quartz particles.

We also conducted clarification experiments by using the polysaccharide-protamine complex as flocculants. The results are shown in Fig. 1b. In these experiments, the protamine dose was fixed at 4×10^{-4} g and the polysaccharides dose was varied. However, the flocculation efficiency of protamine could not be sufficient. Fig. 1b shows the influence of the concentration of polysaccharides. The concentration of protamine was fixed at 4×10^{-3} g/L. As seen in Fig. 1b, the A/A_0 had the minimum value in all polysaccharides, and the minimum value of complex flocculants was much lower than that of the single component addition of protamine. Fig. 1c shows the results of clarification experiments, where protamine and polysaccharides were separately added to the quartz powder suspension. In this experiment, a 2 mL of protamine solution (0.2 g/L) was added to the quartz suspension, and subsequently, a 2 mL of polysaccharide solution (alginate, 0.02-0.2 g/L; κ-carrageenan and pectin, 0.04-0.4 g/L) was added. The concentration of protamine was fixed at 4×10^{-3} g/L (in 100 mL), the same concentrations as in Fig. 1b. The separate addition of protamine and polysaccharides has no flocculation ability.

In our previous study, we have already reported the flocculation ability of the alginate-protamine complex flocculant. Alginate molecule has carboxyl group, and κ-carrageenan and pectin molecules have a sulfonic group. These functional groups have a negative charge at the weak acidic and alkaline pH region. At around the neutral pH (pH 6.5-7.5), protamine molecule has a positive charge because of consisting of many arginines. Thus, κ-carrageenan and pectin molecules should also bind protamine molecules, and the complex is considered to be a positively charged high molecular weight polymer. The present results could reveal that the combination of alginate and protamine was not special and that polysaccharides or polymers with an opposite charge to protamine molecules at a certain pH could form a complex with excellent flocculation ability.

3.2. Influence of mass ratio of polysaccharide and protamine on flocculation efficiency

We considered that the mass ratio of polysaccharides and protamine plays an important role in flocculation efficiency. The clarification experiments were conducted with varying the mass ratio. In these experiments, the mass of protamine was fixed and the mass of polysaccharides was varied. The results are shown in Fig. 2. The abscissa of Fig. 2 represents the mass ratio of polysaccharides and protamine, and the ordinate of Fig. 2 represents the relative absorbance. The concentrations of protamine were shown in the figure.

In all cases, as increasing the mass of protamine, the flocculation efficiency was getting better even at the same mass ratio. For κ-carrageenan and pectin (Figs. 2b and 2c), at a mass ratio of about 1, A/A_0 value tend to show minimum value. On the other hand, in the case of alginate (Fig. 2a), mass ratio dependence of A/A_0 shows a quite different profile depending on the protamine concentration. At the protamine dosage of 6.0×10^{-5} g, 90 % of quartz particles remained in the suspension ($A/A_0 = 0.9$). On the other hand, at the protamine dosage of 4.0×10^{-4} g, only 3 % of quartz particles remained in the suspension ($A/A_0 = 0.03$). The low A/A_0 value was kept relatively wide mass ratio from 0.3 to 0.7. Judging from Fig. 2, the optimal dosage of protamine could be considered as 4.0×10^{-3} g/L for all three polysaccharides. In addition, the optimal mass ratio could be considered as 0.4-0.6 for alginate and 0.1 for κ-carrageenan and pectin, respectively.

3.3. Influence of dosage of complex flocculant on flocculation efficiency

The clarification experiments were also conducted at different doses of complex flocculants. In these experiments, the mass ratio of polysaccharide and protamine was fixed and the dosage was varied. Assuming that all protamine molecules added to the mixture bind to the polysaccharide molecules, the complex flocculant prepared at the same polysaccharide/protamine mass ratio has the same positive charge density even the dosage of complex flocculant was changed. The results are shown in Fig. 3. The selected mass ratio was represented in the figure legend.

As seen in Fig. 3, except for alginate at a mass ratio of 0.4 and 0.6, for all other polysaccharides, In the case, the flocculation caused by the charge neutralization, the flocculation efficiency shows the maximum value as a function of flocculant dosage

[39-41]. In general, the flocculation using inorganic or low-molecular mass flocculants falls into this category. On the other hand, the flocculation caused by the bridging of particles by the flocculants, the flocculation efficiency is kept in a wide range of dosage. In general, the flocculation using large molecular mass flocculants, such as synthesized polymers and polysaccharides fall into this category [42,43]. However, in this study, we cannot decide the flocculation mechanism caused by the polysaccharides. In the case of alginate at mass ratios 0.4 and 0.6, the minimum A/A_0 value was lower than other polysaccharides, and the dosage which gives the minimum A/A_0 value was also lowest among the three polysaccharides. This result suggests that the alginate-protamine complex could be the most promising flocculant among the three polysaccharides-polymer complexes. Based on the results shown in Fig. 3, the minimum A/A_0 values for the three polysaccharides-protamine complex flocculants and the dosage which gives the minimum A/A_0 values are summarized in Table 1. Judging from lesser dosage and lower A/A_0 value, in each complex flocculant, the optimal conditions in terms of mass ratio are regarded as 0.4, 1.0, and 1.0 for alginate, κ-carrageenan and pectin, respectively.

3.4. Application of flocculation model to experimental flocculation efficiency

We have previously proposed a flocculation model derived from taking into account bridging between a flocculant-adsorbed surface on a particle and a bare surface on another particle. By applying this model, the flocculation performance could be evaluated [37]. The detailed derivation of this model would be referred to in the previous paper [37]. Intrinsically, the adsorption equilibrium constant of each complex flocculant on quartz must be determined, but it is very difficult to determine the adsorbed amount of complex flocculant. Thus, we considered the adsorption of complex flocculant onto the quartz particle occurs by the binding between the guanidine or amino group of protamine in complex flocculants and the bare surface of quartz particles. In the previous study [37], the flocculation efficiency and the flocculation mechanism of methylated protein flocculant and associated colloidal flocculant consisting of methyl glycol chitosan and potassium polyvinyl sulfate were investigated. The adsorption of these flocculants followed the Langmuir adsorption isotherm. In this study, we assumed that the adsorption of the complex flocculant onto quartz particles also follows the Langmuir adsorption isotherm. In the case of Langmuir-type adsorption, the binding strength of adsorbate and adsorption site is reflected in the adsorption equilibrium constant. Thus, we considered that the equilibrium adsorption constant of protamine onto quartz particles can be an index of the binding strength of the complex flocculants, and we conducted the adsorption experiments of protamine with quartz powder. The adsorption isotherm of protamine is shown in Fig. 4. When the adsorption of protamine onto quartz particle follows the Langmuir adsorption isotherm, the equilibrium adsorption density is expressed by the following equation.

