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Lactulose formation catalysed by alkaline-substituted sepiolites in milk permeate

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Abstract

Alkaline-substituted (Na^+, K^+) sepiolites were used as catalysts for the formation of lactulose in milk permeate. Besides lactose and lactulose, other carbohydrates, such as galactose and epilactose, produced in side reactions, were determined. The effect of different washing cycles of sepiolite on the isomerisation of lactose and the exchange of cations with the permeate were also investigated. In general, the activity of the sodium sepiolite was higher than that of potassium form. Twenty per cent of lactulose formation (≈1000 mg/100 ml), with respect to the initial lactose, was obtained after 150 min of reaction, using sodium sepiolite washed during 10 cycles. Under these conditions, 25% of lactose degradation was detected, whereas small amounts of epilactose and galactose were formed. The exchange of Na^+ between sepiolite and permeate decreased considerably with the number of washing cycles. The present work shows an appropriate method for obtaining lactulose in milk permeate with acceptable yields and without complicated purification steps. © 2001 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Permeate; Sodium sepiolite; Potassium sepiolite; Lactulose; Lactose

1. Introduction

The cheese industry produces high quantities of whey that represent a major disposal problem. Proteins, the most valuable components of whey, can be recovered by ultrafiltration which is a standard operation in cheese plants. Ultrafiltration of whey generates large amounts of permeate which contains, on a dry weight basis, 80–85% lactose, 8–10% ash and some vitamins (Shay & Wegner, 1986). Although the industry has developed many uses for permeate, a huge surplus still exists (Horton, 1993).

Lactose is used as the raw material to produce several useful derivatives for food and pharmaceutical applications. Large quantities of lactose are converted into lactulose (4-O-β-D-galactopyranosyl-D-fructose) by alkali hydroxide catalysis (Méndez & Olano, 1979). Lactulose is applied to pharmaceuticals for portal systemic encephalopathy and for chronic constipation. It is also applied to infant formula and food since the discovery of its role as a Bifidus factor (Méndez & Olano, 1979; Mizota, Tamura, Tomita, & Okonogi, 1987). Lactulose is relatively expensive to produce, not only because of the low product yield (20–30%) from the reaction, but also the high cost of purification. This is mainly due to the partial degradation of lactulose to galactose, isosacharinic acids and coloured products (Méndez & Olano, 1979).

Previous studies have proved the usefulness of natural and alkaline-substituted sepiolites for efficient lactose isomerisation in aqueous lactose solutions with minimal production of other compounds in side reactions (de la Fuente, Juárez, de Rafael, Villamiel, & Olano, 1999; Troyano, de Rafael, Martínez-Castro & Olano, 1996). Moreover, the use of heterogeneous catalysts allows their easy removal from the media after conversion is accomplished. To the best of our knowledge, no information is available regarding the isomerisation of lactose with alkaline-substituted sepiolites in milk permeate. The aim of this paper was to evaluate the possibility of the use of sepiolite to isomerise milk permeate lactose, avoiding any purification steps, to turn this into a high value-added product.

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2. Materials and methods

2.1. Materials

Sepiolite was supplied by Tolsa S.A. (Madrid) from its Spanish mines. It was a fine powder with the following physical properties: specific gravity, 2; apparent density, 100–120 g l^{-1} and specific surface area (S_{BET}, N_2), 288 m^2 g^{-1} (González, Ibarra, & Chamorro, 1987).

2.2. Alkaline-substituted sepiolites

Sodium sepiolite was prepared following the procedure reported by Mifsud, Corma, and García (1988): 10 g of natural sepiolite was heated at 120 °C with 100 ml 1 N NaOH for 1 h. After the ion-exchange, the resulting solid was thoroughly washed by centrifugation at 5000 r.p.m., by 5, 10 and 15 cycles of 10 min, with 250 ml deionised water. The potassium form of sepiolite was prepared by exchanging the Na^+ in the sodium form of sepiolite in a stirred 1 N solution of KOH at 90 °C and a liquid:solid ratio of 10, for 1 h. After the ion-exchange, the sample was washed with 250 ml deionised water as mentioned earlier. Both types of sepiolite were dried at 115 °C for 15 h, according to Corma and Martín-Aranda (1991).

