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Adsorption of lactose using anion exchange resin by adding boric acid from milk whey

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Abstract

Influence of adding boric acid (BA) on the adsorption behavior of lactose onto an anion exchange resin (IRA402) was investigated. By adding BA, the amount adsorbed of lactose onto IRA402 was increased ca. 20 % compared with without adding BA. In the presence of BA, ca. 70% of the adsorbed lactose could desorb from IRA402, while the absorbed lactose hardly desorbed in the absence of BA. Lactose molecular was considered to bind to tertiary amine group on IRA402 by Maillard reaction. The optimum conditions of the dosage of BA and pH were found at the molar ratio of BA to lactose ranging from 1-2, and pH 7-9. The kinetics and equilibrium of lactose adsorption could be explained by Langmuir adsorption model (best model). In the case of real whey solution, phosphate strongly affected the adsorption behavior and could be removed as precipitation from the whey over pH 10. Whey proteins had little effect on lactose adsorption, which was ca. 30% less than that in the model system. Moreover, the kinds of whey proteins and amino acids had little effect on the amount adsorbed. Minerals in the whey may consider to be also responsible for the decreased adsorption in the whey.

KEYWORDS: adsorption, lactose, milk whey, boric acid, tertahydroxyborate, anion exchange resin

1. Introduction

Whey is a byproduct of the manufacturing process of dairy products such as cheese and yogurt. Approximately 90% of raw milk is produced as whey in the cheese manufacturing process [1-3]. Domestic production of natural cheese in 2020 will be about 45,000 tons, and production volume in Japan has increased by about 30% over the past 10 years. The production of whey, a by-product of this increase, is estimated to be at least 400,000 tons. The chemical oxygen demand (COD) of whey as an indicator of water pollution is 60,000-80,000 mg/L, and lactose in particular has been reported to have the greatest impact on COD levels. The COD standard for wastewater in Japan is 160 mg/L, which indicates that whey has an extremely high environmental impact.

Whey is a byproduct that has a high environmental impact when disposed of in rivers, but efforts are underway to make effective use of it. Efforts include concentrating and drying whey, processing it into whey powder, adding it to confectionery, bread, and ice cream, and adding it to feed livestock such as pigs to improve meat quality. The main constituents of whey are lactose (45-50 g/L), whey proteins such as β-lactoglobulin, α-lactalbumin, and lactoferrin (6-8 g/L), and minerals such as calcium, phosphorus, sodium, potassium, and minerals (80-100 g/L) such as calcium, phosphorus, sodium, potassium, magnesium and so on [4]. Separation/recovery of these components can result in the more effective use of whey. However, since whey tends to spoil at room temperature and is produced in large quantities, effective utilization of whey requires large capital investment and management and maintenance costs for storage facilities for quality control and various processing equipment. As a result, whey processing is not profitable for small and medium-sized producers, and whey is often disposed of as industrial waste, except for some producers who use it as animal feed. At present, whey is mainly treated in septic tanks in Japan, but manufacturers still have to bear the cost of treating whey when it is disposed of. Therefore, it is important to separate and recover lactose from whey to reduce the burden of whey treatment and make effective use of these bio-resources. Although membrane separation using ultrafiltration membranes is used as a large-scale industrial separation method for lactose, a simpler separation method is desirable for relatively small dairy plants [5-7].

Adsorption is one of the most widely used separation methods in many fields because it is easy to operate and often does not require expensive equipment [8-10], and several adsorbents have been employed to remove heavy metals, i.e., ion-exchange resin [11-13], activated carbon [14-16], zeolite [17-19], hydrogel [20,21], etc. Thus, the recovery of lactose from whey by adsorption is recommended because it is considered to be an easy separation method for small- and medium-scale producers. The relatively inexpensive adsorption technique could reduce the BOD load of wastewater even in small-scale plants or producers. The authors think this manner is the practical value of this study.

In this study, for the separation of lactose in whey, we attempted the adsorptive separation of the complex on an anion exchange resin using the reaction in which a polyhydric alcohol compound with a diol structure, such as sugar, forms a negative complex structure with boric acid [22]. This complexation reaction has been used for the analysis of sugars by HPLC and boron-selective anion exchange resins [23,24], but there are few reports on its application to the separation of sugars in liquids. Separation of lactose from milk whey by utilization of boric acid and commercial anion exchange resin and by formation of complexation with lactose boric acid has been not reported yet.

Firstly, batch adsorption experiments using lactose solution (model system) were conducted to investigate the influence of the kind of the counterion of the anion exchange resin on the amount adsorbed of lactose, and the influence of the addition of boric acid on adsorption and desorption abilities on the anion exchange resin. Then, the influences of the molar ratio of boric acid to lactose and the pH of the solution on the adsorption kinetics and equilibrium were also investigated, and the optimum conditions (molar ratio and initial pH) were determined. The adsorption kinetics under the optimum conditions were evaluated using rate constants obtained from the pseudo-second-order rate equation and the Langmuir rate equation, and the saturated amount adsorbed and the adsorption equilibrium constant were obtained from the Langmuir adsorption model. In addition, adsorption experiments were carried out with actual whey solution under the optimum conditions obtained from the lactose model solution experiments, and the adsorption behavior was compared with that of the model solution.

2. Materials and methods

2.1. Materials

Lactose one hydrate, phenol, potassium sodium tartrate, copper sulfate tetrahydrate, Folin-Lowry (phenol) reagent, L(+)-ascorbic acid, and ammonium molybdate were purchased from Kanto Chemical Ltd. (Tokyo, Japan). Boric acid, sulfuric acid, sodium hydroxide, sodium carbonate, hydrochloric acid, sodium sulfate, sodium chloride, sodium nitrate, carminic acid, and L-glutamic acid were purchased from Wako Pure Chemical Ltd (Tokyo, Japan). Bovine serum albumin and β-lactoglobulin were purchased from Sigma-Aldlich Chemical (Missouri, St. Louis, U.S.). Anion exchange resin, IRA402BL CL was purchased from Organo Corporation (Tokyo, Japan).

2.2. Preparation of whey solution

Cow milk was purchased from a general market and was supplied commercially from Hakodate Dairy Corporation Co., Ltd. in Hokkaido prefecture, Hakodate, Japan. A desired amount of the milk was taken in a 500 mL beaker, then, ca. 1 M hydrogen chloride solution was added until the pH of the milk reached at pH 4.6. At the pH, proteins were aggregated and precipitated. After the precipitation, the aggregates of proteins were filtered by a paper filter (5C). The filtered solution was used as a whey solution. The whey solution was diluted and, the pH of the diluted whey solution was adjusted at a desired value if necessary.

In the case of the removal of phosphate ion dissolved in the whey, the pH of the whey solution was adjusted to pH 10 by adding NaOH solution, then a white precipitate was produced. The whey solution was centrifuged (3250 × G, 3000 rpm, 15 min) and filtered using a paper filter (No. 5C). The treated whey solution was used for experiments.

2.3. Preparation of anion exchange resin

IRA402 (anion exchange resin) was used as an adsorbent for lactose in this study. According to the data of the supplier, water retention capacity is about 49-56 %, total exchange capacity 4.2×10^{-3} mol/g-dry, particle size 0.50-0.65 mm, and tertiary amine functional group, by the following procedure, the counter ion of IRA402 anion exchange resin, that is, chloride ion, could be exchanged with hydroxyl ion for the adsorption of lactose. 30 mL of the anion exchange resin was taken in a 100 mL beaker and 50 mL of distilled water was also poured into the beaker to wash the resin with distilled water. After the washing, the resin was dried in a dryer at 50 °C for 24 hours. The dried resin was immersed in distilled water for 24 hours. The resin was taken from distilled water and was wiped with paper gently to remove water from the outer surface of the resin. 60 mL of 1M NaOH aqueous solution per unit mass (g) of the dried resin was added to the resin in an adequate volume beaker, then, the resin was stirred for one hour. After stirring, the resin was collected on a paper filter to separate from the liquid phase by filtration. The resin was rinsed with distilled water and this rinsing was continued until the pH of the rinsed water was confirmed to be the same as the distilled water.

2.4. Procedure of adsorption experiment in the model system.

Desired amounts of lactose solution and boric acid solution were mixed to adjust the desired concentration of lactose and boric acid and the pH of the mixed solution was adjusted to the desired pH value by adding HCl or NaOH solutions. The prepared adsorbent (anion exchange resin, IRA402) the desired amount of distilled water was taken in a 100 mL Erlenmeyer flask. Then, the flask was set at 30 °C. water bath and the solution was stirred at 400 rpm using a magnetic stirrer. After this, the mixed solution was taken in the flask. In almost experiments, 0.1 or 0.5 g (based on dry weight) of adsorbent was used, and the volume of the system was set at 40 or 80 mL. The amount adsorbed of lactose was calculated by the difference between the initial and arbitrary time concentrations of lactose.

2.5. Procedure of adsorption experiments using whey solution

After preparing milk whey by the method described in section 2.2, the pH was adjusted to the desired pH value by adding an appropriate amount of 1 M HCl or 1 M NaOH solution. After that, the whey solution was centrifuged at 3000 rpm for 15 min. The whey solution was filtered again with filter paper (ADVANTEC 5C). In the case of varying the whey protein concentration, whey protein concentration was varied by foam separation to remove whey proteins from the liquid phase. In this operation, the employed apparatus was the same one in our previous study [25-27], and the whey solution was diluted five times to prevent becoming the entire liquid as foam by aeration. Air was used as an aerated gas and the volumetric flow rate was set at 50 cm^3/min, which corresponds to a superficial gas velocity, 0.0537 cm/s. The pH value of the prepared whey solution was adjusted at pH 7 by adding HCl or NaOH solutions. The procedure after this was mostly the same as the procedure described in section 2.4. In addition, the control adsorption experiments were conducted with the lactose solution in which bovine serum albumin (BSA), β-lactoglobulin, (βLG), or L-glutamic acid (Glu), were prepared and added as desired concentrations.

