

# Ca<sup>2+</sup>, Mg<sup>2+</sup> OR Fe<sup>2+</sup> ION-EXCHANGED CANCRINITE-TYPE ZEOLITES AS POSSIBLE HYPOGLYCEMIANT AGENTS

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## Abstract

A nitrate-sodium cancrinite-type zeolite was synthesized and exchanged with calcium (II), magnesium (II) and iron (II) cations. These exchanged zeolites were previously characterized by XRD, BET specific surface area, chemical analysis and FT-IR. XRD confirmed only the presence of the cancrinite phase. Other phases, such as sodalite, were not identified. Different amounts of these ion-exchanged zeolites were put in contact with a glucose solution during variable time. Results showed that these ion-exchanged cancrinites were active for the glucose adsorption, especially those exchanged with Fe; while the Ca<sup>2+</sup>, Mg<sup>2+</sup> and Na<sup>+</sup> cancrinites displayed an adsorption capacity much lower than the Fe<sup>2+</sup> cancrinite. Moreover, the kinetic studies showed that the glucose adsorption capacity by using these modified cancrinites, it is affected by the glucose concentration in the reaction medium. [www.relaquim.com](http://www.relaquim.com)

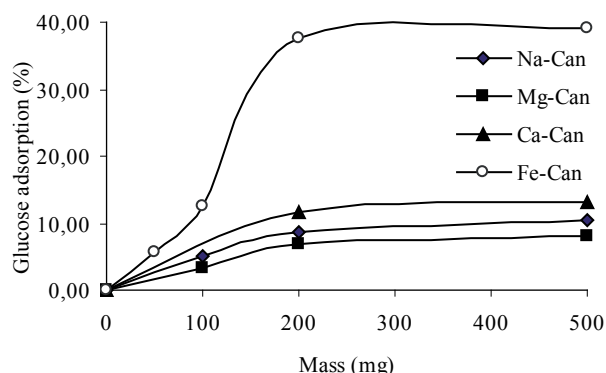
**Key words:** cancrinite, hypoglycemiant agents, diabetes, cationic exchange.

## Resumen

Se sintetizó una zeolita tipo cancrinita sódica y nitrada, y se intercambió con cationes calcio (II), magnesio (II) y hierro (II). Estas zeolitas se caracterizaron, previamente, por difracción de rayos X, área superficial específica BET, análisis químico e infrarrojo con transformada de Fourier. Los datos de DRX confirmaron únicamente la presencia de la fase cancrinita. Otras fases, como la sodalita, no fueron detectadas. Estas zeolitas intercambiadas fueron puestas en contacto con una solución de glucosa a diferentes masas y tiempos de contacto. Los resultados señalaron que estas cancrinitas modificadas fueron activas para la adsorción de glucosa, especialmente las zeolitas intercambiadas con Fe, mientras que las cancrinitas intercambiadas con Ca<sup>2+</sup>, Mg<sup>2+</sup> y Na<sup>+</sup> mostraron una capacidad de adsorción mucho más baja que la cancrinita de Fe. Además, los estudios cinéticos demostraron que la capacidad de adsorción de glucosa por estas zeolitas es afectada por la concentración de glucosa en el medio de reacción. [www.relaquim.com](http://www.relaquim.com)

**Palabras clave:** cancrinita, agentes hipoglicemiantes, diabetes, intercambio catiónico

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Glucose adsorbed by different masses of modified cancrinite zeolites.

## INTRODUCTION

Type-II diabetes or Diabetes mellitus is characterized by the inadequate use of the insulin by human organism; therefore, the glucose levels in the blood are not normal. This type of diabetes can be controlled by diets, exercises and a low ingestion of sugar or carbohydrates to control the glycemia levels. However, when the sugar levels in the blood are very high, several drugs should be frequently administered in order to regulate the glucose concentration in the organism. These drugs are composed of sulfonylureas, which stimulate to the pancreas to produce insulin (White *et al.* 1959). These compounds are very effective but when they are used for long time, their effectiveness is lost. Then, new treatments based on the insulin administration should be started.

