CHARACTERIZATION OF LACTOSE AND DERIVED PRODUCTS IN DAIRY PRODUCT INDUSTRY EFFLUENTS PROCESSING

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The treatment of the effluents of dairy product industries containing lactose is done by a biological process, which reduces considerably the original amount of that sugar. Although the final residual content of lactose is small after treatment, it may cause the eutrophication and/or the superfertilization of the water, which provokes vegetation growth on the water surface, hindering the navigability and increasing the consumption of the dissolved oxygen necessary to the life of the fishes of the river or sea where the treated effluent is poured.

In dairy industry, after proper initial processing steps of waste treatment, lactose, as it is water soluble, may still be present in the outgoing effluents. A complementary step by using organophilic clay adsorption, as a further treatment of these effluents, may enhance antipollution procedures, decreasing its final content in the effluents. The present paper deals with the characterization, by thermal analysis of different lactose products, which may be present in the different processing steps as it dissolves in water and then it is recrystallized from it, as well as after being adsorbed by organophilic clay from those effluents, which are very diluted lactose aqueous solutions.

Introduction

The residual lactose, which is not extracted from dairy industry effluents by conventional methods, provokes the pollution of water and rivers, causing super fertilization of the water and vegetation growth on the water surface. An organophilic clay, made in Brazil, from a smectitic clay with quaternary ammonium salt $[(CH_3)_3NR]^+$ [1], which was characterized in a previous paper [2], was used to study the adsorption of the lactose. Isothermal adsorption measurements were done in concentrations next to those of the industrial effluents at 30°C, to have same environmental conditions and to obtain the adsorption isotherm.

Differential thermal analysis (DTA) has traditionally been used to characterize the nature of clays [3], as well as carbonaceous products [4], and many articles demonstrate that the experimental parameters have a great effect on the resulting thermal analysis curves [5]. Currently, thermogravimetric analysis (TG), differential scanning calorimetry (DSC) and simultaneous TG/DTA have been used to characterize organophilic clays and nanocomposites [6–9]. DSC and modulated DSC have been used for the characterization of hydrated lactose, which can change its structural state or hydration state, depending on the applied drying procedure [10, 11].

The purpose of this paper is to contribute for the characterization, by thermal analysis, of the lactose and of the clays that may be used to treat industrial effluents containing it in low concentrations.

Experimental

Materials and methods

To obtain the organophilic clay (AO), a Brazilian commercial smectitic clay from Verde Claro (VC) was used, which is predominantly calcic [2]. The calcium cation was changed by sodium with carbonate sodium carbonate, and subsequently by an organic radical by reacting with a quaternary salt of ammonium (chloride of hexadecile-trimethyl-ammonium). The organophilic clay was used in the process of lactose adsorption. To measure the lactose amount in each phase, a total organic carbon measurement equipment, Shimatzu model TOC-5000A, was used. The lactose is a commercial monohydrated α-lactose, which is insoluble in methanol, ethanol and ether [12, 13]. X-ray diffraction (XRD) was performed by using the powder method. The equipment was a Philips X'PERT MPD and CoK_α radiation was used. Simultaneous TG/DTA analyses in a TA-Instruments model SDT2960, were performed in platinum crucibles, by using 100 mL min^{-1} of air as the purge gas at a heating rate of 10°C min^{-1}.

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Results and discussion

Through XRD the organic radical presence in the AO structure was indicated by an increase of the basal interlayer distance to 23.37 Å of this clay, when compared to the previous value of the original VC clay, which was 15.16 Å.

The lactose adsorption at 30°C was studied using aqueous concentrations from 200 to 1000 mg L^{-1} by using the AO, obtained from VC clay. The behavior of the adsorbate in solution was analyzed by the Freundlich isotherm, shown in Fig. 1, which can be expressed by the equation $X/m=K_f C_e^{1/n} f$, where X is the mass of adsorbed solute, m is the clay mass, K_f is a constant related to the capacity of adsorption (L mg^{-1}) and n_f is a non-dimensional constant, which depends on the shape of the isotherm. C_e refers the equilibrium concentration in (mg L^{-1}) [14]. The agreement with the Freundlich method was confirmed as shown in Fig. 1, by a very good correlation coefficient (0.9753), showing a mean adsorption of 38.40 mg of lactose per gram of clay. Experimental K_f and n_f values were, respectively 0.031 and 0.9429.