2.6. Procedure of desorption experiments

The adsorbents which were used in the adsorption experiments were used once in the desorption experiments. The experimental conditions were as follows; 0.015 M lactose solution or 0.015 M boric acid/lactose mixed solution; adsorbent 1.0 g-dry; volume 40 mL; pH 7. After the adsorption experiment, the loaded adsorbents were collected by filtration using a paper filter (No. 2). The adsorbents were rinsed with distilled water to wash the outer surface of the adsorbents. After this, the collected lactose-loaded adsorbent was taken in 40 mL of 1M NaCl solution in a 100 mL Erlenmeyer flask. At the desired time, a portion of the solution was sampled and the lactose concentration was determined.

2.7. Determination method of lactose, boric acid, phosphate, and proteins

Lactose concentration was determined spectrophotometrically (486 nm) by the phenol sulfuric acid method [28]. The Boric acid concentration was determined spectrophotometrically (585 nm) by the carminic acid method [29]. Phosphate concentration was determined spectrophotometrically (880 nm) by the molybdenum blue method [30]. Protein concentration was determined spectrophotometrically (725 nm) by the Lowry method [31]. Bovine serum albumin was employed as a standard protein to make the determination line for the Lowry method. V-630 spectrophotometer (JASCO Co. Ltd., Japan) was used for these measurements described above.

3. Results and Discussion

3.1. Effect of adding boric acid on adsorption of lactose onto anion exchange resin

Fig. 1 shows a typical result of the influence of the counter ions on the time course of the amount adsorbed of lactose, X_t. In the case of chloride ion (solid circle), X_t was 5.0×10^{-5} mol/g, on the other hand, in the case of hydroxyl ion, X_t was 7.5×10^{-4} mol/g, respectively. The binding strength between the tertiary amine functional group and chloride ion was considered to be stronger than that between the tertiary amine functional group and hydroxyl ion included in IRA402. For the usage of IRA402 for lactose adsorption, this result suggested that the exchange of the counter ion from chloride ion to hydroxyl ion was adequate for this purpose in this study. Therefore the IRA402 which has a hydroxyl ion as a counter ion was used in this study. The preparation procedure was described in section 2.3.

Fig. 2 shows the influence of adding boric acid on the typical time course of the amount adsorbed of lactose, X_t. The equilibrium of the adsorption was required for ca. 30 - 45 hours. At the equilibrium state, X_t was 4.4×10^{4} mol/g and 5.4×10^{4} mol/g without (open circle) and with (solid circle) adding boric acid, respectively. X_t with boric acid was 1.22 times higher than X_t without boric acid. The photographs of IRA402 were shown in the graphical abstract. The color of the resin after adsorption without boric acid was extremely different from the other resins. The reason was considered that the lactose molecule has a carbonyl functional group and IRA402 has a tertiary amine functional group, and in the case without boric acid, lactose molecules could bind with the amine functional group within the resin, resulting in the Maillard reaction [32], which is non-enzymatic browning reaction, occurred on the resin surface. Moreover, desorption experiments were conducted to confirm the degree of release of lactose from the resin. The results are shown in Fig. 3. The loaded adsorbents were obtained from the adsorption experiments as follows: the adsorption experiment was conducted with 1 g-dry IRA402 resin and 80 mL of 0.015 M lactose and 0.015 M lactose-boric acid (role ratio of one to one) at pH 7, respectively. In the ordinate of Fig. 3, C_{dmax} represents the maximum concentration of lactose in case of releasing all amount adsorbed of lactose in the 40 mL of 1 M NaCl solution, and was defined as,

$$C_{\mathrm{dmax}} = X_{\mathrm{e}}\, m \,/\, V. \tag{1}$$

Where X_e, m, and V are the equilibrium amount absorbed of lactose, the mass of adsorbent used in the adsorption experiments, and the volume of the eluent solution, respectively. Thus C/C_{dmax} represents the frequency of desorption of lactose from the resin surface. According to the amount adsorbed, the values of C_{dmax} with and without adding boric were acid 1.41×10^{-2} M and 2.32×10^{-2} M, respectively. The value of C/C_{dmax} without boric acid (ca. 0.1) is smaller than that with boric acid (ca. 0.7). It could be considered that the fact should support the assumption of the Maillard reaction at the resin surface. At the early stage of the Maillard reaction should seem to be a reversible reaction.

As seen in Fig. 1, the adsorption equilibrium state reached about 50 hours. Thus, as the adsorption time has proceeded, the Maillard reaction would be irreversible. It is well known that ion exchange resin has many pores. At the close surface of the near entrance part of the pore, the adsorption could be irreversible, resulting in the available adsorption sites should decrease. The addition of boric acid would enhance both the adsorption and the desorption of lactose with IRA402.

3.2. Influence of the molar ratio of boric acid and lactose and the initial and the equilibrium pH values on the amount adsorbed of lactose.

Fig. 4 shows the influence of the molar ratio of lactose to boric acid and the initial pH on the equilibrium amount adsorbed of lactose, X_e. The experiments were carried out with 0.01 M of the initial concentration of lactose, 40 mL of liquid volume, and 0.5 g of ion exchange resin for 72 hr of the adsorption time. At both pH 7 and 9, X_e increased up to the molar ratio of 2, and at higher molar ratios, X_e decreased. X_e in the case of the initial pH of 7 was slightly higher than that in the case of the initial pH of 9 at a molar ratio of 2, but overall, there was no significant difference between X_e at molar ratios of 1 and 2. Lactose is a disaccharide sugar that is formed by the β-1$\rightarrow$4 glycosidic linkage of β-D-glucose and β-D-galactose and has two cis-diol structures [33]. On the other hand, in an aqueous solution, the following equilibrium relationship for boric acid is established [34].

$$B(OH)_3 + H_2O \leftrightarrow B(OH)_4^- + H^+ \quad ; pK_a = 9.24 \tag{2}$$

The tetrahydroxyborate ion, $B(OH)_4^-$, is formed in the alkaline region [34]. In complexation, the tetrahydroxyborate ion binds with the cis-diol part, L, as follows [35,36].

$$B(OH)_4^- + L \leftrightarrow BL^- + 2H_2O \tag{3}$$

$$B(OH)_4^- + 2L \leftrightarrow BL_2^- + 4H_2O \tag{4}$$

As described above, it could be considered that X_e in the case of the molar ratio 2 was rather higher than that at the case of the ratio 2 because tetrahydroxyborate ion could bind with cis-diol part up to two parts.

Fig. 5 shows the relationship between the equilibrium amount adsorbed of lactose, X_e, and the equilibrium pH. The amount adsorbed increased very abruptly up to the ca. 18 hours in all experimental conditions, after this, it slowly reached the adsorption equilibrium state. The adsorption equilibrium was found to reach 30-45 hours as same as in Fig. 2. Only in the case of the experimental condition of pH 7 and molar ratio 2, X_t seemed to increase slightly linearly after about 24 hours, but this is not considered to be a significant diffusion-limited process.

The experimental conditions were almost the same as in Fig. 4, but only the initial pH was varied from pH 2 to pH 11. In the range of pH 7-9, X_e reached the maximum value for both the molar ratios 1 and 2. The reason could be considered that in the acidic region, the lactose-borate complex is less likely to form, and in the alkaline region, the competitive adsorption between OH^- and lactose-borate complexes onto ion exchange resin was caused. The fractions of tetrahydroxyborate ion are ca. 0.01 and 0.4 at pH 7 and 9, respectively, which are calculated from the equilibrium relationship (Eq. (2)). The relatively high X_e at pH 7 may be related to the release of OH^- ions from adsorbent (ion exchange resin).

Judging from the results shown above, the most optimum initial experimental conditions were considered as the molar ratio 1 and 2, the initial pH 7-9. In further experiments, these initial conditions were employed.

3.3. *Evaluation of adsorption kinetics of lactose on anion exchange resin with adding boric acid*

In particular, it is important to evaluate the adsorption kinetics for the determination of the operating time of adsorption operation in terms of practical operation. Fig 6 shows the typical time course of the amount of lactose adsorbed at a time, t, X_t. There was little difference depending on the experimental conditions, indicating that the adsorption equilibrium was reached in ca. 24 hr. The kinetics equations of the pseudo-second order and the Langmuir are expressed by the following equations.

$$X_\mathrm{t} = \frac{kX_\mathrm{e}^2 t}{1 + kX_\mathrm{e} t} \tag{5}$$

$$X_\mathrm{t} = X_\mathrm{e}\left[1 - \exp\left(-(k_a C_e + k_d)t\right)\right] \tag{6}$$

Where, k, in Eq. (5), and k_a and k_d, in Eq. (6) are the adsorption rate constant for the pseudo-second order adsorption kinetics, the adsorption rate constant and the desorption rate constant for Langmuir adsorption kinetics, respectively. These rate constants were determined by fitting of the data to Eqs. (5) and (6) using a least squares regression, respectively. The estimated rate constants are summarized in Tables 1 and 2 with the coefficient of determination, R^2. There were no large differences, particularly in the k values except for the experimental condition of pH 7 and the molar ratio 2. The k_a values also were mostly the same without large differences. The K value is defined by the ratio of k_a to k_d, which corresponds to the equilibrium adsorption constant of Langmuir adsorption. In the case of the molar ratio 2, the K value was about two times larger than that in the case of the molar ratio 1. It has been reported that the adsorption equilibrium constant for bidentate adsorption was larger than that for monodentate adsorption [37]. According to the reaction scheme shown in Eq. (3) and (4), it is considered that the tetrahydroxyborate ion could bind with two lactose molecules, resulting that might make bidentate type adsorption within the anion exchange resin.

