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Research Article
Desiccant Properties Comparison of Natural Bio-polymers

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Abstract

Background and Objective: Desiccants are substances used in the dehumidification process which is vital in order to avoid the degradation of materials. Silica gel is the most prominent type of desiccant used and today the world has developed an interest in bio-polymers due to certain demerits of silica. Hence this study was conducted to investigate the desiccant properties of the four commercial flours wheat, corn, potato and gram and to compare them with the common silica gel desiccant. **Materials and Methods:** The bio-polymers were dried under vacuum at 120°C and were studied over time using Near-Infrared spectroscopy for their-OH combination peak which appears at around 5200 cm^{-1} and the derivative spectra were analyzed to recognize the specific-OH groups involved in the hydrogen bonding process. Further, the gravimetric analysis was used to study the rate of adsorption and their long term efficacies were detected using data loggers. **Results:** The results clearly indicated that adsorption of water occurs at C1, C2+C3, C4 and C6-OH groups for wheat and corn flour while potato and gram flour showed only three peaks attributing to C1, C2+C3 and C6-OH. Further, it was observed that C1 and C2+C3-OH groups have a similar and the highest rate. **Conclusion:** The rates of adsorption of all flours were greater than both analytical grade and commercial silica while corn flour was found to be an outstanding desiccant compared to conventional silica desiccant.

Key words: Near-Infrared spectroscopy, adsorption, Bio-desiccant, gravimetric, commercial silica, analytical grade

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Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Dehumidification is a vital process in different aspects and can be achieved in two major ways either by cooling the air to a temperature lower than the dew point or by using a sorbent material. The latter is more preferred as the temperature lowering is energy intensive[1]. Sorbents are materials capable of attracting and holding gases or liquids and desiccants are a subset of sorbents that specifically have an affinity for water vapor and thus a good desiccant is a material with a greater adsorption capability, low regeneration temperature[2], high surface area and low cost[3]. Desiccants have a wide array of industrial and agricultural applications such as in textile mills, post-harvest crop storage[4] electronics, pharmaceuticals, food and storage in order to prevent corrosion and condensation[5,6]. In case of electronics, the comfortable humidity level for most items is 45-60% and thus intensifies the necessity of desiccants[7]. In pharmaceuticals too, the damage made by moisture is massive and includes degradation of active intermediates, reduction of tablet hardness, discoloration, reduction of drug potency, development of unpleasant odors etc. and the appearance in pharmaceutical intermediates, preparations and finished products substantially depend on the desiccant used[8]. In many of the applications above, silica gel serves as the common desiccant and this property of silica is due to the presence of siloxane groups on the surface which transform in to hydroxyl groups and polarize thus forming hydrogen bonds with the nearby water molecules. The next layer of water arises due to the intermolecular hydrogen bonding and continues up to several layers[5]. Also it is noteworthy that there are some limitations like low sorption capacity and high regeneration temperature associated with such conventional desiccants and the same fact has encouraged studies on advanced desiccant materials such as composite desiccants and also chemical and natural polymer desiccants[6].

The growing interest on bio-desiccants is normally attributed to their eco-friendliness, bio-degradability, cheapness and availability[9]. Although the scientific literature available on bio-desiccants is scarce, starch and starch derivatives are being used as desiccants in industry since a long time. Such materials include corn grits, corn starch, enzyme modified corn grits and other starch-based materials and have been mainly used for the dehydration of ethanol in industry[10-13]. In general, the efficacy of bio-desiccants is due to the carbohydrate structure where the adsorption of water occurs through interacting with free-OH groups via hydrogen bonds[14]. These bio-desiccants are mainly polysaccharides made up of D-glucose units linked together via α-glycosidic bonds[15] and starch is such a polysaccharide and is a mixture of amylose and amylopectin[16,17]. Several studies on bio-desiccants reveal that chemical grade amylose, amylopectin and starch from potato, microcrystalline cellulose, amylose acetate, dextran and dextrin do show significant desiccant activity and have been characterized using second and fourth derivatives of Near-Infrared spectroscopy (NIR) for their molecular adsorptions[18]. But it is noteworthy that the commercially available flours which are also mixtures of amylose and amylopectin have not been screened for their desiccant ability.