Figure 2 shows the TG and DTA curves of the original monohydrate lactose (Lac60c.000) and after being dissolved and recrystallized in water (Lacrecr.000). Both were dried at 60°C prior to analysis for 24 h and they do not show practically any mass loss due to free water until about 120°C. From this temperature to about 175°C, the original lactose shows a mass loss on the TG curve, due to the loss of its hydration water, characterized by the endothermic sharp peak seen in that range of temperature [15]. The recrystallized lactose shows a very small mass loss of hydration water. This indicates that after the solubilization of the monohydrate lactose in water and recrystallization by drying the solution at 60°C, until constant mass, mostly anhydrous lactose is formed, with a very little presence of the hydrated phase, as characterized by the little endothermic peak on the corresponding DTA curve at about 150°C. There are no significant mass losses for both samples
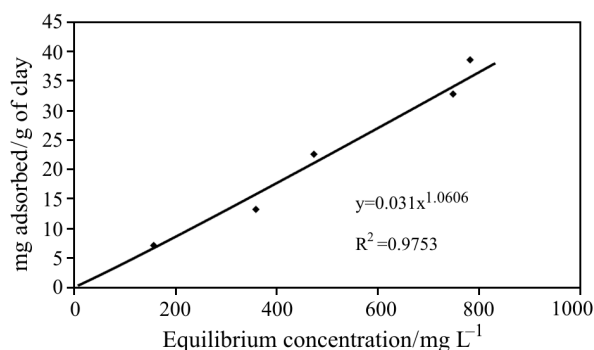
when heated from 150 to 240°C. During this period the monohydrated lactose shows a crystallization peak at 180°C and a subsequent melting peak, while the anhydrous sample only shows a melting peak at 230°C. This indicates that the original lactose was partially amorphous as alpha monohydrate phase [16] and during the analysis it was crystallized to the beta anhydrous phase and then melt. Just after melting, both samples present total decomposition and burning steps, as seen in Fig. 2.
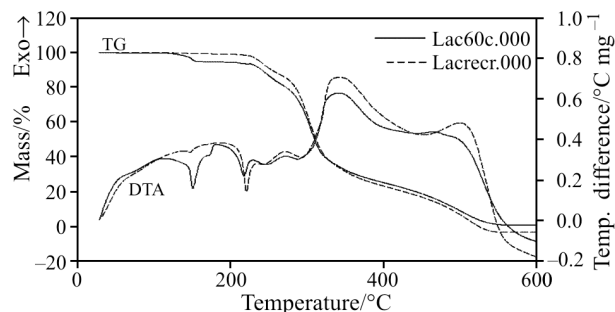
Fig. 2 TG and DTA curves of the original monohydrate lactose (Lac60c.000) and after being recrystallized (Lacrecr.000), both dried at 60°C prior to analysis

Figure 3 shows the TG, DTG and DTA of the original VC clay and of AO clay obtained after reaction with salt quaternary of ammonium. From TG curves is noticed that the AO clay presents a smaller content of free and/or adsorbed water in the pores than the VC clay. Through the DTG curves, which represent the rate of mass loss for each case as a function of the temperature, the several stages of mass loss are better visualized from the respective DTG peaks. It can be seen that the AO clay loses its free and/or adsorbed water even at 140°C. The VC clay presents a larger loss of water, which occurs up to 210°C. This indicates a stronger link with the mineral structure of the clay. From 350 to 600°C the characteristic dehydroxylation DTG peak occurs. In the DTG curve of the AO clay, from 150 to 350°C there is the pyrolysis and beginning of the organic material
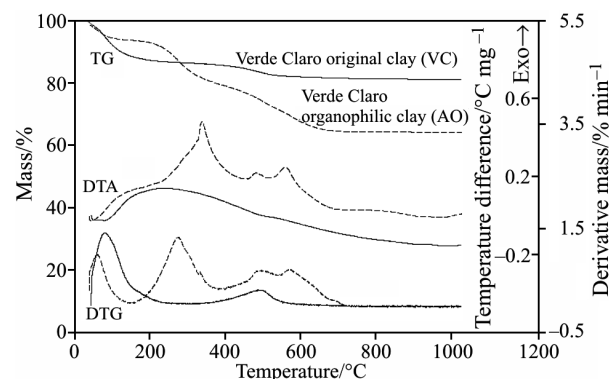
Fig. 1 Adsorption isotherm of the lactose by the VC organophilic clay at 30°C

Fig. 3 TG, DTG and DTA curves of the VC and AO clays

burnout, characterized by the respective exothermic DTA peak. The second step of the residual organics burnout after 400°C, occurs simultaneously to the dehydroxylation of the clay structure, which are better identified by the respective DTG peaks.

Figure 4 shows the TG and DTG curves of dried samples at 60°C, of the AO clay, after it has been immersed in water without lactose (AOH$_2$O) and after immersed in the solution containing 1000 ppm of lactose (AO1000). All samples were analyzed after a drying step at 60°C. As can be seen, the curves of the samples AOH$_2$O and AO1000 do not show significant differences in their thermal behavior and they show a little higher organic matter release and burnout than the AO clay during the heating process in air between 150 and 375°C.
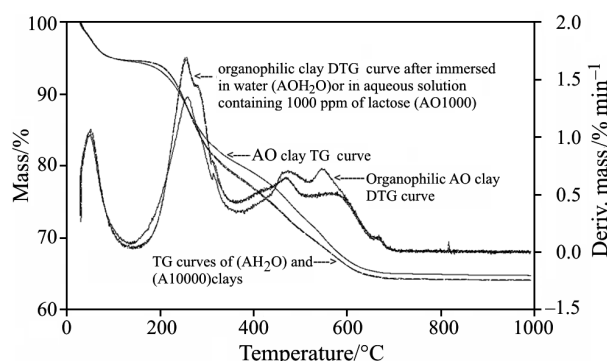