$$X_p = K_p X_{sp} C_p / (1 + K_p C_p) \tag{8}$$

Where C_p, K_p, and X_{sp} denote the equilibrium concentration, the equilibrium adsorption constant, and the saturated adsorption density for protamine, respectively. The Langmuir plot of the data shown in Fig. 4 gave a good linear relationship. The equilibrium adsorption constant, K, and the saturated adsorption density, Xs, could be determined as 1.54×10^2 L/g and 1.07×10^{-3} g/g-quartz by a least-squares method. The solid curve in Fig. 4 was the calculated line of Langmuir isotherm (Eq. (8)) using the two adsorption parameters.

The fitting results are shown in Figs. 5-7. The data of Figs. 5-7 are the same data shown in Fig. 3. The estimated parameters are summarized in Table 2. The results of the model calculation were considered to be in good agreement with the experimental data. However, as θ_a approached to 1, deviations of the calculated values and the experimental data were also observed at high θ_a range. The reason is considered as follows. For each complex flocculant, in the region of θ_a greater than θ_a which gives the maximum value of η (0.2 for alginate, and 0.4 for κ-carrageenan and pectin), the fractional coverage of the particle surface by the complex flocculants is high. The complex flocculants have the same positive charge, thus the bridging flocculation was considered to be prevented by the electrostatic repulsion force. It was confirmed that the flocculation model can be applied to the flocculation using the complex flocculants.

3.5. Influence of flocculant properties on optimal flocculation

Based on the estimated parameters summarized in Table 2, the following three parameters are calculated, that is, the ion-binding number, α, the optimum coverage, θ_{opt}, and the residual concentration, C_{opt}, of the complex flocculant left in the aqueous phase after flocculation, by the following equations.

$$\alpha = n/m \tag{9}$$

$$q_{opt} = 1/(1 + \alpha) \tag{10}$$

$$C_{opt} = 1/(\alpha K) = 1/(\ \alpha K_p) \tag{11}$$

The calculated parameters are summarized in Table 3, and the relationship of α, θ_{opt}, C_{opt}, and K_b are shown in Fig. 8 for each complex flocculant. In all cases, α decreased with increasing θ_{opt}, and the lower θ_{opt}, the more binding points appeared (Fig. 8a). It can be considered that the lower the θ_{opt}, the greater the adsorption intensity of the complex flocculant. In addition, as with θ_{opt}, α decreased with increasing C_{opt} for all complex flocculants (Fig. 8c). Higher α is associated with the lower θ_{opt}, and stronger adsorption intensity, whereas lower α is associated with weaker adsorption intensity and increase C_{opt}. As seen in Fig. 8b, θ_{opt}, decreased with increasing K_{b}. Combined with a discussion about Figs. 8a-c, the more binding points the greater K_{b}. The θ_{opt} of κ-carrageenan and pectin are comparable, but the K_{b} differs greatly. For alginate and pectin, K_{b} was similar, but θ_{opt} was significantly different. To discuss the reason in detail, the total number of acidic groups and molecular weights of the three polysaccharides are focused.

The total number of acidic groups of three kinds of polysaccharides was determined by conductometric titrations [44,45]. In addition, the molecular weight of polysaccharides was determined by measuring the intrinsic viscosity and using the Mark-Houwink-Sakurada equation [46]. The intrinsic viscosity, $[\mu]$, is expressed as follows using the Mark-Houwink-Sakurada equation.

$$[\mu] = K_{\mathrm{MHS}}\, M^{\beta} \tag{12}$$

Where K_{MHS} and β are the Mark-Houwink-Sakurada constant, and M is a molecular weight of polysaccharide. The determined total number of acidic groups and the molecular weight of polysaccharides are summarized in Table 4.

As seen in Fig. 8a, for all three complex flocculants, the lower θ_{opt}, the larger α, and the greater K_{b}. By comparison of three complex flocculants, for κ-carrageenan and pectin, θ_{opt} was similar but K_{b} was different, on the other hand, for alginate and pectin, K_{b} was almost the same but θ_{opt} was different. The difference between carrageenan and pectin may be due to the difference in the total number of acidic groups. The total number of acidic groups of pectin (4.48×10^{-3} mol/g) is about 2.4 times higher than that of carrageenan

(1.89×10^{-3} mol/g). The larger amount of protamine adsorbed onto pectin than carrageenan may have caused a significant difference in K_b. Although the molecular weight of alginate (193,000) is about 2.4 times that of pectin (82,000), θ_{opt} at the same K_b value is larger for pectin than for alginate. This result suggests that the pectin complex is larger than that of alginate when compared with the protamine binding complex. Thus the two particles can be easily bound across the electric double layer. This suggests that the three-dimensional structure of protamine-binding pectin and alginate is different. Finally, the performance of the alginate, carrageenan, and pectin-protamine complex flocculants was comprehensively compared based on the wide range of optimal flocculant dosage, a large number of ionic bonds, the low optimal coverage, the large adsorption constant K_b, and the low optimal flocculant concentration, the protamine-alginate complex flocculant was considered to have the highest performance.

4. Conclusion

The authors conducted the flocculation experiments with polysaccharide-protamine complex flocculants. Alginate, κ-carrageenan, and pectin were employed as typical polysaccharides. The flocculation ability of three polysaccharide-protamine complex flocculants were investigated on the flocculation ability, the mass ratio, and the dosage of these complex flocculants. It was found that the optimum mass ratio of polysaccharide and protamine was found as 0.4 for alginate and 1.0 for κ-carrageenan and pectin. The optimum dosage of protamine was found as 0.4 mg for all complex flocculants. By applying the flocculation model to the experimental results, the data agreed well to the model, and some model parameters were determined by a least-squares method. Based on the estimated parameters, the optimum fractional coverage, θ_{opt}, the ion-binding number, α, and the optimum residual flocculant concentration, C_{opt}, were calculated. It was found that the lower θ_{opt}, the much ion-binding number, and the greater the binding constant. Judging from the relationship of the parameters, the total number of acidic groups of each polysaccharide, and the molecular weight, the alginate-protamine complex was the most effective flocculant.