Nowadays, new alternatives based on zeolites can also be considered. Because of their well-know adsorption properties, they can reduce the glucose concentration in blood. Concepción-Rosabal *et al.* (1997) tested exchanged natural clinoptilolites with diverse cations, and they found that these modified zeolites could be used as glucose adsorbents. However, the heterogeneity, normally present in the natural zeolite ores, could be an undesirable ele-

ment. Therefore, synthetic-instead of natural- zeolites could be considered. Previously, Sherman and Chao (1989) had tested zeolites X and Y modified with  $K^+$  and  $Ca^{2+}$ . They found that those zeolites were able to separate different saccharides. Likewise, Heper *et al.* (2007) established studies of adsorption kinetics at  $50^\circ C$  by  $Na^+$ ,  $NH_4^+$ ,  $Ca^{2+}$  and  $Mg^{2+}$  forms of zeolite Y contacted with aqueous solutions containing glucose and/or fructose. They found a selective adsorption of the glucose or fructose depending on the cationic form. These cations form complexes with the hydroxyl group of the adsorbed sugar, leading to a selective adsorption according to the orientation of the hydroxyl group (Nobre *et al.* 2009)

On the other hand, Buttersack *et al.* (1993) studied dealuminated zeolites Y and found that Si/Al ratio had a significant influence on the sugar's selective adsorption.

Taking into account these results, it is possible to consider the use of zeolites for adsorption of glucose.

In that sense, our group has tested cancrinite-type zeolites to relieve diverse pathologies such as stomach acidity (Linares *et al.* 2005) and hypercholesterolemia (Linares *et al.* 2008). Cancrinites have a Si/Al ratio equal to 1, which is favourable for the cationic exchange procedures (Buttersack *et al.* 1993). Therefore, this work represents a new opportunity offered by modified cancrinite zeolites as a glucose adsorbent.

## MATERIALS AND METHODS

A nitrate-sodium cancrinite zeolite was synthesized according to the previously reported procedure (Hackbarth *et al.* 1999). Then, this cancrinite was ion-exchanged with 0.01M  $Ca^{2+}$ ,  $Mg^{2+}$  or  $Fe^{2+}$  solutions by using a ratio of 10 mL salt solution/g zeolite. The slurry was kept in reflux for 24h, centrifuged and the solid was refluxed again twice.  $Fe^{2+}$  oxidation state was preserved by

using a N<sub>2</sub> atmosphere during the reflux condition. After the last reflux, the slurry was centrifuged again and solids were washed off with abundant distilled water and dried at 80°C for 18 h in a convection oven. Samples were identified as Na-Can (sodium-cancrinite), Mg-Can (magnesium-cancrinite), Fe-Can (iron (II) cancrinite) and Ca-Can (calcium-cancrinite). Obtained solids were characterized by techniques such as: X-ray diffraction (XRD), Fourier transforms infrared spectroscopy (FT-IR), N<sub>2</sub> physisorption measurements and chemical analysis. XRD analyses were performed in a Siemens 5000 diffractometer with CuK $\alpha$  radiation (1.542 Å) for crystalline phase detection from 5 to 80° (2 $\theta$ ). The presence of functional groups and an evaluation of purity of solids were achieved by FT-IR. Spectra were recorded in a Perkin-Elmer 283 spectrometer in the 4000-400 cm<sup>-1</sup> range. Physisorption measurements were carried out in a Beckman Coulter SA 3100 instrument; BET surface areas were determined by nitrogen adsorption at -196°C with an Ar/N<sub>2</sub> ratio of 70/30. Inductively Coupled Plasma Emission Spectroscopy (ICP) using a Perkin Elmer ICP/ 5500 instrument was used to analyze the chemical compositions of the original and exchanged zeolites.

Characterized cancrinites were contacted with 3mL of a glucose solution (100 ppm) at different masses: 50, 100, 200 and 500 mg for 60 min. In order to determine the contact time, 100 mg of solids were also put in contact with a glucose solution at 15, 30, 45 and 60 min. Solids were centrifuged and analyzed by FT-IR. The quantitative determination of glucose was performed by enzymatic techniques whose coloured complex was followed by UV-Visible at 506 nm.