Thus, this study was aimed to compare the desiccant properties of the natural bio-polymers, wheat, corn, potato and gram flours as studied by NIR spectroscopy and gravimetry and also determining their long-term efficacies in order to substitute currently available silica gel desiccant.

MATERIALS AND METHODS

Study area: This research project was conducted from June, 2019 to April, 2020.

Sample preparation: The four commercially purchased flour samples were sieved through 38 μm sieve and about 0.15 g of each sample was evacuated and dried at 120°C using a vacuum ceramic heater (BA Electric Bunsen from Electro thermal, Staffordshire, U.K.) controlled by an external vacuum pump (Edwards, West Sussex, U.K) as shown in Fig 1. The samples were cooled to room temperature and the initial weight was recorded before gravimetric and near-infrared measurements which were taken simultaneously.

Near Infrared (NIR) measurements: Each dried sample was placed on the transflectance accessory of spectrometer (Perkin-Elmer Ltd, Cambridge, UK) equipped with a deuterated tri-Glycine sulfate detector and was exposed to the atmospheric air in the room (Fig. 2) while maintaining the humidity at 60% and temperature at 22°C. The evolution of the adsorption peak of water vapor was analyzed by NIR spectrometer in every 30 min over a period of 7 hrs. NIR spectra were collected in the range of 10000-4000 cm^{-1} and a total of 30 scans were obtained at a resolution of 16 cm^{-1} per time. All NIR spectra were transformed to log (1/R) format and the second and fourth derivatives of the spectra were obtained using the program after automatic smoothing.

Gravimetric measurements: Each dried and cooled sample was placed in the pre-weighed glass container and exposed

Fig. 1: Sample evacuation apparatus

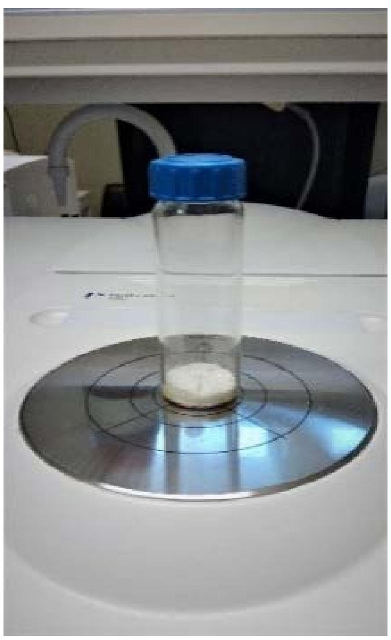

Fig. 2: Placement of sample on the transflectance accessory of NIR spectrometer

to the atmospheric air and the weight measurements were taken once in every 30 min until there was no any significant difference between two consecutive readings.

Long term efficacy check: Initially 3.0 g of each flour was placed in small semi-permeable packets separately and 0.3% of sodium propionate by initial weight was added as a preservative. Then each packet was kept in an air-tight zip-lock polythene bag separately along with a data logger to check the variation of surrounding humidity and temperature (Tiny tag Plus 2-TGP 4017, UK). The logger was launched to detect the parameters once in an hour over a period of 3 days. For the purpose of comparison the same procedure was followed for commercially available silica gel packets and analytical grade silica.

RESULTS

The results of this research work show that all the flour samples (bio-polymers) used in this study adsorb water molecules from the surroundings at different rates. Corn flour adsorbs more water than wheat, potato and gram flours. Furthermore, corn flour adsorbs more than twice the amount of water than gram flour. The study confirmed that corn flour is the best desiccant among the ones studied in this study.

The analysis of the NIR spectra acquired during the evolution of water adsorption revealed the behavior of the OH groups attached to different carbon atoms of the glucose units in the bio-polymer matrix of the flour samples.