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Captions of figures and tables

Fig. 1. Influences of (a) protamine and (b, c) polysaccharide dosages on the relative absorbance, A/A_0. The concentration of quartz suspension was 3.0 g/L.

Fig. 2. Influence of mass ratio of polysaccharide and protamine on specific absorbance, A/A_0, of quartz suspensions for (a) alginate, (b) κ-carrageenan, (c) pectin.

Fig. 3. Influence of polysaccharide-protamine complex dosage on the relative absorbance, A/A_0 for (a) alginate, (b) κ-carrageenan, and (c) pectin.

Fig. 4. Adsorption isotherm of protamine onto pulverlized quartz particle surface. Solid curve is calculated from Eq. (8).

Fig. 5. Flocculation efficiencies of alginate-protamine complex flocculant as a function of the fractional coverage of the quartz surface by flocculant. The mass ratio was (a) 0.4, (b) 0.6, and (c) 0.8. The solid line represents the model prediction calculated using Eq. (2). The parameters used in the calculation is listed in Table 2.

Fig. 6. Flocculation efficiencies of *k*-carrageenan-protamine complex flocculant as a function of the fractional coverage of the quartz surface by flocculant. The mass ratio were (a) 1.0, (b) 1.2, and (c) 1.4. The solid line represents the model prediction calculated using Eq. (2). The parameters used in the calculation is listed in Table 2.

Fig. 7. Flocculation efficiencies of pectin-protamine complex flocculant as a function of the fractional coverage of the quartz surface by flocculant. The mass ratio were (a) 1.0, (b) 1.2, and (c) 1.6. The solid line represents the model prediction calculated using Eq. (2). The parameters used in the calculation is listed in Table 2.

Fig. 8. Relationship between (a) the fractional coverage of the quartz surface by flocculant at maximum flocculation efficiency and number of ionic bond on quartz particle, (b) the equilibrium constant and the fractional coverage of the quartz surface by flocculant at maximum flocculation efficiency, (c) the optimum additional concentration and number

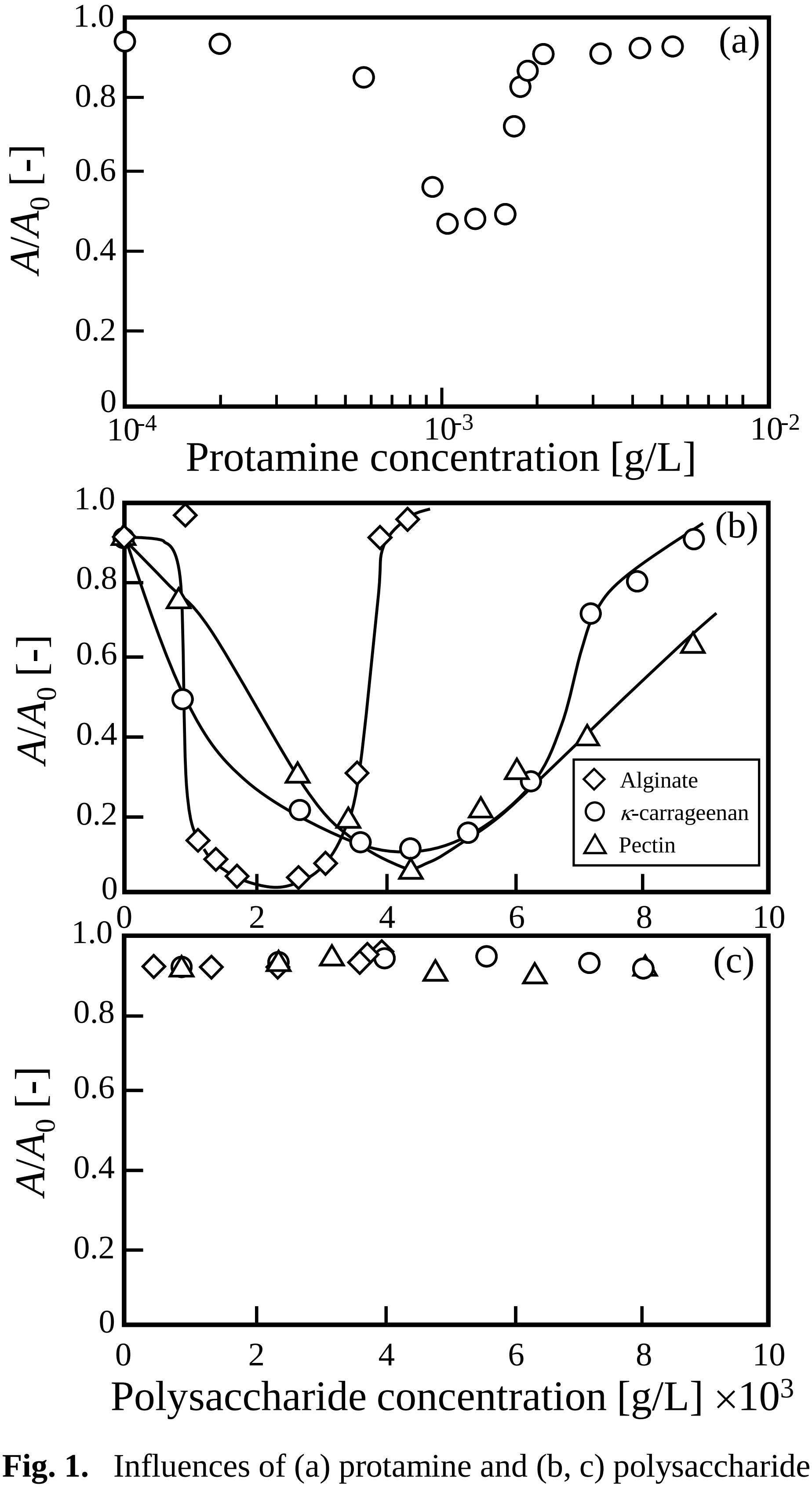
of ionic bond on quartz particle.

Table 1 Summary of the optimal dosage of complex flocculant and A/A_0 values at the dosage.

Table 2 Model parameters estimated from model calculation of quartz suspension flocculation by polysaccharide-protamine complex flocculant.

Table 3 Estimated values of α, θ_{opt}, and C_{opt} from model calculation.