## RESULTS AND DISCUSSION

The XRD pattern of the Na<sup>+</sup> cancrinite sample shows reflections attributed to the nitrated-cancrinite-type zeolite that was consistent with the P<sub>63</sub> spatial group (ICDD-PDF# 38-0513) (Robson and Lillerud 2001) (Fig. 1). Other phases, such as sodalite, were not detected by XRD. XRD patterns for the exchanged cancrinites were similar to that reported by nitrate-sodium cancrinite.

On the other hand, FT-IR spectrum (Fig. 2) of the synthesized sodium cancrinite-type zeolite showed different bands: a band at 1425 cm<sup>-1</sup> was assigned to the presence of nitrate anions occluded in the zeolite framework structure. The band placed at

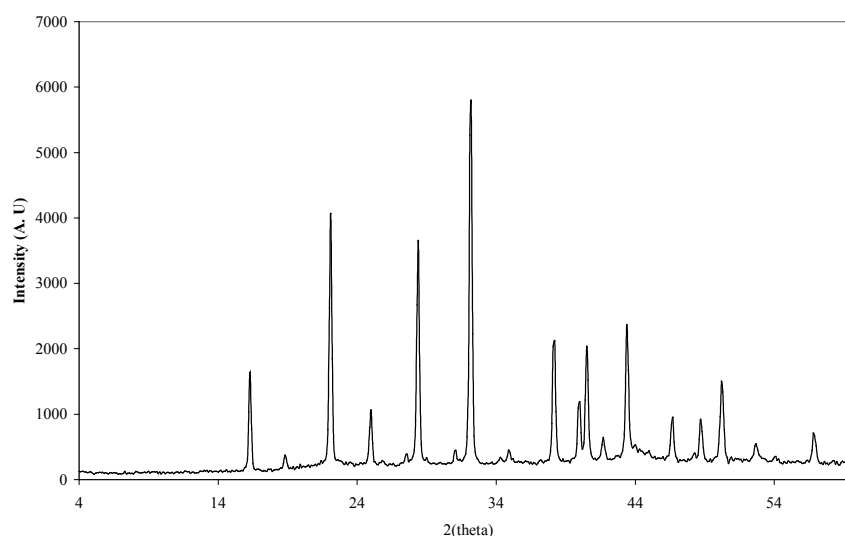


Figure 1. Powder XRD pattern of synthesized cancrinite zeolite.

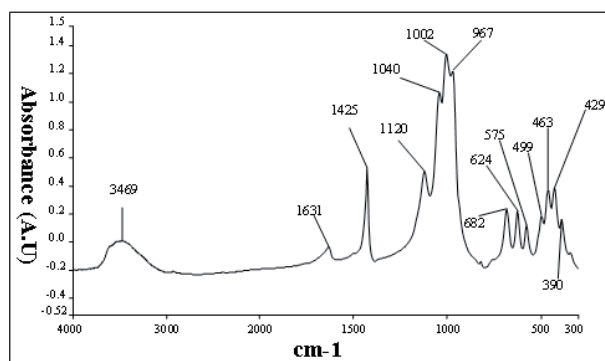


Figure 2. FT- IR spectrum of synthesized nitrate-sodium cancrinite.

$1631\text{ cm}^{-1}$  corresponds to water molecules localized inside the cancrinite cavity, while bands in the region between  $1095$  and  $500\text{ cm}^{-1}$  were attributed to Si-O-Al bonds (Hackbarth *et al.* 1999).

Likewise, Table 1 shows the chemical analysis and textural properties of exchanged cancrinites. Because Mg and Ca are di-valence cations, they are exchanged in minor proportion in comparison to monovalence cations.

The BET specific surface area of Na-Can is quite low if it is compared to other zeolites whose pores are free. The presence of nitrate anions occluded inside the framework structure is responsible for this low surface area (Hackbarth *et al.* 1999). As the pores are blocking, the BET area is almost entirely the external area of these solids. The micropores area is quite negligible. These results are expanded to the other exchanged cancrinites.