3.3. Evaluation of adsorption equilibrium of lactose on anion exchange resin with adding boric acid

We employed Langmuir adsorption isotherm to evaluate the adsorption equilibrium in this study, because the adsorption site of anion exchange resin (IRA402) is the quaternary ammonium group, and the complex of cis-diol (lactose) and tetrahydroxyborate ion should have a negative charge. Langmuir isotherm is expressed by the following equation.

$$X_e = \frac{KX_sC_e}{1+KC_e} \tag{7}$$

Where X_s is the saturated amount adsorbed of lactose. The adsorption isotherms are shown in Fig. 7. As seen in Fig. 7, it was found that X_e reached X_s for each experimental condition. The adsorption parameters, K and X_s, for Langmuir isotherm, were determined by fitting of the data to Eq. (7) using a least squares regression. The values of K and X_s are summarized in Table 3. The lines drawn in Fig. 7 are the calculated values using K and X_s determined; the dotted line for pH 7 and molar ratio 1, the solid line for pH 9 and molar ratio 1, the dashed-dotted line for pH 7 and molar ratio 2, and the dashed line for pH 9 and molar ratio 2, respectively. In the case of the molar ratio 1, K and X_s were not difference was not substantially different between pH 7 and 9. For both pH 7 and 9, X_s at the molar ratio 1 was about 1.2 times larger than X_s at the molar ratio 2. In the case of pH 9 and the molar ratio 9, X_s was estimated larger than the other three cases as 0.846×10^{-3} mol/g. According to the supplier's data, the anion exchange resin (IRA402) has the total adsorption sites as 4.2×10^{-3} mol/g. Comparing these values, the value of X_s at pH 9 and the molar ratio 1 corresponds to only ca. 20 % of the supplier's data. It is considered that if in the case of the molar ratio 2, bidentate adsorption may occur, X_s at the molar ratio 2 should be only naturally estimated lower than X_s at the molar ratio 1. Since the adsorption of the complex to the resin is probably due to electrostatic attraction, it is reasonable to assume that both the adsorption kinetics and the adsorption equilibrium are of the Langmuir-type adsorption mechanism although the adsorption kinetic data is statistically in good agreement with the pseudo-sesond order adsorption kinetics equation. Judging from these experimental results, future experiments were conducted at pH 7 with the molar ratio 1, which requires less boric acid and allows for easier pH adjustment.

There have been many papers that apply several kinetics and adsorption isotherm equations to experimental kinetics data or adsorption equilibrium data and determine the statistically optimal equation by correlation coefficient or coefficient of determination. However, for example, Freundlich isotherm has been derived empirically and does not have some physical meanings. Moreover, It has been reported that there are many cases in which Freundlich isotherm could be explained by two Langmuir isotherms [38-44]. Not only judging from statistical parameters, it is necessary to consider the types of adsorbent, the experimental isotherm profiles, and the overall interpretations of the results of the batch adsorption experiments for the adequate kinetic and adsorption equilibrium isotherm equations. It is very likely possible that the adsorption kinetics and adsorption equilibrium relationship of the adsorption experimental data using adsorbents with a finite number of quantitative functional groups could be expressed by the Langmuir kinetics and isotherm equations. The adsorption isotherms shown in Figs. 7, 10, and 11 sufficiently show that the saturated amount adsorbed is reached as the equilibrium concentration increases, and a Langmuir adsorption equilibrium relationship is likely established. If the adsorption rate data in the same system are likely to follow the Langmuir adsorption equilibrium, it is quite natural to assume that the rate model will also follow the Langmuir type. The pseudo-second order kinetic model equation was also applied because the pseudo-second order kinetic model equation is considered to be derived from the Langmuir kinetic equation [45-51].

3.4. Influence of coexisting substances in whey solution on adsorption of lactose on anion exchange resin with adding boric acid

3.4.1. Influence of phosphate ion on adsorption of lactose

In preliminary experiments, when the pH of the whey solution was raised above 7, the solution became cloudy. Furthermore, in the adsorption experiments, it was difficult to reproduce the experiments because the white precipitated substance adhered to the surface of the resin and was visually confirmed. Phosphate and calcium are two of the most abundant minerals in milk. The concentrations of phosphate and calcium in milk are about 2.9×10^{-2} mol/L and about 2.5×10^{-2} mol/L, respectively. More than 70% of calcium is present in casein micelles. Casein micelles are colloidal particles consisting of four components α_{S1}–, α_{S2}–, β–, and κ– caseins dispersed in milk, and are composed of small particles called submicelle, which are bound together via calcium phosphate [4]. The white precipitated substance observed over pH 7 was considered to be calcium phosphate. By varying the pH of the whey solution, the white precipitate was removed by centrifugation and filtration, and the relationship between the pH value and the phosphate concentration was investigated. After preparing the whey solution as described in section 2.5, the pH value of the whey solution was adjusted to the desired value, and then the solution was centrifuged at 3250×G (3000 rpm) for 15 min. The supernatant solution (whey solution) was filtered by filter paper (Advantec, No. 5C). Fig. 8a shows the relationship between the phosphate concentration and pH. As increasing pH value, the phosphate concentration decreased from 1.97×10^{-2} mol/L (pH 4.6) to 1.23×10^{-3} mol/L (pH 12). This result suggests that phosphate was captured in the white precipitated substance and removed from the liquid phase. Lactose adsorption experiments were carried out using the whey solution, which was adjusted at pH 10, centrifuged, and filtered, and then pH was adjusted at pH 7. Fig. 8b shows the time course of the amount adsorbed of lactose, in which the results of two experiments (run1 and run2) are shown. The reproducibility of the experiment was very good, indicating that there is no significant variation between the data of the two runs. Compared with the results of adsorption experiments conducted under the same conditions with the model system shown in Fig. 1 (open circle symbol), the amount adsorbed at 24 hours is 0.727×10^{-3} mol/g for the model system, while the amount adsorbed at 96 hours is 0.583×10^{-3} mol/g for the whey system, indicating that the adsorption rate was also slower and the amount was also lower than those for the model system.

3.4.2. Influence of whey proteins on adsorption of lactose

The whey protein concentration was varied by foam separation to investigate the influence of the whey protein concentration on the adsorption of lactose on the resin. Fig. 9 shows the typical time course of the whey proteins and lactose within the column. Before conducting foam separation, phosphate ions were removed from the whey solution by adjusting pH 10, centrifugation, and filtration, then the whey solution was diluted five times and was adjusted to pH 7 to prevent not becoming the entire solution to foam by aeration [25]. When the solution was used in the adsorption experiment, moreover the solution was diluted two times (ten-fold dilution of the original whey solution) and pH was adjusted to pH 7. The whey protein concentration decreased from 0.35 g/L to 0.15 g/L for up to 2 hours, while the lactose concentration was kept constant (0.03 mol/L). The adsorption experiments were carried out by varying the whey protein concentration in the whey solution in this manner. The typical result is shown in Fig. 10. Boric acid was added to the solution at the molar ratio of 1. As seen in Fig. 10 there was no difference in the time course of X_t even though the initial whey protein concentration was different (0.175 and 0.075 g/L). The open circle symbol corresponded to X_t of the model system (without whey proteins). The X_e (t = 70 min) of the model system was ca. 0.7×10^{-3} mol/g, while the X_e (t = 70 min) of the whey system (triangle symbols) was ca. 0.5×10^{-3} mol/g, which was 30% lower than that of the model system. These results suggest that the presence of proteins in the system was getting lower the amount adsorbed of lactose, however, the variation in the protein concentration did not affect the amount adsorbed of lactose.

3.4.3. Influence of amino acid and kinds of protein on adsorption of lactose

In the previous section, it was suggested that the difference in the concentration of whey proteins did not affect the adsorption of lactose, but the presence of the whey proteins could affect the adsorption of lactose. The difference in the amount adsorbed of lactose between the model system and the whey system was considered to be caused by other substances and types of proteins contained in the whey. Milk whey contains β-lactoglobulin (βLG, 3-4 g/L), α-lactalbumin (ca. 1.5 g/L), and bovine serum albumin (BSA, ca. 0.3-0.6 g/L), which make up ca. 80 % content of the total milk whey proteins [52]. In addition, the major amino acid constituents of milk whey are glutamic acid (Glu, ca. 0.04 g/L), tryptophan (0.002 g/L), and glycine (ca. 0.007 g/L), which make up ca. 75 % of the total amino acids content of milk whey [53]. βLG, BSA, and glutamic acid were employed as typical proteins and amino acids for the adsorption experiment. The concentration of protein (βLG and BSA) and the amino acid were adjusted to 0.075 g/L and 0.004 g/L in the solution, and the pH was adjusted to pH 7. The results are shown in Fig. 11. The time courses of the amount adsorbed of lactose in the model system were mostly the same even though any additive was added to the system, while the time courses of the amount adsorbed of lactose in the whey system were ca. 30 % lower than those in the model system, and were almost the same with the result shown in Fig. 10 (open triangle symbol). Each isoelectric point of βLG, BSA, and Glu is 4.9, 5.2, and 3.25, respectively. They should have a negative charge at pH 7, with which the adsorption experiments were conducted. Based on these experimental results, it is unlikely that the decrease in lactose adsorption in the whey system is due to the influence of proteins or amino acids at pH 7. Since whey also contains various vitamins and chlorine as a major mineral [4], it is assumed that these are influencing factors.