2.3. Treatments

Milk permeate was obtained by passing skim pasteurised milk through a Minitan System (Millipore) with a 10 kDa ultrafiltration membrane. Samples were subsequently heated at constant temperature (90 °C) in a silicone oil bath with stirring and thermostatic control (±1 °C). When the solution reached the desired temperature, an appropriate amount of sepiolite (washed for 5, 10 or 15 cycles) was added and the mixture was stirred during the process. Samples (10 ml) were periodically withdrawn for analysis after 30, 60, 90, 120 and 150 min. Sepiolite loading was 15.0 g l^{-1} of milk permeate.

The pH of the samples was measured before and after thermal treatments with a pH-meter MicropH2001 (Crison Instruments, Barcelona, Spain).

2.4. Analytical determinations

All analytical determinations were carried out at least in duplicate. Carbohydrate determination was done by means of gas chromatography of their trimethylsilyl ethers using a 3 m×1.0 mm inside diameter stainless steel column (Chrompack, Middelburg, The Netherlands), packed with 2% OV-17 on nonsilanised 120/140 Volaspher A-2 (Merck, Darmstadt, Germany), following the method described by Olano, Calvo, and Reglero (1986).

Cation content was analysed by atomic spectrophotometry. Sodium and potassium were determined by atomic emission at wavelengths of 589 and 766.5 nm, respectively. Calcium and magnesium were measured by atomic absorption with a multielement hollow cathode lamp. Matrix interference was controlled following the method described by Juárez and Martínez-Castro (1979).

Colour development was measured as the absorbance at 420 nm of the samples, following the method of Meydav, Saguy, and Kopelman (1977).

3. Results and discussion

In general terms, treatments of permeate with alkaline-substituted sepiolites resulted in the isomerisation of lactose into lactulose. Small amounts of epilactose and galactose were also formed as a consequence of disaccharide degradation (Méndez & Olano, 1979; Troyano et al., 1996).

Fig. 1 shows the changes in carbohydrate content during the treatment of permeate with sodium sepiolite. The formation of lactulose, epilactose and galactose and the degradation of lactose were influenced by the number of washing cycles. The activity of sepiolite decreased with the number of washing cycles. The highest isomerisation of lactose was attained when 5 cycles of washing were applied. Lactulose reached values near 1200 mg/100 ml after 60 min of reaction, which represents about 25% of lactose conversion. The amounts of epilactose and galactose formed were close to 80 and 400 mg/100 ml, respectively. Under these conditions, a considerable degradation of disaccharides was observed, since the decrease of lactose content was about 2000 mg/100 ml (40% of initial concentration).

When the sodium sepiolite was washed using 10 cycles, it took 150 min of reaction to reach the maximum amount of lactulose formed (≈1000 mg/100 ml), which represents 20% of initial lactose. Under these conditions, the decrease of lactose was 1100 mg/100 ml (25% of initial concentration), i.e. slightly higher than the concentration of lactulose present. The formation of epilactose and galactose was about 50 and 150 mg/100 ml, respectively. These contents were considerably lower than those observed after 5 cycles washing. Hardly any differences were obtained between the treatments performed after 10 and 15 cycles of washing with deionised water.

With respect to potassium sepiolite, the effect of washing cycles on the isomerisation of lactose and the degradation of disaccharides was similar to that shown for sodium sepiolite. However, potassium sepiolite was less active than sodium sepiolite, as can be observed in Fig. 2. Values of about 1000 mg/100 ml of lactulose were only obtained after 150 min of treatment with