The results and findings in this study are presented in Fig. 3-8. Figure 3 showed the NIR spectra of the bio-polymer samples measured in the region 10000-4000 cm^{-1}. The CH second overtones and OH combinations absorb in the region 9200-7600 cm^{-1}, the CH combinations and OH first overtones absorb in the region 7500-5950 cm^{-1}, the OH combinations of water molecules adsorbed to OH groups on carbohydrate molecules and hydrogen bonded to other water molecules absorb in the region 5300-5100 cm^{-1} and the CH combination frequencies absorb in the region 4500-4000 cm^{-1}. Figure 4 showed the evolution of NIR spectra measured on wheat flour sample at 60% humidity and 22°C over 7 hrs. The combination frequencies of OH vibrations of the water molecules that are adsorbed through hydrogen bonding to different OH groups on glucose molecular units give rise to a broad band in the region 5300-5100 cm^{-1}. All the flour samples used in this study showed similar adsorption bands in the region 5300-5100 cm^{-1}. This band is broad and comprises of several absorptions. These absorptions are revealed in their second and fourth derivative profiles. The second and fourth derivative profiles of an NIR spectrum of wheat flour sample are shown in Fig. 5. The second derivative profile is still broad and shows some features of underlying bands in the regions 5300-5200 and 5200-5125 cm^{-1}. However, the fourth derivative profile reveals four clearly resolved absorption bands at 5241, 5211, 5181 and 5160 cm^{-1}. As mentioned