Atra et al. (2005) investigated ultra- and nanofiltration for recovery of whey proteins and lactose and reported that the yield of lactose was ca. 90 % by using polyamid nanofilter (RA55 MILLIPORE) under 30ºC [54]. Cuartas-Uribe et al. (2009) studied the separation of lactose from whey ultrafiltration permeate using nanofiltration and reported that the recovery of lactose ranged in 84.6-89.1 % by using DS-5 DL (GE-OSMONICS, US) which is made of a thin-film composite with polyamide surface on polysulfone support and polyester matrix [55]. Souza et al. (2010) studied integrated processes (microfiltration, ultrafiltration, ion exchange, reverse osmosis, and spray-drying) to separate and purify lactose from whey and reported that lactose was purified as 88.5 % by a single-stage ultrafiltration and also was purified as 97.7 % by a second stage ultrafiltration [56]. Ding et al. (2016) studied the shear-enhanced ultrafiltration to concentrate whey protein and lactose and reported that recovery of lactose was 30% using polyethersulphone ultrafiltration membranes [57]. Sánchez-Moya et al. (2020) studied the separation of lactose from sheep whey with ultrafiltration and reported that the recovery of lactose was 10% by using a polysulfone ultrafiltration membrane in the filtration of whey [5]. Zhang et al. (2020) investigated a combination of ultrafiltration, electrodialysis, and nanofiltration to produce low-lactose milk powder, and reported that the recovery of lactose was 44% by ultrafiltration [58]. Based on the results of Figs. 10-11, the recovery of the adsorption method in this study was 58-60% in the model system for lactose, and 40-42% in the actual system with whey. Even in the case of ultrafiltration, a recovery rate of about 40% has been reported in some cases, and this method can be considered to be doing well as a simple treatment method in small-scale plants.

3.5. Limitation of the present adsorption process

Although the addition of boric acid made it possible to regenerate IRB402, the desorption efficiency was only about 70%, and about 30% of boric acid remained in IRA402, which means that complete regeneration of the resin may be difficult. Although it is only an assumption, since the binding ability of IRA402 and chlorine ions is very strong, it may be possible to regenerate IRA402 by adding NaCl and so on. Another problem is that it is necessary to remove boric acid from the desorption solution after lactose is desorbed from IRA402. This problem can be solved by using a special ion exchange resin for boric acid.

The necessity to remove minerals and vitamins from the actual whey is also an issue for further study.

4. Conclusions

The adsorption separation of lactose using an anion exchange resin with the addition of boric acid was studied from both fundamental and applied aspects with the aim of effective utilization of whey and reduction of environmental pollution. The following results were obtained.

1. By exchanging the counter ion of the anion exchange resin (IRA402) from chloride ion to hydroxide ion, lactose could be adsorbed onto IRA402, and the amount adsorbed of lactose was 14.2 times larger.
2. The addition of boric acid enabled the desorption of lactose from anion exchange resins, and resulted in 72% desorption of lactose from IRA402, and the desorption rate (%) increased 6.7-fold.
3. The binding between tetrahydroxyboronate ion and the cis-diol of lactose is considered to be the most likely adsorption species.
4. The optimal amount of boric acid and pH were 1:1 in the molar ratio of boric acid to lactose and pH 7-9.
5. Langmuir-type adsorption equilibrium relationship was established.
6. The recovery of the adsorption method in this study was 58-60% in the model system for lactose, and 40-42% in the actual system with whey.
7. The amount of lactose adsorbed from the actual whey solution was 35% lower than in the model system. It was suggested that coexisting minerals, vitamins, and chlorine ions influenced the amount of lactose adsorbed from the whey solution.

In further studies, we will conduct a more detailed analysis of the effect of pH on the amount adsorbed of lactose and will extend this study to a fixed-bed adsorption operation and separation of boric acid from a practical point of view. The reuse of waste contributes to

SDG's (Sustainable Development Goals subjected by the United Nations) and we could propose one of the contribution manner for SDG’s in this study.

Credit authorship contribution statement

Hideo Maruyama: Planning the experiments of this research, Conducting the experiments, Analysis of the experimental data, Writing original manuscript. Hideshi Seki: Advising experimental method, Discussions about results, Writing-Reviewing and Editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Nomenclature

C = concentration of metal ion within the column [mol/m^3]

C_{dmax} = the maximum concentration of lactose by releasing lactose [mol/m^3]

C_{i} = initial concentration of of lactose [mol/m^3]

C_t = concentration of lactose at time, t [mol/m^3]

k = adsorption rate constant defined in Eq. (5) [kg/(mol min)]

K = equilibrium adsorption constant defined in Eq. (7) [m^3/mol]

k_{a} = adsorption rate constant defined in Eq. (6) [m^3/(mol min)]

k_{d} = desorption rate constant defined in Eq. (6) [min^{-1}]

m = mass of anion exchange resin [kg]

R = removal efficiency of metal ion [-]

t = time [min]

X_{e} = equilibrium amount adsorbed of lactose [mol/kg]

X_{s} = saturated amount adsorbed of lactose [mol/kg]

X_t = amount adsorbed of lactose at time, t [mol/kg]

V = volume of liquid [m^3]

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Figures and tables captions

Fig. 1. Influences of the counter ions of anion exchange resin (chlorine ion and hydroxyl ion), on lactose adsorption onto anion exchange resin, IRA402. Experimental conditions: lactose 0.015 M; boric acid 0.015 M; solution volume 80 mL; IRA402 1.0 dry-g; initial pH 7.

Fig. 2. Influence of boric acid on lactose adsorption onto IRA402 anion exchange resin. Experimental conditions: lactose 0.01 M; boric acid 0.01 M; solution volume 40 mL; IRA402 0.5 dry-g; initial pH 7.

Fig. 3. Influence of boric acid on lactose desorption from anion exchange resin, IRA402 with 1 M NaCl solution. Experimental conditions: (desorption) solution volume 40 mL; IRA402 1.0 dry-g; initial pH 7. :(adsorption) solution volume 80 mL; IRA402 1.0 dry-g; initial pH 7.

Fig. 4. Influence of the molar ratio of boric acid and lactose on the equilibrium adsorption density, Xe, onto anion exchange resin, IRA402, for initial pH 7 (●) and pH 9 (○) , respectively. Experimental conditions: lactose 0.01 M; IRA402 0.5 dry-g; solution volume 40 mL.

Fig. 5. Change in equilibrium adsorption density, Xe, of lactose onto anion exchange resin, IRA402 for the molar ratio, 1 (○) and 2 (●), respectively. The other experimental conditions are same as Fig. 4.

Fig. 6. Typical time course of the amount adsorbed of lactose onto IRA402. Fitting of the data to Eq. (5) for the pseudo-second order adsorption kinetics (Fig. 6a) and Eq. (6) for the Langmuir adsorption kinetics (Fig. 6b). The lines represent the calculated values using estimated the adsorption parameters (Tables 1 and 2).

Fig. 7. Adsorption isotherms of lactose onto IRA402. Lines correspond to the calculated values using Eq. (7) and the estimated adsorption parameters listed in Table 3. Experimental conditions: lactose 0.01 M; IRA402 0.5 dry-g; solution volume 40 mL.

Fig. 8. (a) Influence of pH on concentration of phosphate ions in the milk whey solution after centrifugation and filtration. (b) Typical time course of the amount adsorbed of lactose from milk whey solution after reducing phosphate ions. Experimental conditions: lactose 0.015 M; boric acid 0.015 M; IRA402 1.0 dry-g; solution volume 80 mL; the initial pH 7.

Fig. 9. Typical time course of concentrations of milk whey protein and lactose within the foam separation column. The initial lactose and protein concentrations were 0.03 mol/L and 0.35 g/L, respectively.

Fig. 10. Typical time course of the amount adsorbed of lactose from milk whey for different protein concentrations. Experimental conditions: lactose 0.015 M; boric acid 0.015 M; IRA402 1.0 dry-g; solution volume 80 mL; initial pH 7.

Fig. 11. Typical time course of the amount adsorbed of lactose from milk whey and the model solutions containing protein and amino acid. The experimental conditions: lactose 0.015 M; boric acid 0.015 M; IRA402 1.0 dry-g; solution volume 80 mL; initial pH 7.

Table 1 The adsorption parameters, k and X_e, estimated from fitting of the data to Eq. (5) for the pseudo-second order adsorption kinetics.

Table 2 The adsorption parameters, k_a, k_d and K, estimated from fitting of the data to Eq. (6) for Langmuir adsorption kinetics.

Table 3 K and X_s estimated from fitting of the data to Eq. (7) for the Langmuir isotherm.