Table. 4 The Mark-Houwink-Sakurada constant and Molecular weight of polysaccharide.



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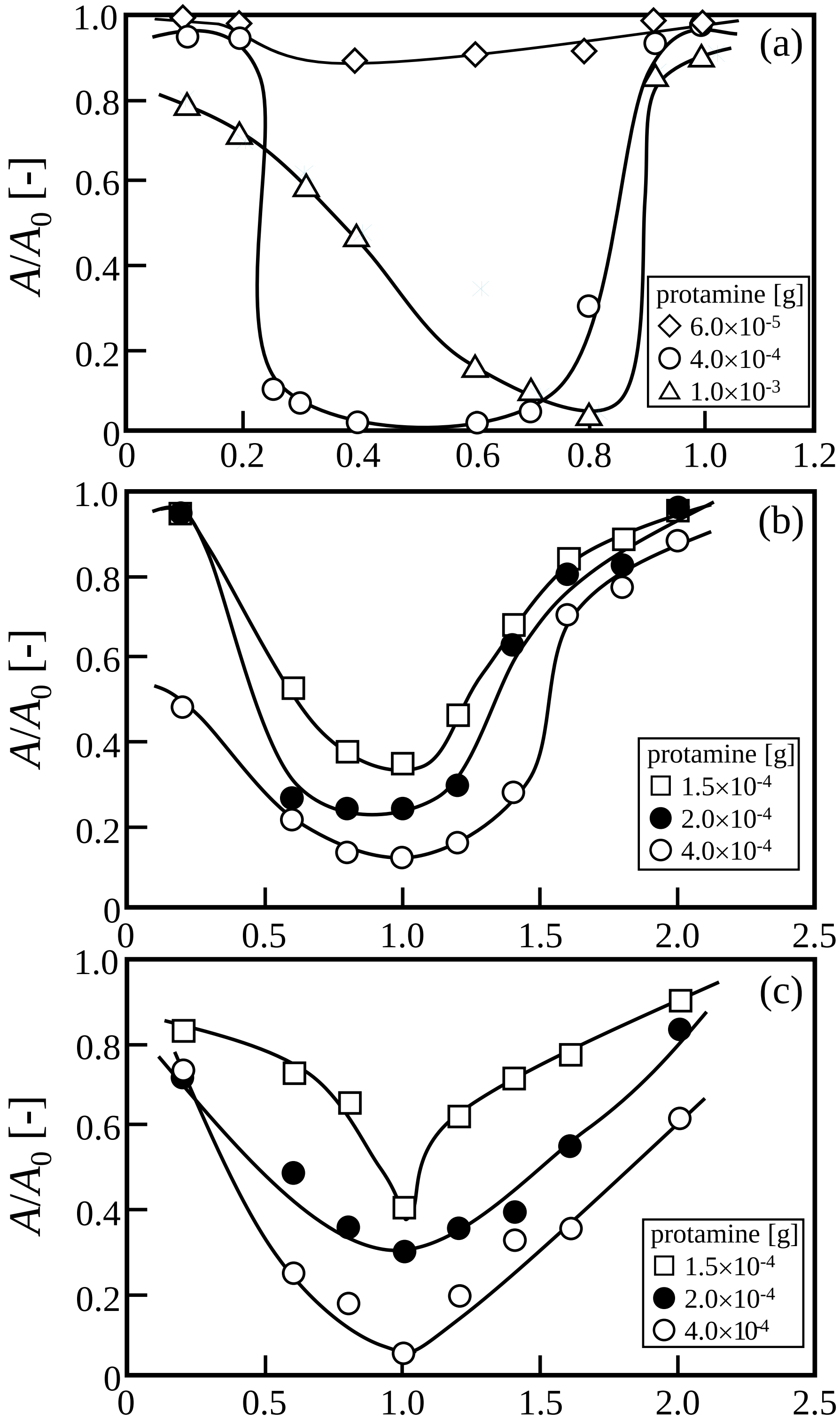


Fig. 2. Influence of mass ratio of polysaccharide and protamine on specific absorbance, A/A_0, of quartz suspensions for (a) alginate, (b) κ-carrageenan, (c) pectin