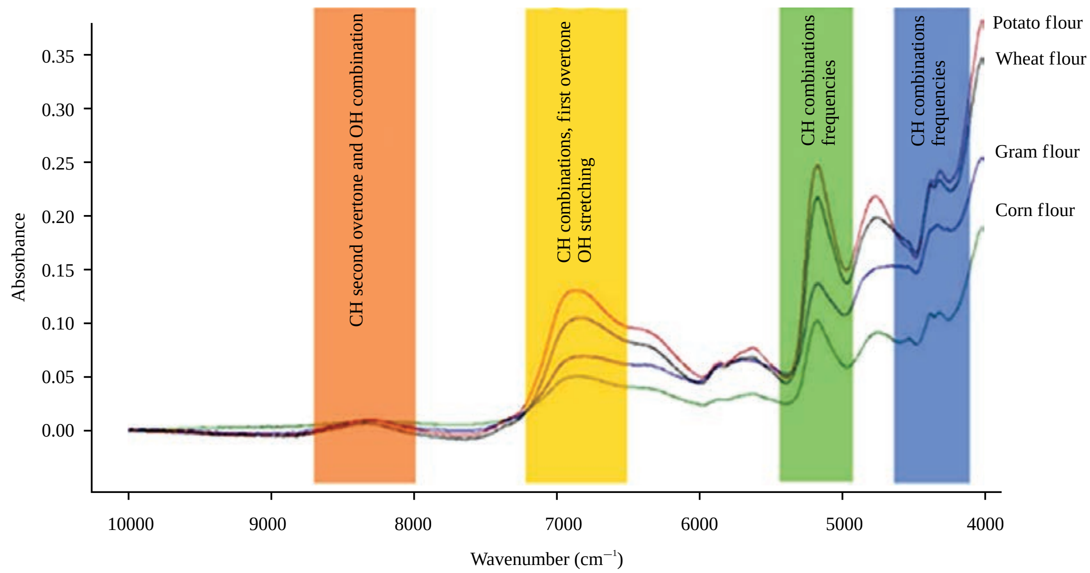

Fig. 3: Near-Infrared band assignments for commercial flour samples

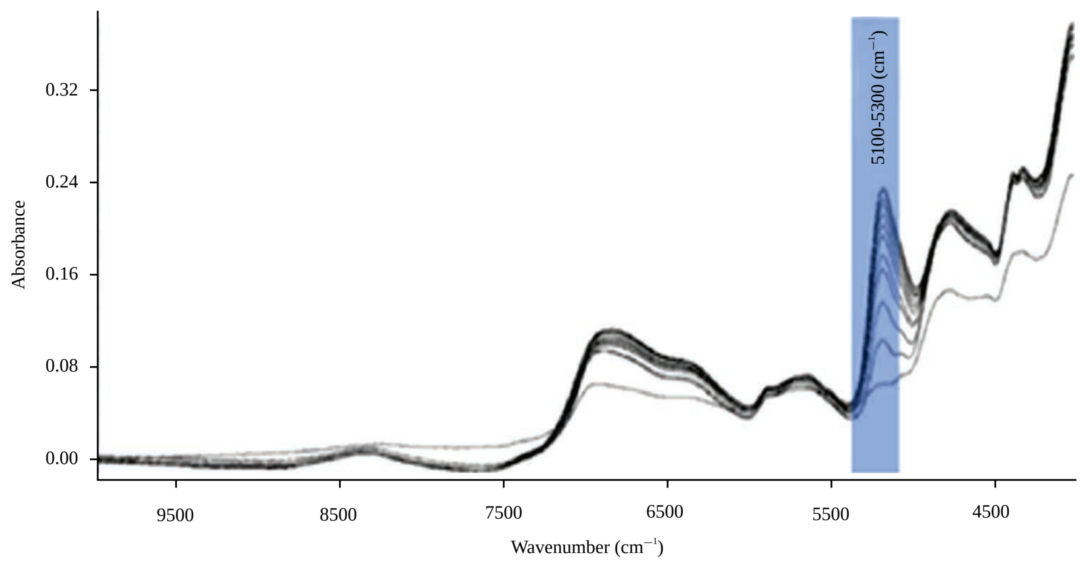

Fig. 4: NIR absorption spectrum for the water adsorption on wheat flour (10,000-4000 cm^{-1})

above, the bands at 5241, 5211, 5181 and 5160 cm^{-1} arise from the water molecules attached to the glucose ring OH groups at positions C1, C2, C3, C4 and C6. These bands were extensively studied for wheat, potato, gram and corn flour samples. The results show that all the OH groups on the glucose molecules of all the samples were involved in the adsorption of water molecules. Their rate of adsorption over time are indicated by their increase in intensities over time.

In order to attribute the resolved fourth derivative peaks to specific-OH groups on different carbon atoms in a glucose unit, further analysis was carried out using analytical grade amylose, amylopectin and cellulose and the spectrum obtained for each flour was compared with the spectra of reference materials. The absorption bands so identified and their peak positions in the fourth derivatives of the NIR spectra of the flour samples are shown in Fig. 6. The peak positions so identified in the flour samples are given in Table 1. One should be reminded that these bands are absorptions from the water molecules and not from the OH groups attached to the glucose units. Most of the peak