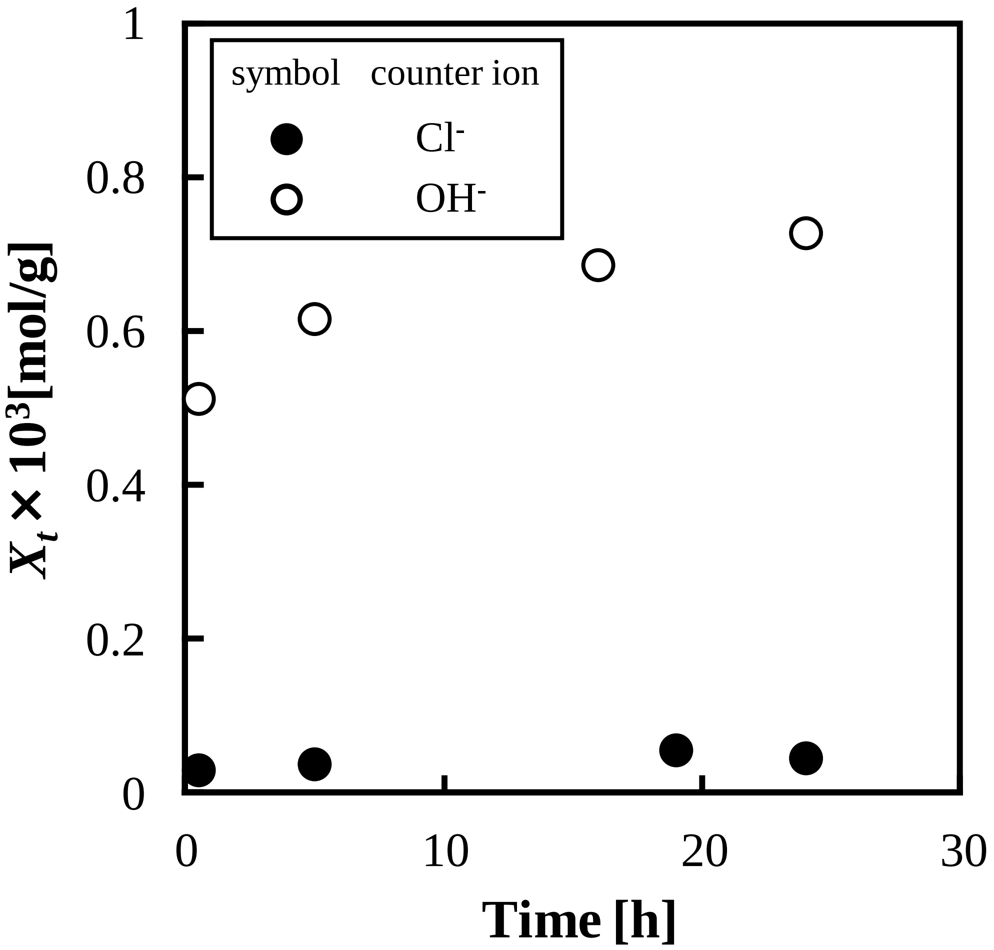

Fig. 1. Influence of the counter ions, chlorine and hydroxyl ion, of anion exchange resin (IRA402) on the amount adsorbed of lactose onto IRA402. Experimental conditions: the initial concentration of lactose 0.015 M and boric acid 0.015 M; the volume of the solution 80 mL; IRA402 1.0 g-dry; the initial solution pH 7.

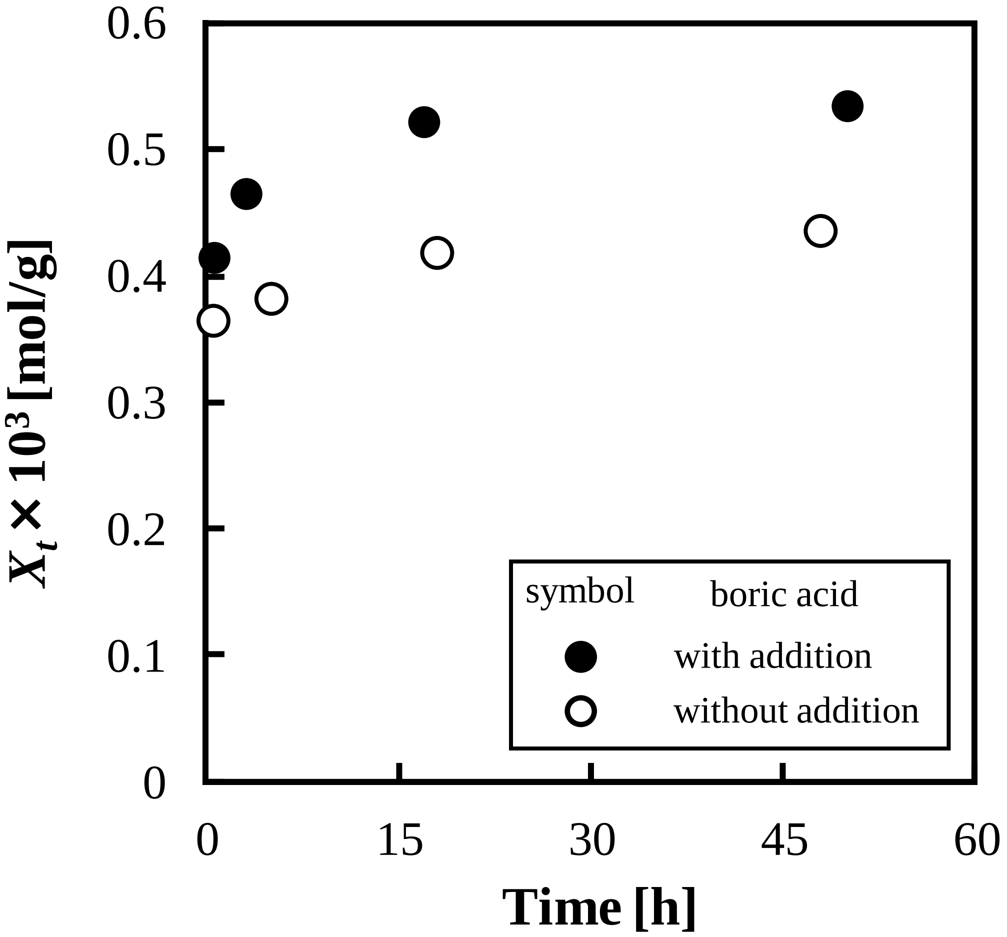

Fig. 2. Influence of boric acid on lactose adsorption onto IRA402 anion exchange resin. Experimental conditions: lactose 0.01 M; boric acid 0.01 M; solution volume 40 mL; IRA402 0.5 dry-g; initial pH 7.

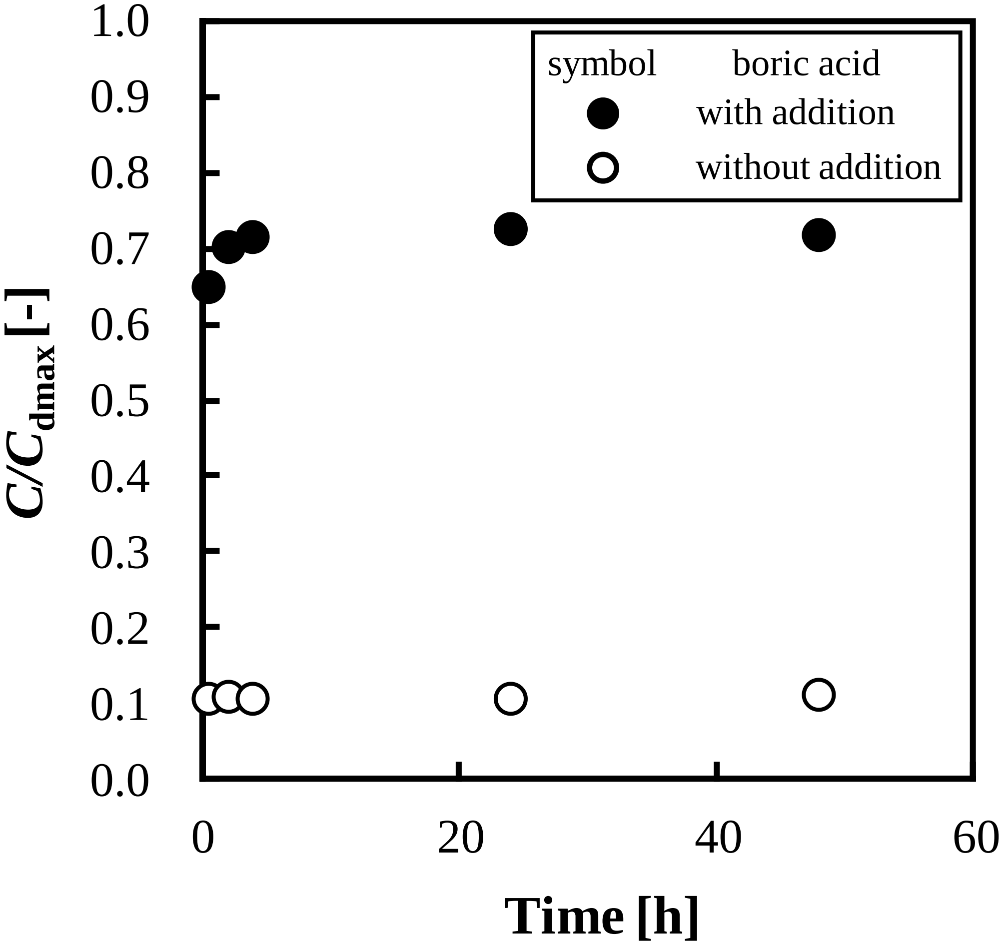

Fig. 3. Influence of boric acid on lactose desorption from anion exchange resin, IRA402 with 1 M NaCl solution. Experimental conditions: (desorption) solution volume 40 mL; IRA402 1.0 dry-g; initial pH 7. :(adsorption) solution volume 80 mL; IRA402 1.0 dry-g; initial pH 7.