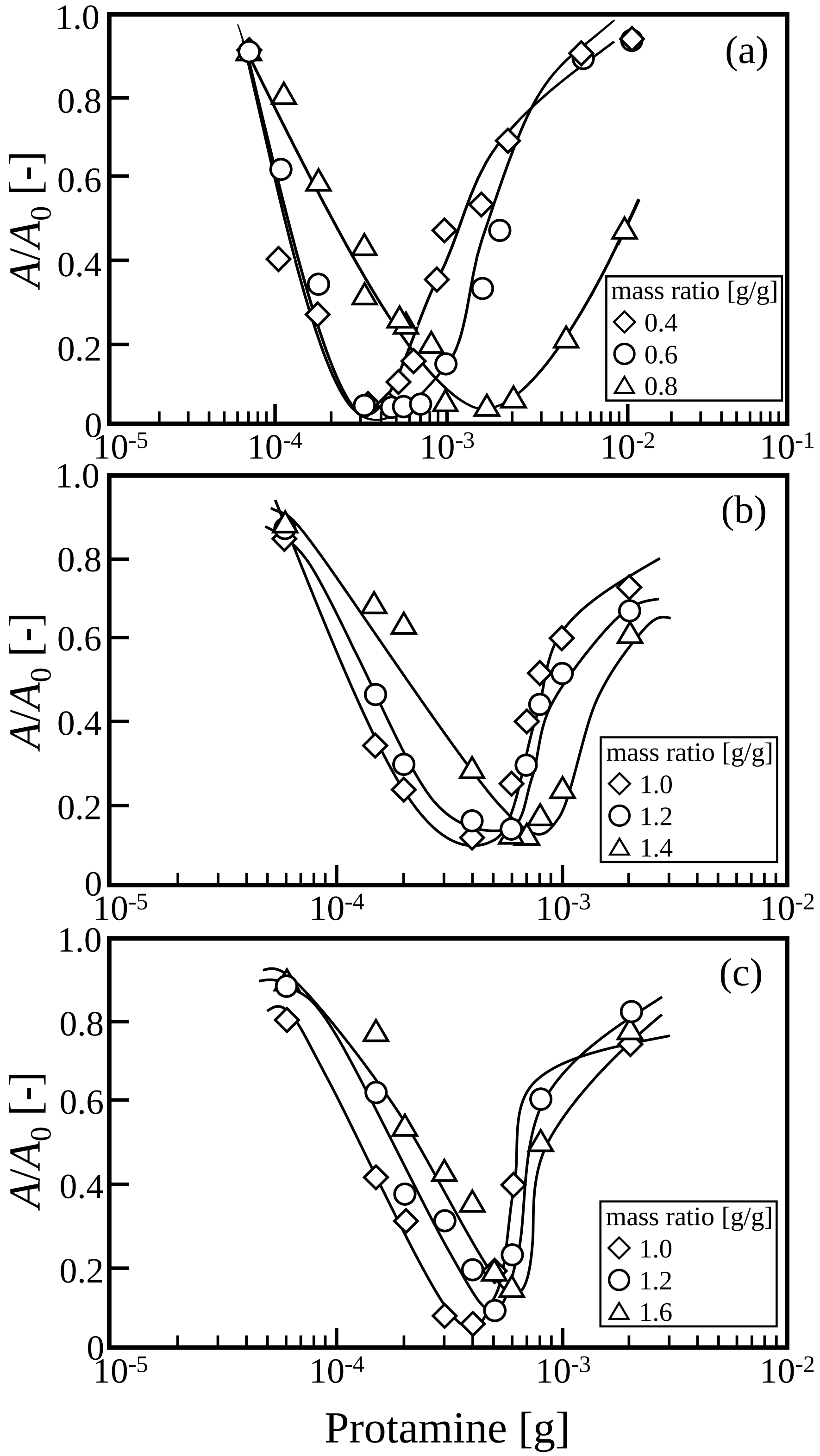
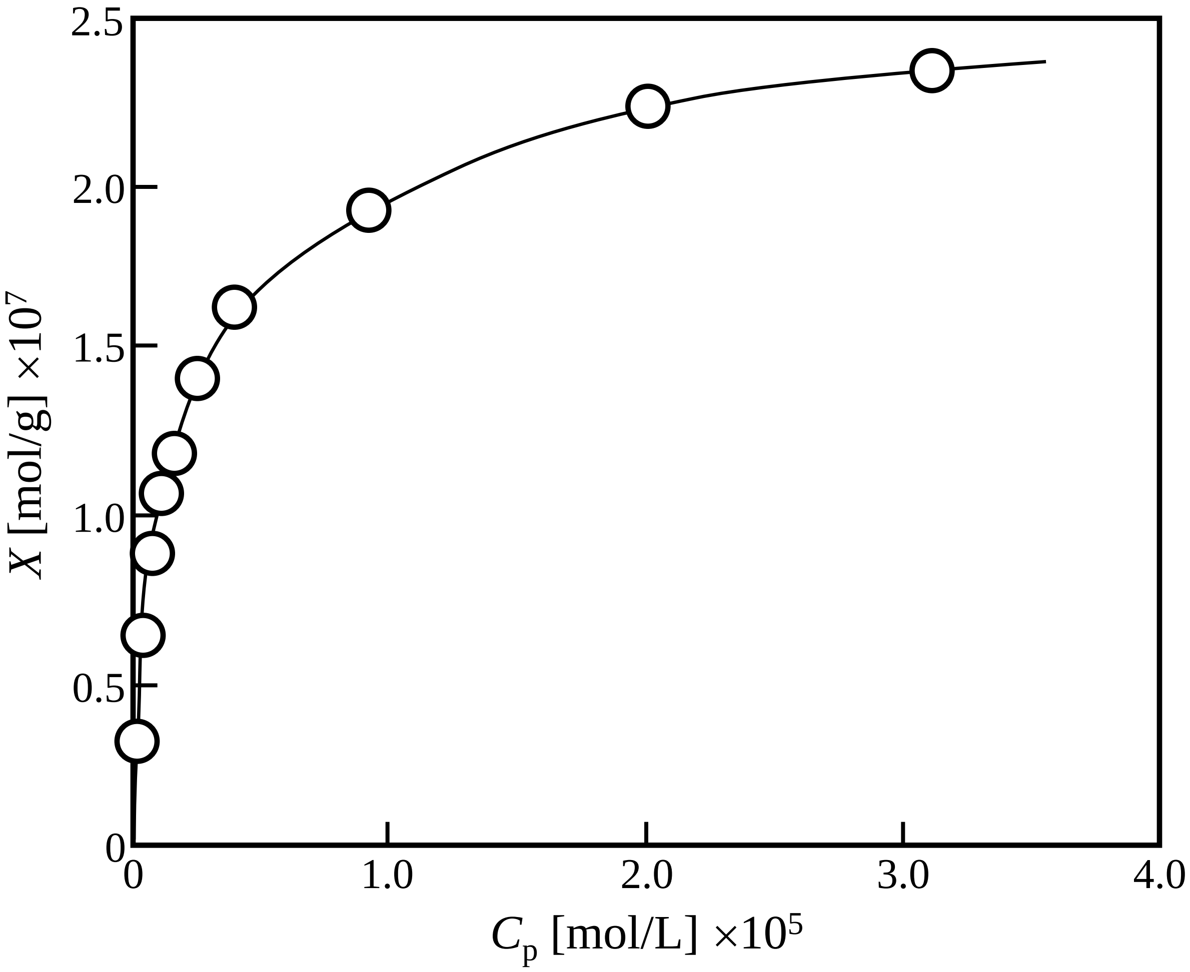


Fig. 3. Influence of polysaccharide-protamine complex dosage on the relative absorbance, A/A_0 for (a) alginate, (b) κ-carrageenan, and (c) pectin.