**Table 1.** Chemical analysis and textural properties of exchanged cancrinites

Exchanged cancrinite	Metal-exchange (%)	BET Surface Area ( $\text{m}^2/\text{g}$ )
Na-Can	100	9
Mg-Can	---	29
Ca-Can	16	43
Fe-Can	10	---

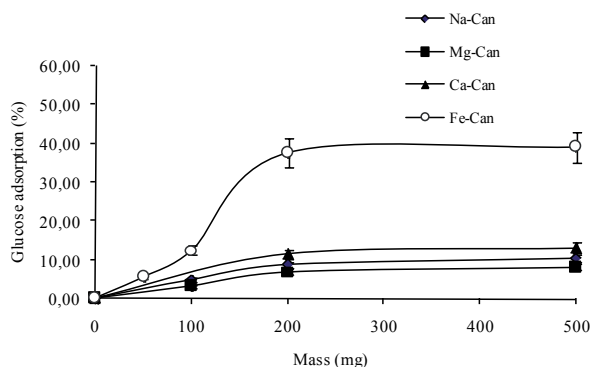


Figure 3. Glucose adsorbed by different masses of modified cancrinite zeolites.

When, the Na-Can is exchanged with  $\text{Mg}^{2+}$  or  $\text{Ca}^{2+}$  cations, the BET surface area is slightly increased in comparison to Na-Can. Due to the fact that,  $\text{Mg}^{+2}$  and  $\text{Ca}^{2+}$  cations are di-valences, they allow a major access to the cancrinite pores

The previously characterized samples were, then, tested as glucose adsorbents. As it is depicted in Fig. 3, the adsorption process is largely enhanced during the first 200 mg sample; after that, the adsorption rate remains constant until the 500-mg sample. A possible explanation could be associated to mass transference troubles. This glucose adsorption takes place on the external crystal surface due to the pore blocking showed by the cancrinite type-zeolites as showed in Table 1 (Hackbarth *et al.* 1999).

On the other hand, it was observed a preference on the glucose adsorption when Fe-Can ( $\sim 40\%$ ) was used in comparison with the other ion-exchanged zeolites ( $\sim 5\text{--}10\%$ ). According to literature (Wolowiec and Drabent 1985),  $\text{Fe}^{2+}$  can produce a stable complex with glucose molecules while glucose interactions with  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  zeolites are weaker (Angyal 1984). Mg-cancrinite showed the lowest adsorption capacity among all the tested cations. According to Heper *et al* (2007),  $\text{Mg}^{2+}$ -zeolite Y presents lack of free space inside the zeolite pores to accommodate glucose. The reason for

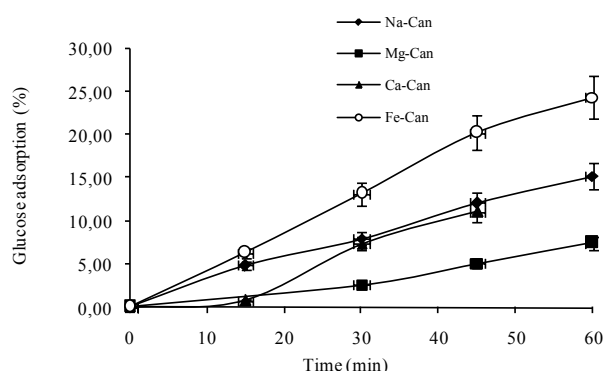


Figure 4. Influence of contact time on the glucose adsorption by modified cancrinite zeolite (100 mg).

this could be a higher affinity of the zeolite to Mg<sup>2+</sup> or a greater hydration layer of Mg<sup>2+</sup> resulting in its inability to leave the cages.

Previously, Sherman and Chao (1989) and Kulprathipanja (1991), had reported the preference of Ca<sup>2+</sup> and K<sup>+</sup> cations for fructose or glucose molecules. However, K<sup>+</sup> and Na<sup>+</sup> are considered non-complex ions, as it has been reported that sugars and univalent cations form very weak complexes in comparison to divalent cations (Churm 1996, Nobre *et al.* 2009)

Concepción-Rosabal *et al.* (1997) reported the use of Fe<sup>2+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> ion-exchanged clinoptilolites as glucose adsorbent. They found an adsorption order similar to our results: Fe >> Mg > Ca ≈ Na. However, no comparison related to the glucose adsorption capacity could be established because the glucose concen-

tration in the Concepción-Rosabal's work was not reported.