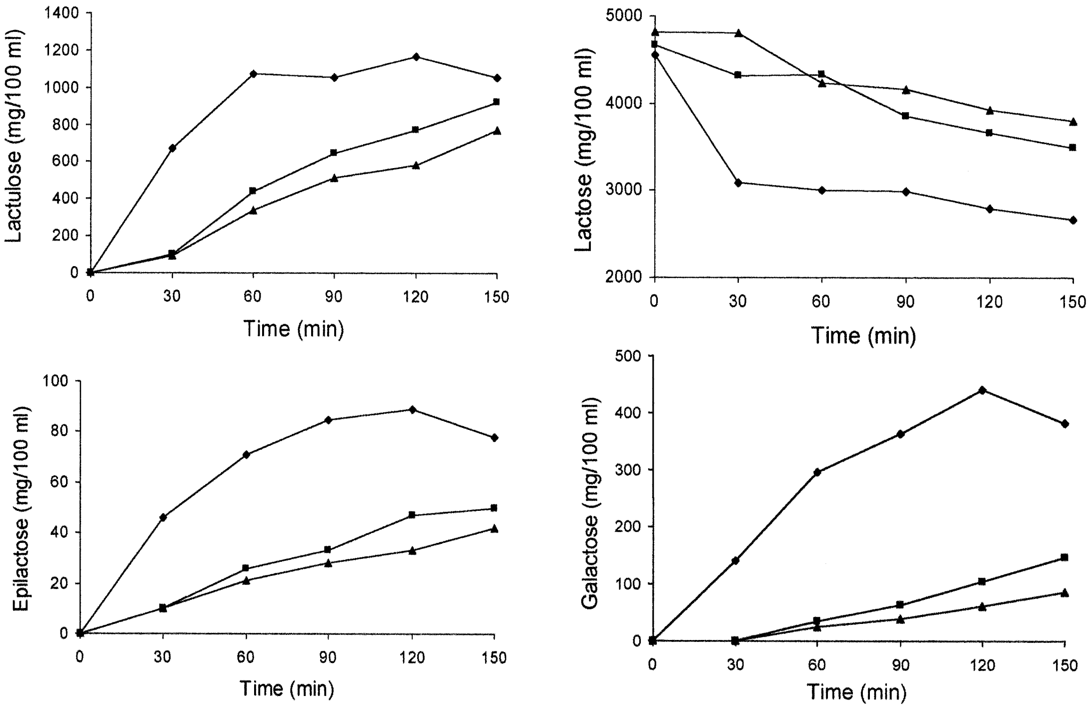

Fig. 1. Formation of lactulose, epilactose and galactose and lactose degradation during permeate treatment with sodium sepiolite after 5 (◆), 10 (■) and 15 (▲) cycles of washing with deionised water.

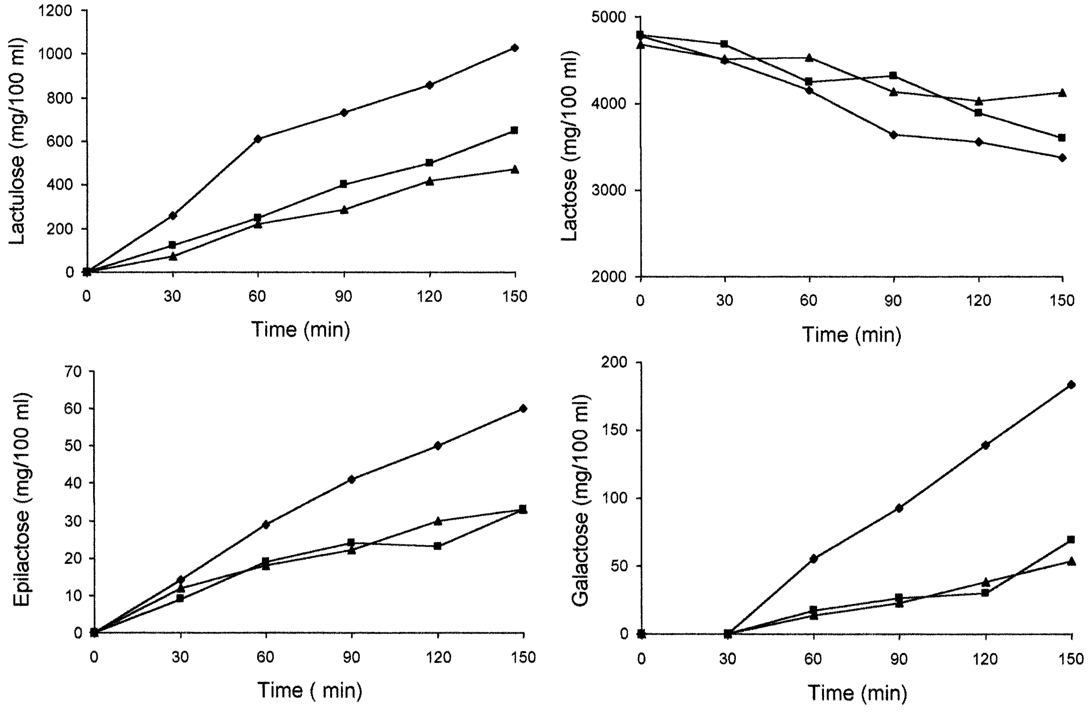

Fig. 2. Formation of lactulose, epilactose and galactose and lactose degradation during permeate treatment with potasium sepiolite after 5 (◆), 10 (■) and 15 (▲) cycles of washing with deionised water.

sepiolite washed during 5 cycles. In general, lower levels of epilactose and galactose were observed as compared with the amounts found using sodium sepiolite. These results are in agreement with those obtained by de la Fuente et al. (1999) for the isomerisation of lactose in aqueous solutions.