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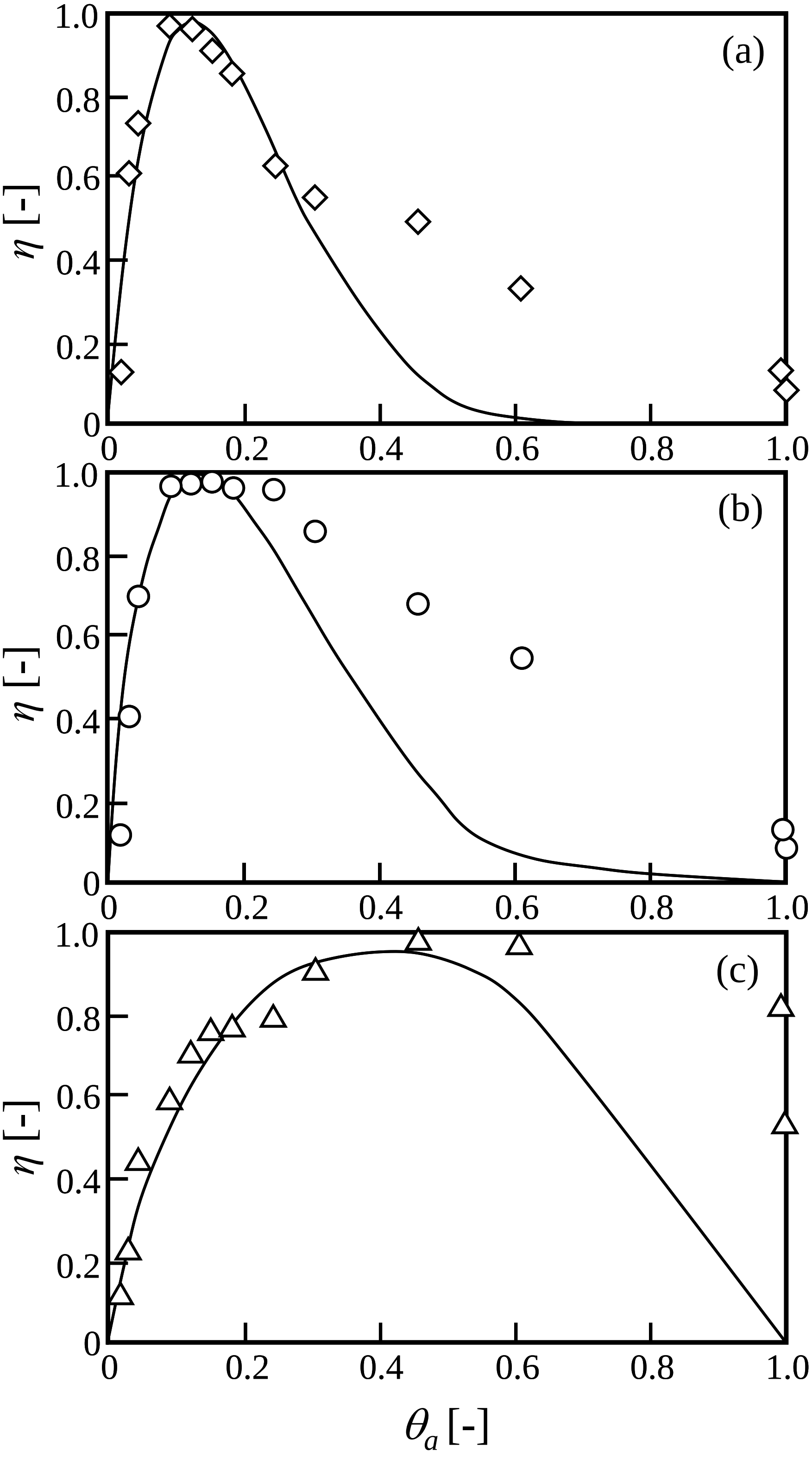

Fig. 5. Flocculation efficiencies of alginate-protamine complex flocculant as a function of the fractional coverage of the quartz surface by flocculant. The mass ratio was (a) 0.4, (b) 0.6, and (c) 0.8. The solid line represents the model prediction calculated using Eq. (2). The parameters used in the calculation is listed in Table 2.