Likewise, the time influence on the glucose adsorption was also determined for modified cancrinites using 100 mg of sample (Fig. 4). In general, the adsorption of glucose increased as contact time is increased.

A maximum adsorption was determined at 60 min of contact time. This time is ideal if gastric functions are carried out (Linares *et al.* 2005). On the other hand, the adsorption behaviour by exchanged cations was similar to that reported for mass influence.

In order to investigate the controlling mechanism of adsorption processes such as mass transfer or chemical reaction, the pseudo-first-order and pseudo-second order equations were applied to model the kinetics of glucose adsorption onto exchanged cancrinites

The possibility of adsorption data to follow Lagergren pseudo-first order kinetics (Lagergren 1898) is given by:

$$dq/dt = K_1 (q_e - q) \quad (1)$$

by integrating Eq (1), the kinetic rate expression becomes:

$$\log(q_e - q_t) = \log q_e - (K_1 * t) / 2.3 \quad (2)$$

The first order rate constant  $K_1$  can be obtained from the slope of plot between  $\log(q_e - q)$  versus time  $t$ .

**Table 2.** Pseudo-first and pseudo-second order adsorption kinetics for the glucose adsorption onto exchanged cancrinites

Exchanged cancrinite	Pseudo-first order				Pseudo-second order		
	$q_e$ exp (mg/g)	$q_e$ (mg/g)	$K_1$ (min) <sup>-1</sup>	$r^2$	$q_e$ (mg/g)	$K_1$ (g(mg.min)) <sup>-1</sup>	$r^2$
Na-Can	0.457	0.468	0.035	0.93	0.871	0.0190	0.68
Mg-Can	0.224	0.259	0.025	0.90	-0.132	0.085	0.84
Ca-Can	0.457	0.543	0.030	0.91	-0.102	0.155	0.60
Fe-Can	0.733	0.859	0.037	0.93	26.64	1.84E-5	0.05



A pseudo-second order model proposed by Ho and McKay (Ho and McKay 1999) can be used to explain the sorption kinetics. This model is based on the assumption that the adsorption follows second order chemisorptions (Ho 2004). The pseudo-second order can be expressed as:

$$dq/dt = K_{11} (qe - q)^2 \quad (3)$$

$$dq/(qe - q)^2 = K_{11} dt \quad (4)$$

Integrating Eq 4 simplifies it to:

$$t/qt = 1/(K_{11} \cdot qe^2) + t/qe \quad (5)$$

where  $t$  is the contact time, min,  $qe$  and  $qt$  are the amount of glucose adsorbed by zeolite (mg/g) at equilibrium and at any time  $t$ . A plot between  $t/qt$  versus  $t$  gives the value of the constant  $K_{11}$  ( $\text{g}(\text{mg} \cdot \text{min})^{-1}$ ) and also  $qe$ , mg/g, can be calculated.

In this study, the pseudo-first order model fitted better when compared with the pseudo-second order according to  $r^2$  and  $qe$  values (Table 2). Therefore, the adsorption data in the present study could show a

physical adsorption which will depend on the glucose concentration (Kushwaha *et al.* 2008). A major glucose concentration could increase the adsorption capacity of cancrinites.

## CONCLUSIONS

New solids, the ion-exchanged cancrinite-type zeolites, could be used as hypoglycemic drugs. The best results were obtained with  $\text{Fe}^{2+}$  cancrinites while the  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Na}^+$  cancrinites displayed much lower adsorption than that of  $\text{Fe}^{2+}$ . Similarly, the influence of time on the glucose adsorption showed that  $\text{Fe}^{2+}$  cancrinite was more active at short contact times than that showed by the ion-exchanged zeolites with other cations.

## ACKNOWLEDGEMENT

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