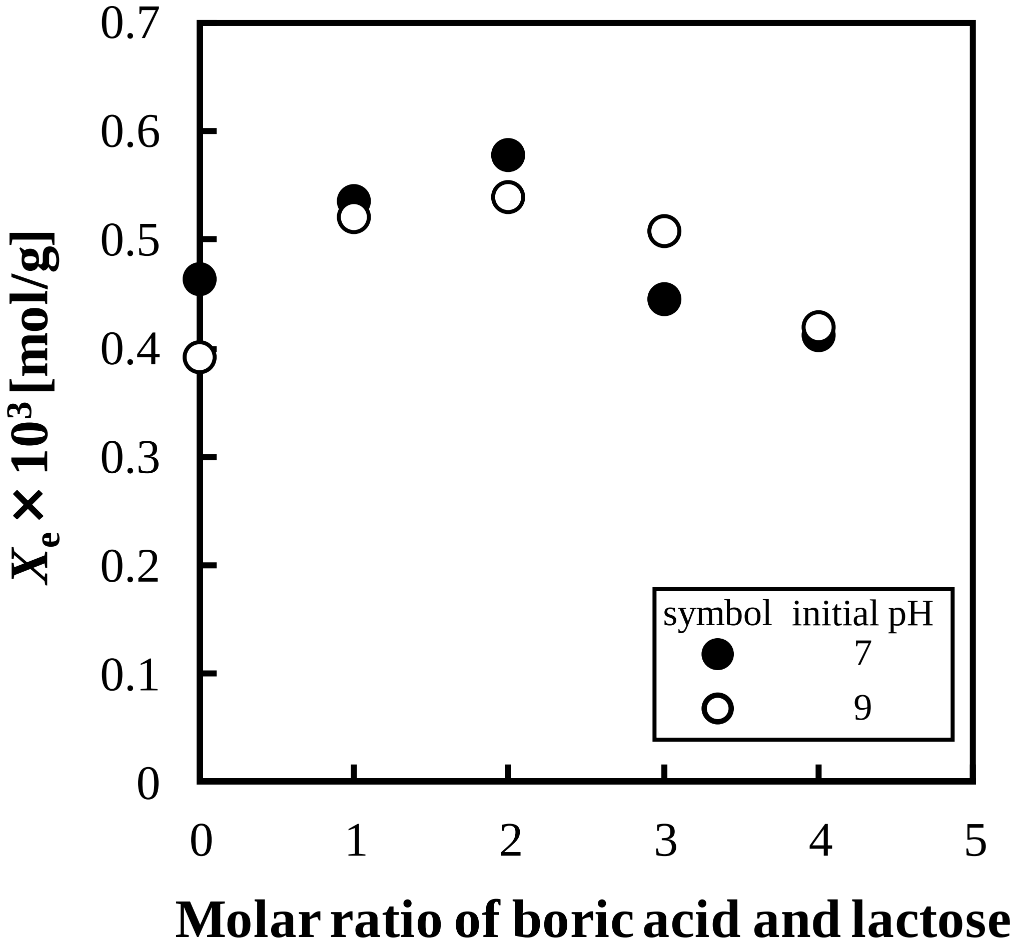

Fig. 4. Influence of the molar ratio of boric acid and lactose on the equilibrium adsorption density, X_e, onto anion exchange resin, IRA402, for initial pH 7 (●) and pH 9 (○) , respectively. Experimental conditions: lactose 0.01 M; IRA402 0.5 dry-g; solution volume 40 mL.

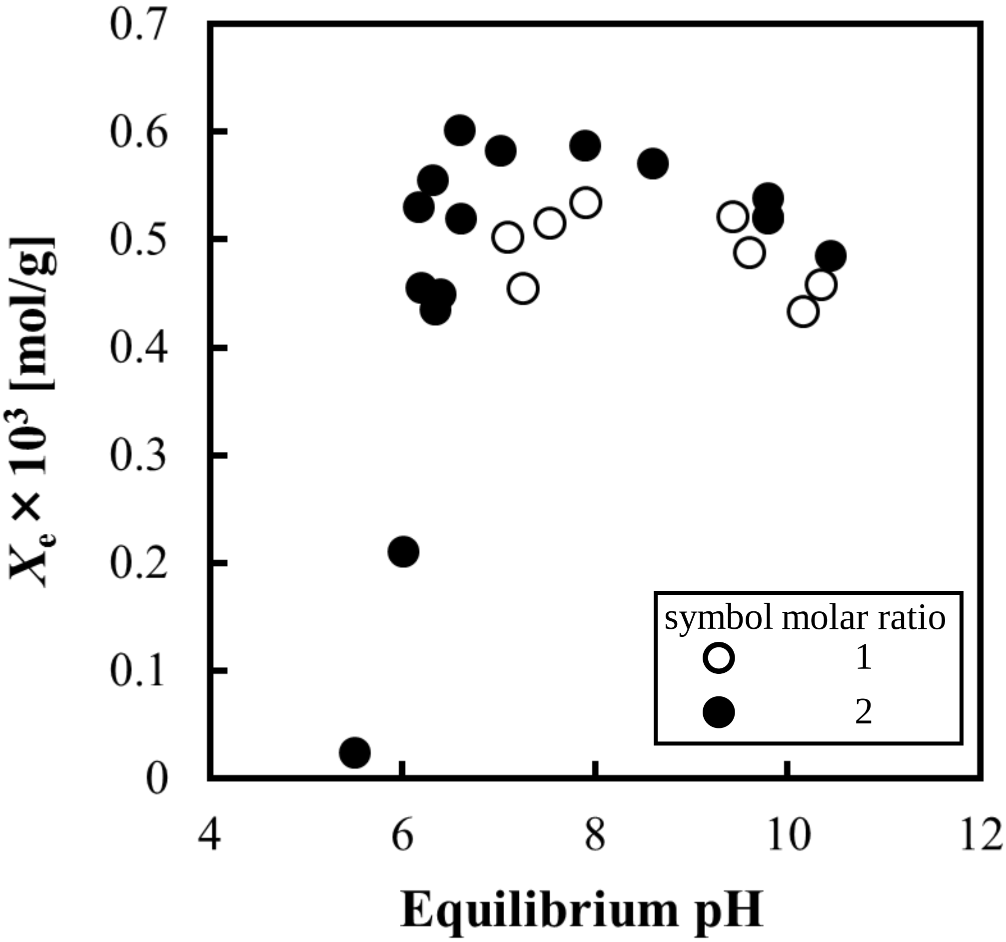

Fig. 5. Change in equilibrium adsorption density, X_e, of lactose onto anion exchange resin, IRA402 for the molar ratio, 1 (○) and 2 (●), respectively. The other experimental conditions are same as Fig. 4.

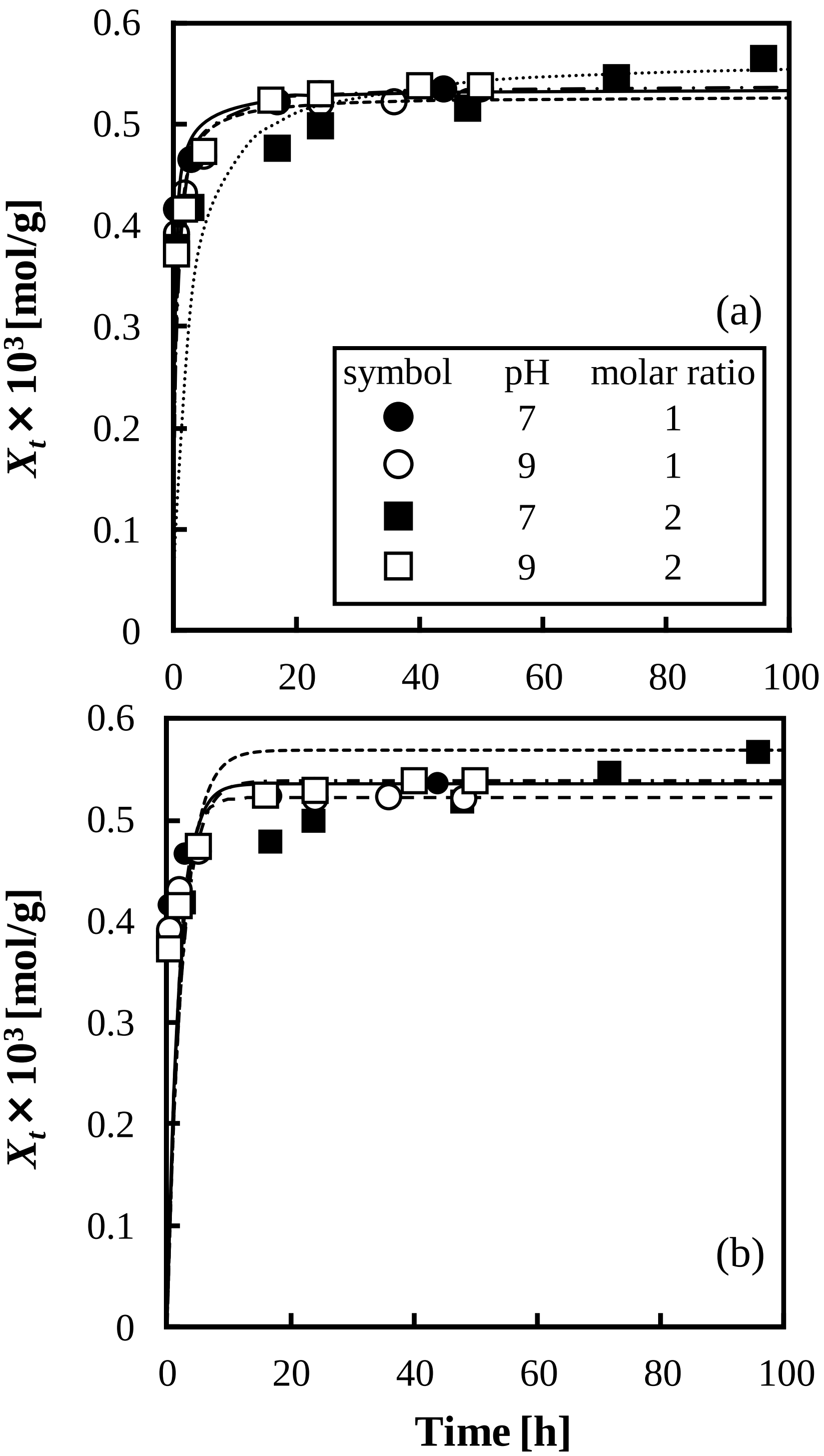

Fig. 6. Typical time course of the amount adsorbed of lactose onto IRA402. Fitting of the data to Eq. (5) for the pseudo-second order adsorption kinetics (Fig. 6a) and Eq. (6) for the Langmuir adsorption kinetics (Fig. 6b). The lines represent the calculated values using estimated the adsorption parameters (Tables 1 and 2).