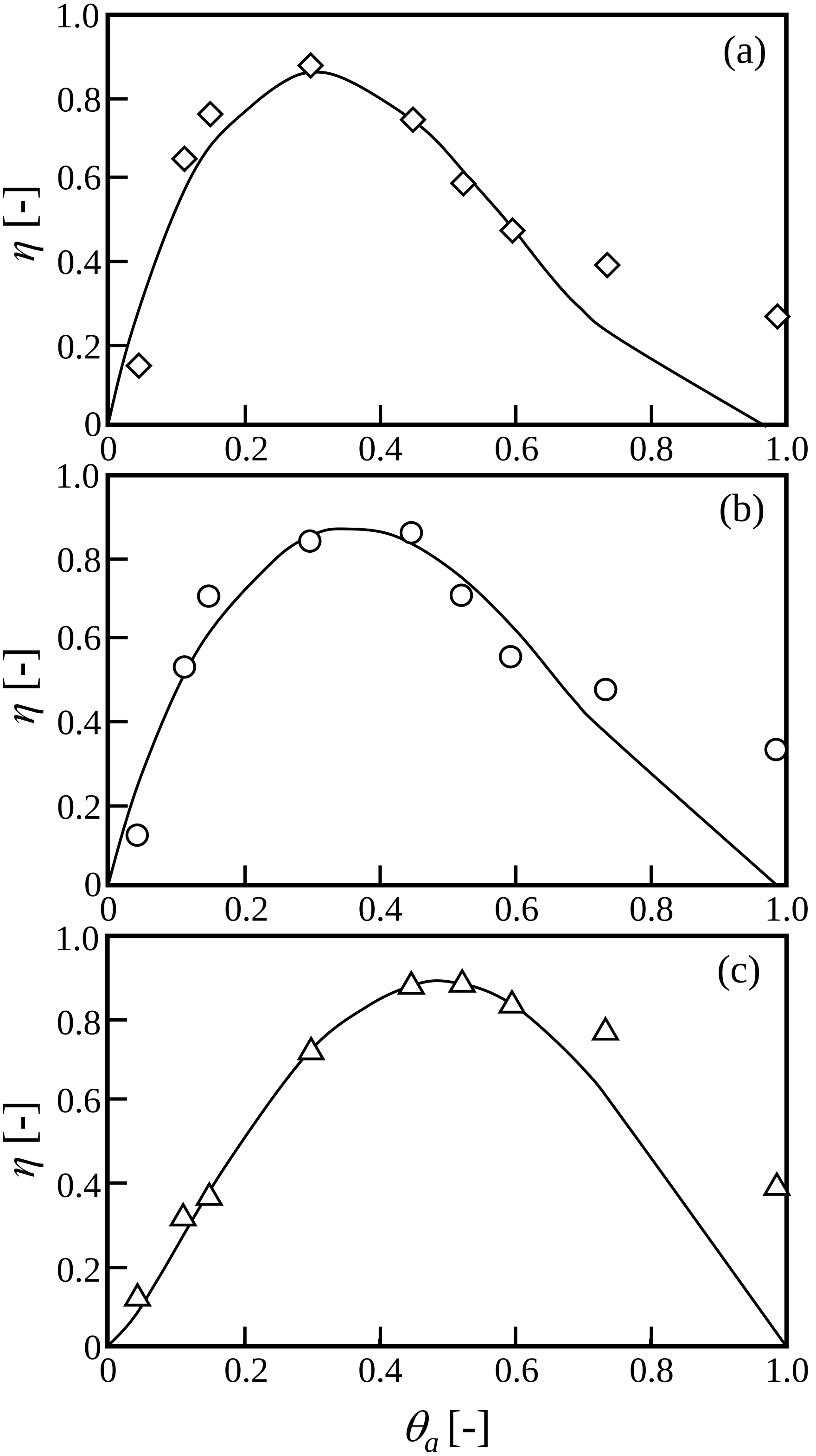

Fig. 6. Flocculation efficiencies of *κ*-carrageenan-protamine complex flocculant as a function of the fractional coverage of the quartz surface by flocculant. The mass ratio were (a) 1.0, (b) 1.2, and (c) 1.4. The solid line represents the model prediction calculated using Eq. (2). The parameters used in the calculation is listed in Table 2.

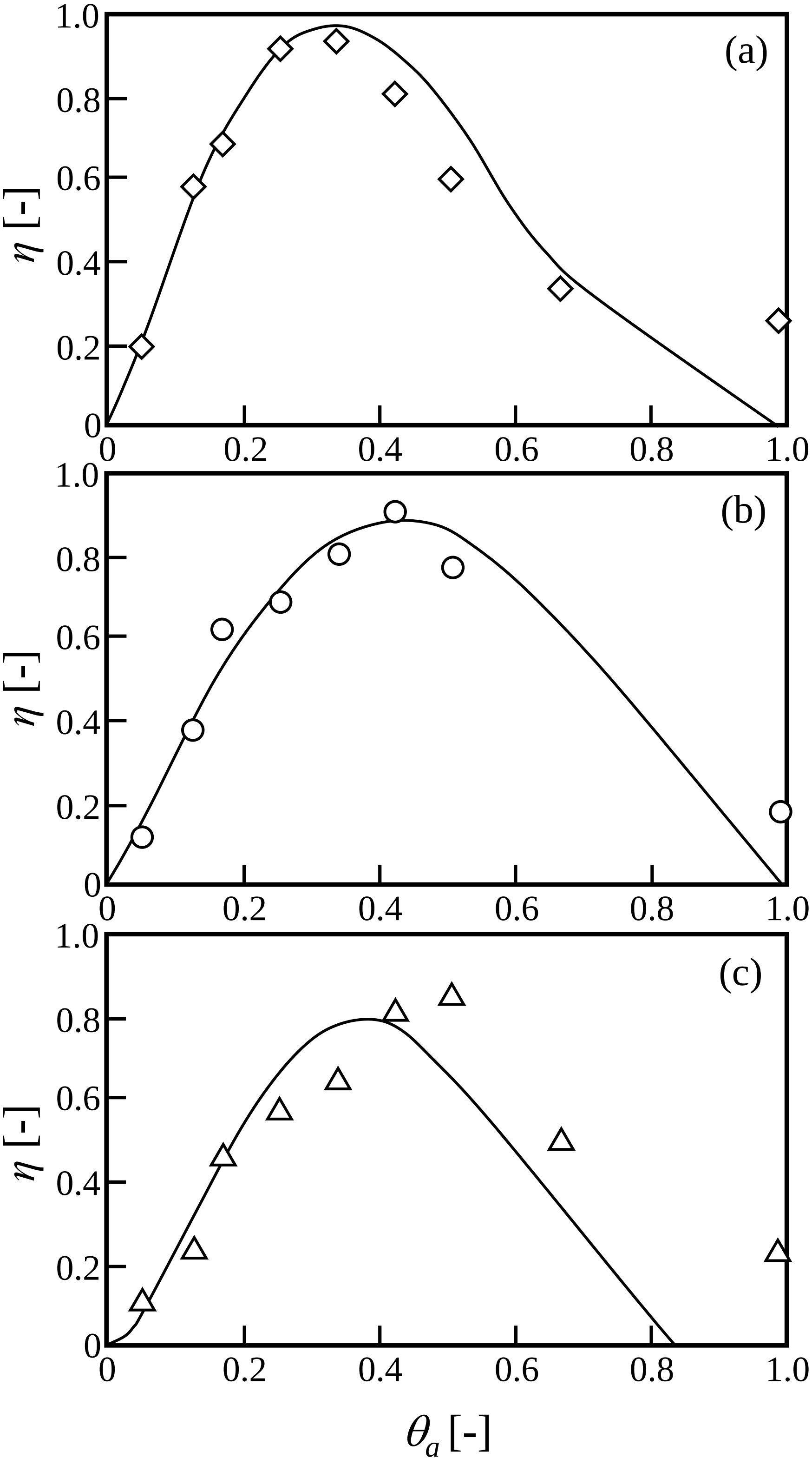

Fig. 7. Flocculation efficiencies of pectin-protamine complex flocculant as a function of the fractional coverage of the quartz surface by flocculant. The mass ratio were (a) 1.0, (b) 1.2, and (c) 1.6. The solid line represents the model prediction calculated using Eq. (2). The parameters used in the calculation is listed in Table 2.