Fig. 4 TG and DTG curves of AO clay, after immersed in water (AOH$_2$O), and after immersed in aqueous solution with 1000 ppm of lactose (AO1000)

Per the adsorption isotherm results, the estimated amount of lactose that is adsorbed by the organophilic clay is very small, practically between 0.3 and 0.5%, and the samples obtained after adsorption present practically very similar TG and DTA curves, avoiding, by direct visual analysis, to note significant differences. However, their DTA curves present resulting exothermic peaks due to the burnout of the organic matter, through which one can identify the presence of the adsorbed lactose as follows.

When the DTA curve of a dried sample obtained after adsorption of lactose in a specific case is subtracted from the AOH$_2$O sample DTA curve, this difference appears, as shown in Fig. 5, including some endothermic peaks due to the incipient melting of the lactose, which is discontinued because of its following decomposition and burning from the organophilic clay structure. This corresponds to the DTA curve that would be obtained, if the AOH$_2$O sample was used as reference during analysis and allows one to identify, by thermal analysis, the presence of the lactose adsorbed by the organophilic clay.
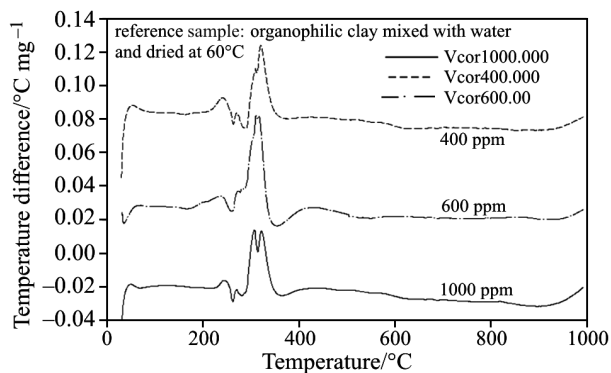

Fig. 5 Differences between DTA curves of organophilic clay after adsorption of lactose from solutions with 400, 600 and 1000 ppm of lactose monohydrate

Conclusions

The adsorption of lactose by Verde Claro organophilic clay occurs according to the Freundlich isotherm, and indicates low adsorbed amounts, which do not allow one to quantify them by usual thermal analysis procedures.

The thermal analysis qualitative identification of the presence of the lactose adsorbed by the organophilic clay, in this case, may be done by the characterization of its melting and following decomposition and burnout peaks from a DTA curve obtained from the difference between the DTA curve of the specific organophilic clay after adsorption, and the DTA of the organophilic clay only mixed with water, after drying both samples at 60°C.

References

1 G. Y. Sheng and S. A. Boyd, Clays Clay Miner., 46 (1998) 10.
2 F. V. Valenzuela Díaz, Proc. Ítal.-Braz. Min. Eng. Congr., São Paulo 1994, p. 124.
3 P. Souza Santos, Ciência e Tecnologia de Argilas, 2nd Ed., Edgard Blucher, São Paulo 1992, p. 277.
4 R. W. Soares, V. J. Menezes, M. V. A. Fonseca and J. Dweck, J. Thermal Anal., 49 (1997) 657.
5 J. Wieckowska, Thermochim. Acta, 134 (1988) 359.
6 J. Dweck, P. M. Büchler and F. K. Cartledge, J. Therm. Anal. Cal., 64 (2001) 1011.
7 T. X. Liu, Z. H. Liu, K. X. Ma, L. Sheng, K. Y. Zeng and C. B. He, Compos. Sci. Technol., 63 (2003) 331.

8 Z. Yermiyahu, I. Lapides and S. Yariv, J. Therm. Anal. Cal.,
   69 (2002) 317.

9 Z. Yermiyahu, A. Landau, A. Zaban, I. Lapides and
   S. Yariv, J. Therm. Anal. Cal., 72 (2003) 431.

10 V. L. Hill, D. Q. M. Craig and L. C. Feely, Int. J. Pharm.,
    161 (1998).

11 S. Rückold, K. H. Grobecker and H. D. Isengard,
    Food Control, 12 (2001) 401.

12 J. G. Zadow, J. Dairy Sci., 62 (1984) 2654.

13 S. T. Yang and E. M. Silva, J. Dairy Sci., 78 (1995) 2541.

14 S. Sharmasakar, W. F. Jaynes and G. F. Vance,
    Water Air Soil Poll., 119 (2000) 257.

15 S. Yariv, D. Ovadyahu, A. Nasser and U. Shuali,
    Thermochim. Acta, 207 (1992) 103.

16 D. O. Corrigan, A. M. Healy and O. I. Corrigan,
    Int. J. Pharm., 235 (2002) 193.