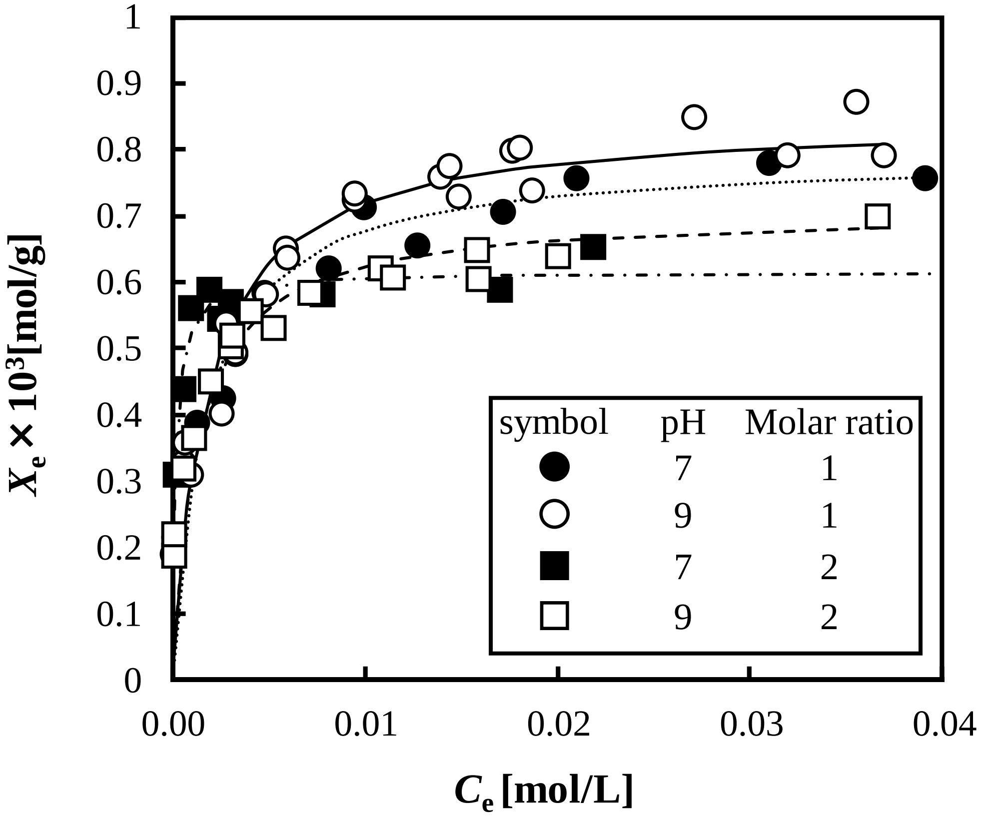

Fig. 7. Adsorption isotherms of lactose onto IRA 402. Lines correspond to the calculated values using Eq. (7) and the estimated adsorption parameters in table 3. Experimental conditions: lactose 0.01 M; 0.5 g-dry resin (IRA 402); solution volume 40 mL.

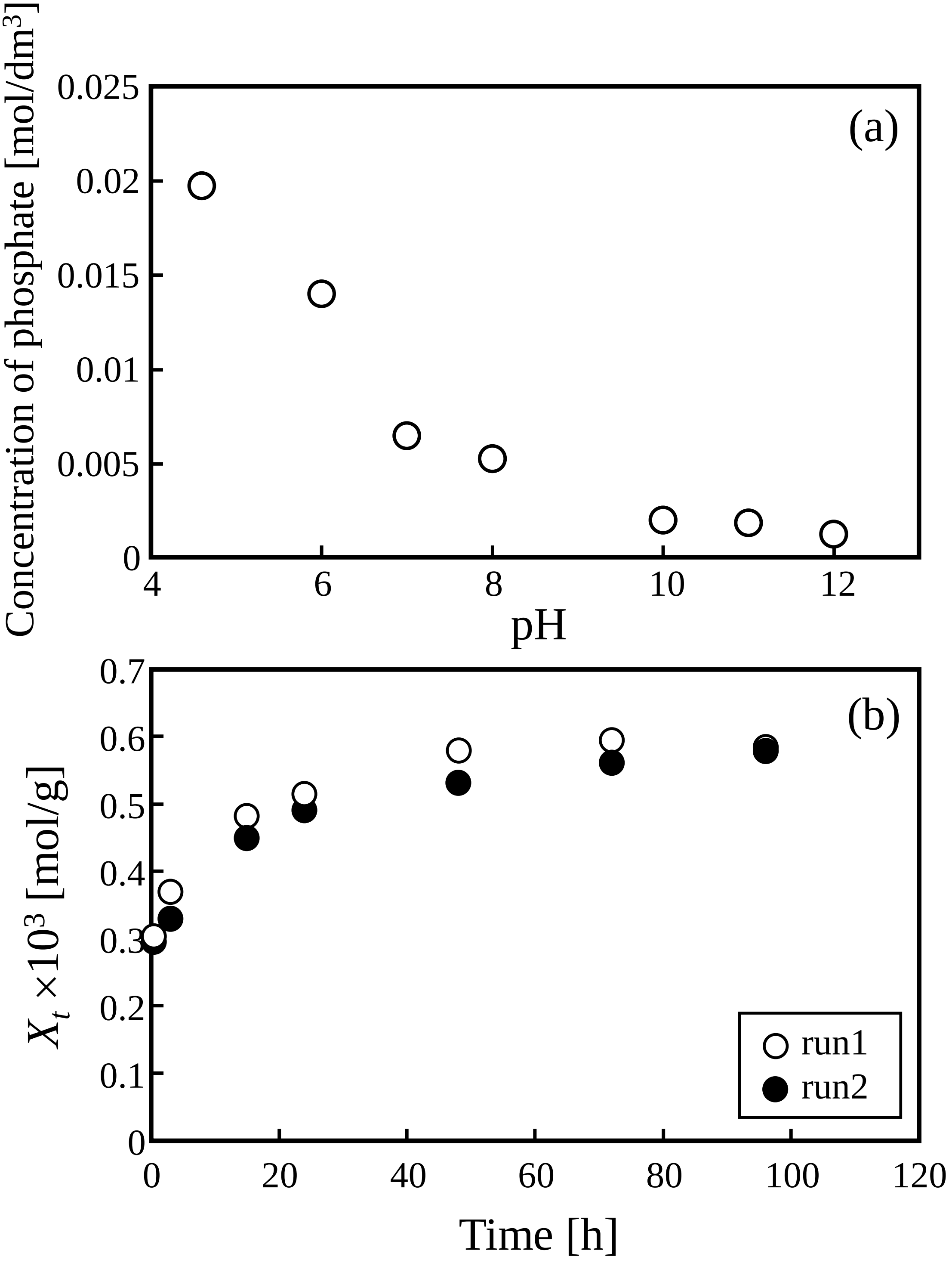

Fig. 8. (a) Influence of pH values on concentration of phosphate ions in the milk whey solution after removing the precipitate by centrifugation and filtration. (b) Typical time course of the amount adsorbed of lactose from milk whey solution after reducing phosphate ions. Experimental conditions: lactose 0.015 M; boric acid 0.015 M; 1.0 g-dry resin (IRA402); solution volume 80 mL; the initial pH 7.