The catalytic activity of alkaline-substituted sepiolites is mainly due to the replacement of Mg^{++} by alkaline

Table 1
Effect of the number of washing cycles of Na-sepiolite on pH and colour development during lactose isomerisation at 90 °C in milk permeate

Time (min)	5 cycles		10 cycles		15 cycles	
	pH	Abs[a]	pH	Abs[a]	pH	Abs[a]
30	9.29	0.3292	8.94	0.0966	8.76	0.0289
60	8.69	0.6794	8.97	0.1259	8.87	0.0653
90	8.48	0.8709	8.86	0.1403	8.60	0.1010
120	8.41	0.9766	8.69	0.1950	8.61	0.1347
150	8.14	0.9869	8.45	0.2081	8.40	0.1530

[a] Absorbance at 420 nm.

Table 2
Effect of the number of washing cycles of K-sepiolite on pH and colour development during lactose isomerisation at 90 °C in milk permeate

Time (min)	5 cycles		10 cycles		15 cycles	
	pH	Abs[a]	pH	Abs[a]	pH	Abs[a]
30	9.14	0.0573	8.45	0.0529	8.69	0.0230
60	8.80	0.1057	8.53	0.0658	8.57	0.0496
90	8.56	0.1747	8.49	0.0860	8.56	0.0512
120	8.38	0.1975	8.57	0.0973	8.50	0.0702
150	8.06	0.2576	8.46	0.1136	8.24	0.0922

[a] Absorbance at 420 nm.

Table 3
Effect of the number of washing cycles of alkaline-sepiolites on the cation composition (mg/l) in milk permeates

Treatment	Washing cycles	Na^+	K^+	Mg^{++}	Ca^{++}
None		340	1540	63	326
Na-sepiolite	5	1220	1460	36	127
	10	685	1420	42	142
	15	480	1400	40	141
K-sepiolite	5	650	2660	46	185
	10	445	1760	31	157
	15	365	1520	31	164

ions (Corma & Martín-Aranda, 1991). Although sepiolite has a considerable capacity of adsorption for metals (Brigatti, Fanchini, Frigieri, & Gardinali, 1999), repeated washing treatments may release Na^+ or K^+ giving rise to a decrease in the catalytic activity.

Tables 1 and 2 show pH values and colour development during the reactions studied. The initial pH value of permeate was 6.7 and increased more than 2 pH units after mixing with sepiolite. The rises in pH decreased with the number of washing cycles. During the reaction, a progressive decrease of pH was observed, probably due to the formation of acidic compounds. Thus, among the fragmentation products most commonly detected in alkaline sugar reactions are lactic, pyruvic, propionic and acetic acids (Hodge & Osman, 1976).

For all treatments, the absorbance at 420 nm was found to increase with the heating time, as a consequence of the formation of coloured compounds during the reaction. The pH and colour development decreased with the increase of washing cycles, in agreement with the observed lower degradation of lactose.

Since the lactulose has to be isolated in a relatively pure form in order to be used as a food ingredient or in therapeutic applications, the content of cations, mainly Na^+, should be taken into account. Table 3 shows the cation composition of milk permeate after the different treatments with both types of sepiolite. A considerable increase in the contents of Na^+ and K^+ was observed in the permeate treated with 5 cycles-washed sodium and potassium sepiolite, respectively and the rise of alkaline cations decreased markedly with the number of washing cycles. The amount of the other cations (Ca^{++} and Mg^{++}) decreased in all cases. In general, hardly any difference was found in the contents of minerals in permeate after 10 and 15 cycles of sepiolite washing.

These results indicate that the control of washing cycles is critical in optimising conditions for lactose isomerisation in order to obtain lactulose in milk permeate. Under optimum conditions, lactose in permeate was efficiently isomerised to lactulose without causing any significant formation of coloured compounds. Lactulose, lactose and small amounts of epilactose and galactose mainly compose the resulting solution and the unreacted lactose can be easily removed by crystallisation.

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