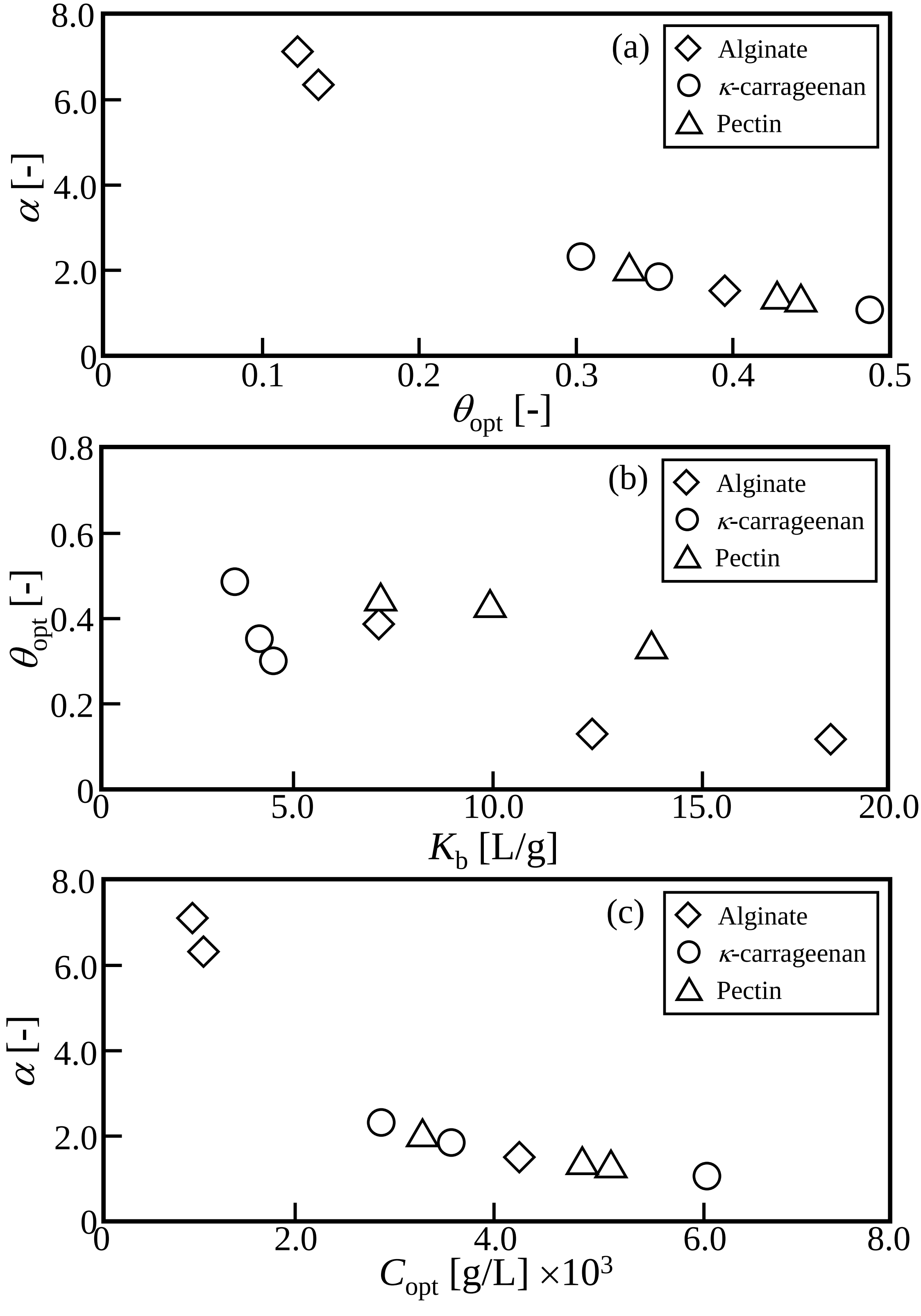

Fig. 8. Relationship between (a) the fractional coverage of the quartz surface by flocculant at maximum flocculation efficiency and number of ionic bond on quartz particle, (b) the equilibrium constant and the fractional coverage of the quartz surface by flocculant at maximum flocculation efficiency, (c) the optimum additional concentration and number of ionic bond on quartz particle.

Table 1

Summary of the optimal dosage of complex flocculant and A/A_0 values at the dosage.

	mass ratio [g/g]	optimal dosage polysaccharide [g]	 protamine [g]	A/A_0 [-]
alginate	0.4	1.2×10^{-4}	3.0×10^{-4}	0.026
	0.6	3.0×10^{-4}	5.0×10^{-4}	0.019
	0.8	1.2×10^{-3}	1.5×10^{-3}	0.020
κ-carrageenan	1.0	4.0×10^{-4}	4.0×10^{-4}	0.120
	1.2	7.2×10^{-4}	6.0×10^{-4}	0.118
	1.4	9.8×10^{-4}	7.0×10^{-4}	0.115
pectin	1.0	4.0×10^{-4}	4.0×10^{-4}	0.061
	1.2	6.0×10^{-4}	5.0×10^{-4}	0.091
	1.6	9.6×10^{-4}	6.0×10^{-4}	0.149

Table 2

Model parameters estimated from model calculation of quartz suspension flocculation by polysaccharide-protamine complex flocculant.

polysaccharide	mass ratio	γ	K_b	A_f	n	m
alginate	0.4	0.54	18.5	1.09	7.13	0.99
	0.6	0.54	12.5	0.73	4.83	0.76
	0.8	0.54	7.06	0.42	1.01	0.66
κ-carrageenan	1.0	0.22	4.36	1.35	2.16	0.94
	1.2	0.22	4.04	1.26	1.76	0.95
	1.4	0.22	3.41	1.74	1.41	1.33
pectin	1.0	0.19	14.0	0.89	2.66	1.33
	1.2	0.19	9.88	0.63	1.63	1.22
	1.6	0.19	7.11	1.34	2.02	1.60

Table 3

Estimated values of α, θ_{opt}, and C_{opt} from model calculation

polysaccharide	Mass ratio	α	θ_{opt}	C_{opt}
Sodium alginate	0.4	7.16	0.12	0.91×10^{-3}
	0.6	6.37	0.14	1.02×10^{-3}
	0.8	1.54	0.39	4.21×10^{-3}
κ-carrageenan	1.0	2.30	0.30	2.81×10^{-3}
	1.2	1.84	0.35	3.52×10^{-3}
	1.4	1.06	0.49	6.12×10^{-3}
pectin	1.0	2.00	0.33	3.25×10^{-3}
	1.2	1.34	0.43	4.85×10^{-3}
	1.6	1.26	0.44	5.14×10^{-3}

Table. 4 The Mark-Houwink-Sakurada constant and Molecular weight of polysaccharide.

polysaccharide	K_{MHS}	β	Molecular weight
Sodium alginate	$7.3\times10^{-5\ a,b}$	$0.92^{a,b}$	193,551
κ-carrageenan	$3.1\times10^{-3\ d}$	0.95^{d}	301,796
Pectin	$9.55\times10^{-5\ a,c}$	$0.73^{a,c}$	82,593

[a] Ref. [46]
[b] Ref. [47]
[c] Ref. [48]
[d] Ref. [49]