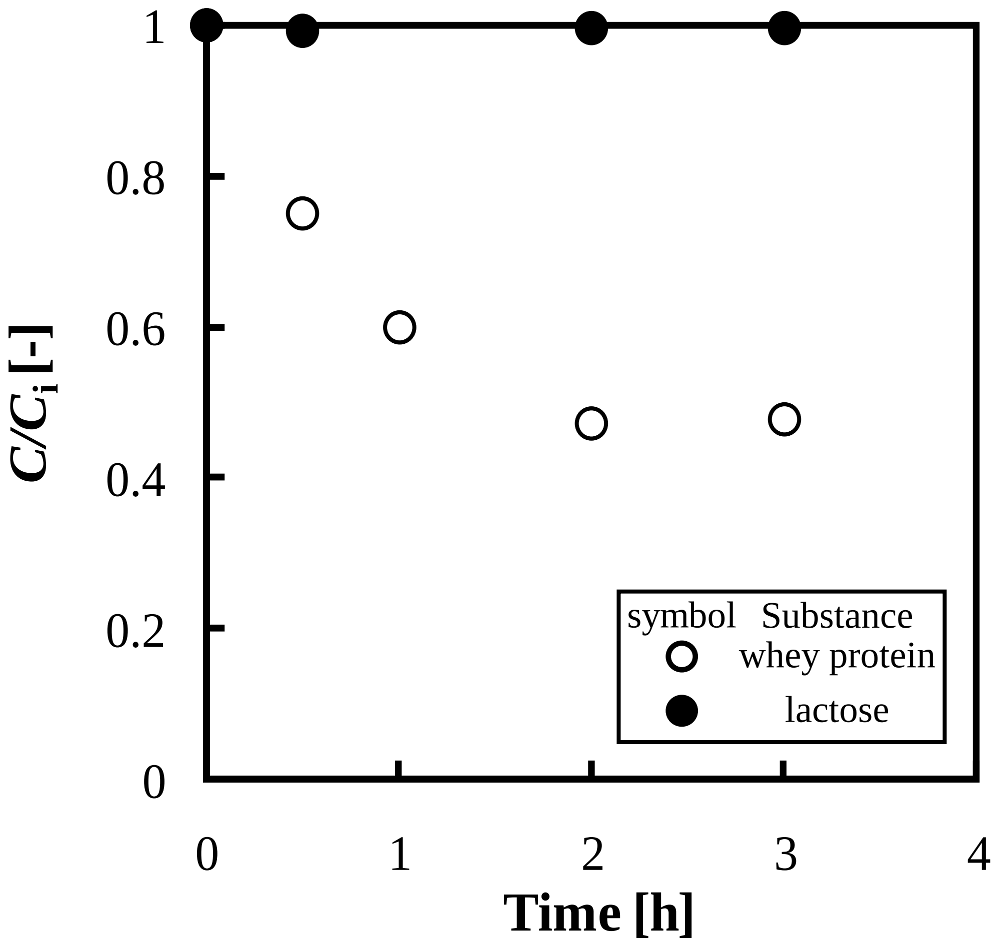

Fig. 9. Typical time course of concentrations of milk whey protein and lactose within the foam separation column. The initial lactose and protein concentration were 0.03 mol/L and 0.35 g/L, respectively.

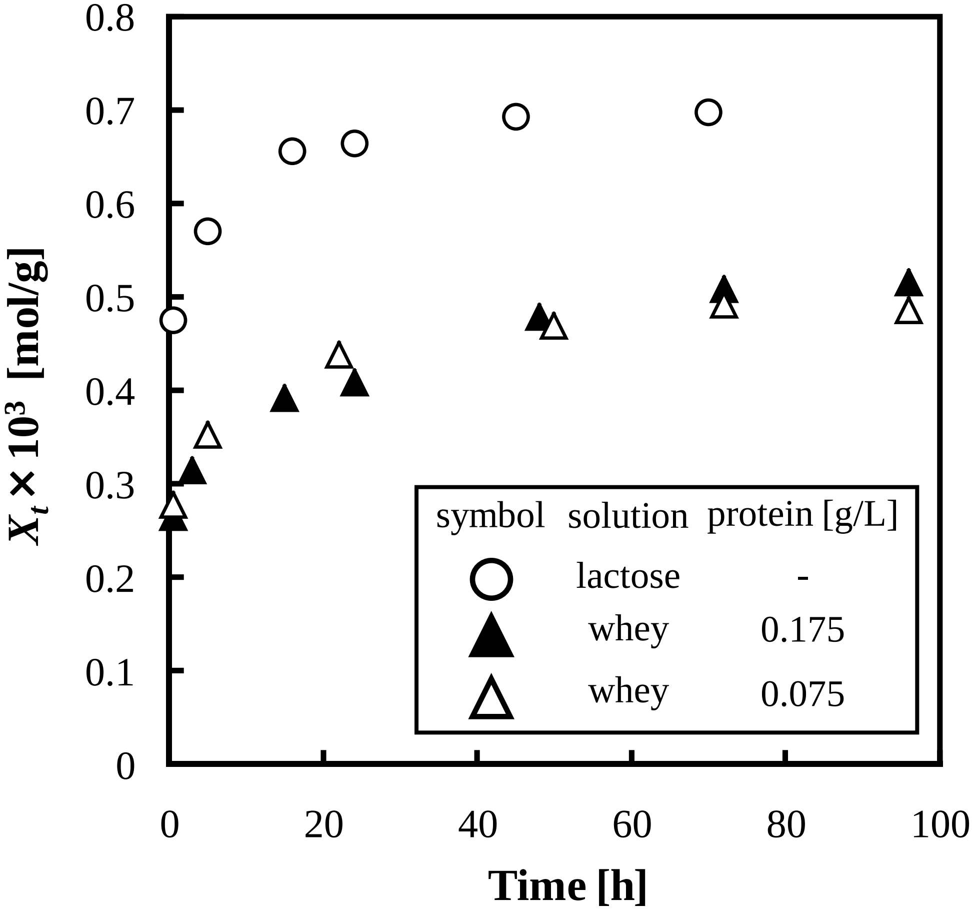

Fig. 10. Typical time course of the amount adsorbed of lactose from milk whey for different protein concentrations. Experimental conditions: lactose 0.015 M; boric acid 0.015 M; 1.0 g-dry resin (IRA402); solution volume 80 mL; initial pH 7.

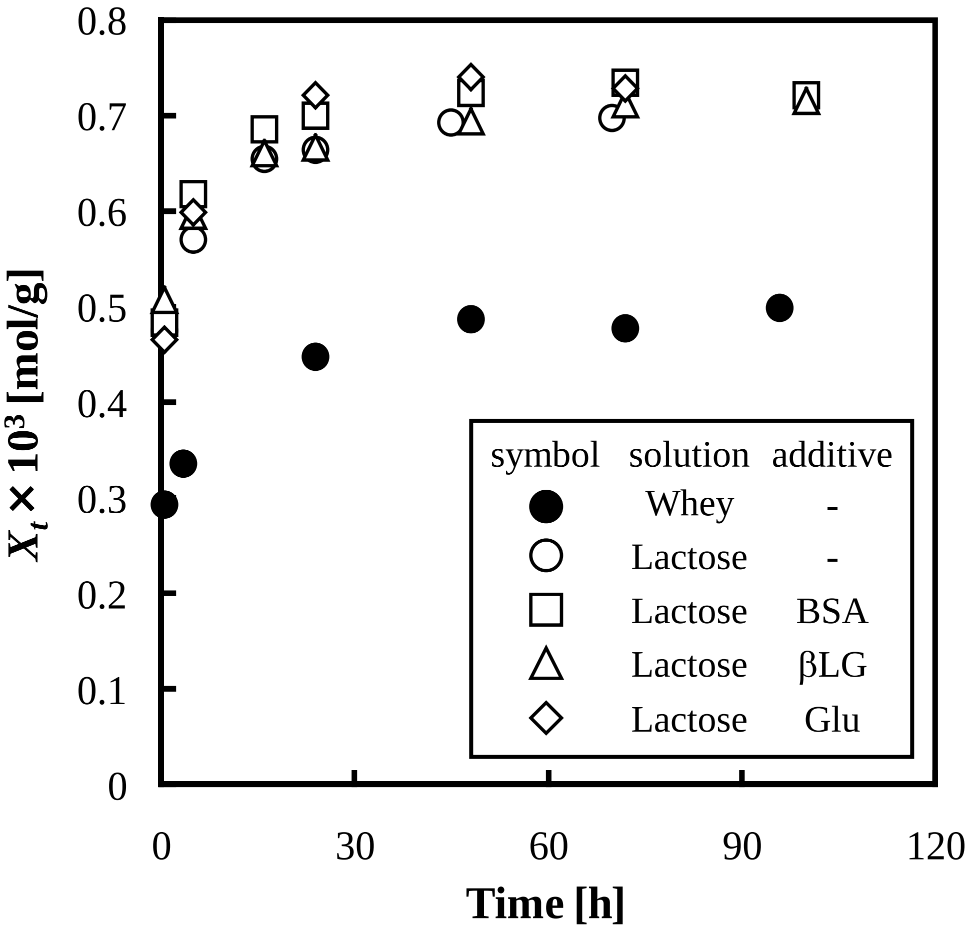

Fig. 11. Typical time course of the amount adsorbed of lactose from milk whey and the model solutions containing protein and amino acid. The experimental conditions: lactose 0.015 M; boric acid 0.015 M; 1.0 g-dry resin (IRA402); solution volume 80 mL; initial pH 7.

Table 1 The adsorption parameters, k and X_e, estimated from fitting of the data to Eq. (5) for the pseudo-second order adsorption kinetics.

pH	molar ratio	$X_e \times 10^3$ [mol/g]	$k \times 10^{-3}$ [g/mol·h]	R^2
7	1	0.535	6.17	0.990
7	2	0.573	0.88	0.990
9	1	0.528	4.69	0.990
9	2	0.540	3.79	0.990

Table 2 The adsorption parameters, k_a, k_d and K, estimated from fitting of the data to Eq. (6) for Langmuir adsorption kinetics.

pH	molar ratio	k_a [L/mol･h]	k_d [/h]	K [L/mol]	R^2
7	1	104.4	0.169	617	0.925
7	2	97.6	0.103	1086	0.871
9	1	111.0	0.238	466	0.858
9	2	115.7	0.119	973	0.925

Table 3 K and X_s estimated from fitting of the data to Eq. (7) for the Langmuir isotherm.

pH	molar ratio	K [L/mol]	$X_s \times 10^3$ [mol/g]	R^2
7	1:1	593	0.791	0.911
7	1:2	5869	0.615	0.911
9	1:1	547	0.846	0.924
9	1:2	760	0.706	0.924