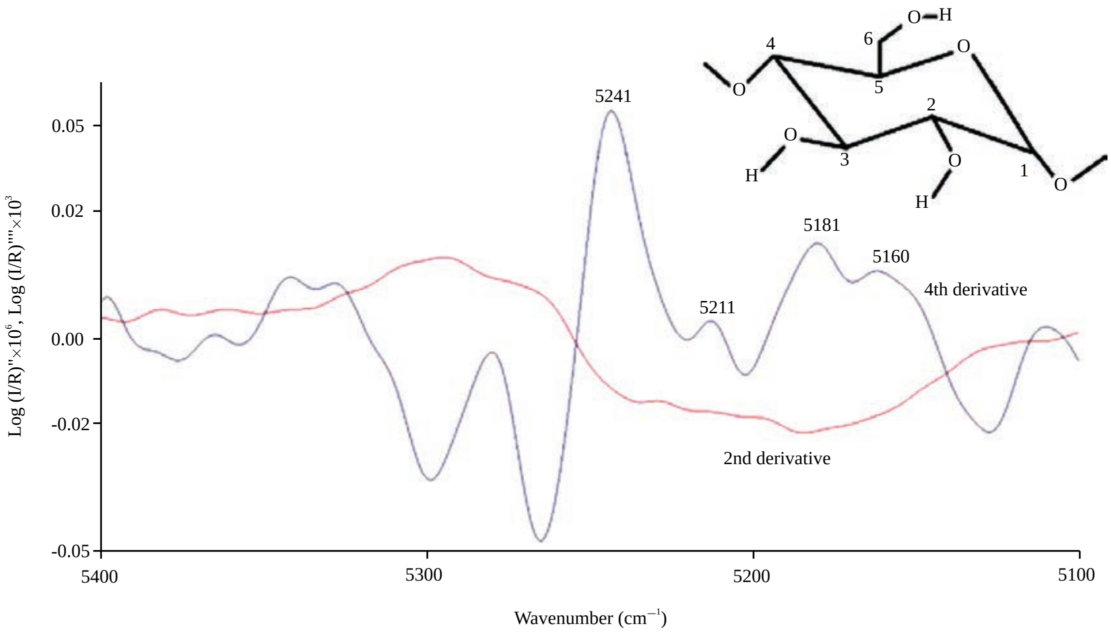

Fig. 5: Second and fourth derivative profiles of NIR spectra for wheat flour (5300-5100 cm^{-1})

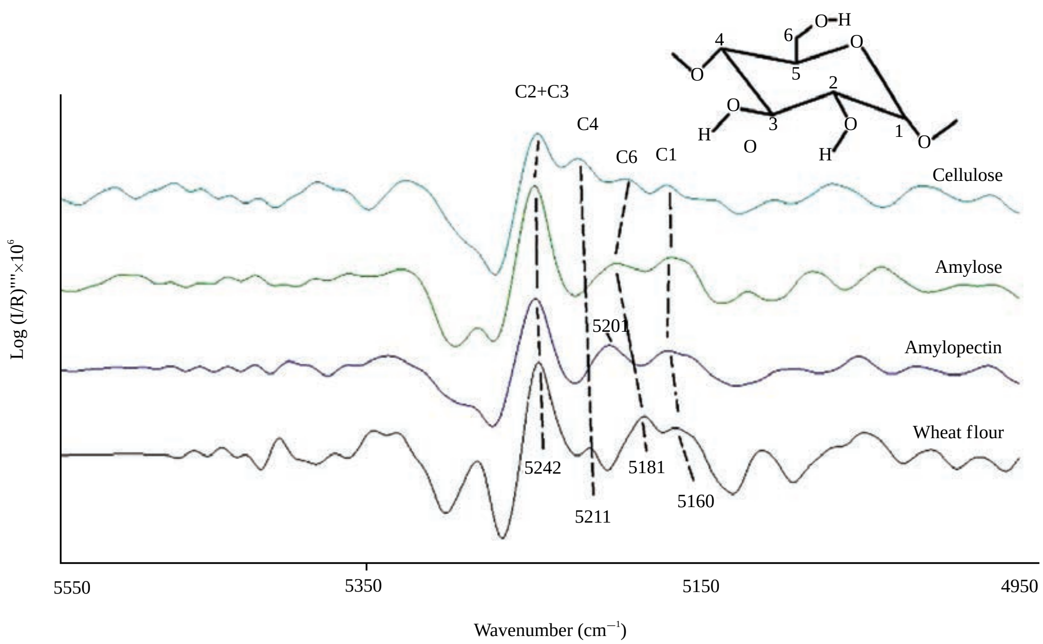

Fig. 6: Comparison of fourth derivative profile of wheat flour (5300-5100 cm^{-1})

Table 1: Band assignment of specific OH groups determined from the 4th derivative NIR spectra of all the flour samples

	Adsorption peaks corresponding to specific -OH groups (cm^{-1})			
Type of flour	C2+C3 OH	C4 OH	C6 OH	C1 OH
Wheat	5243	5211	5181	5160
Corn	5244	5221	5184	5167
Potato	5245	-	5189	5165
Gram	5244	-	5193	5169

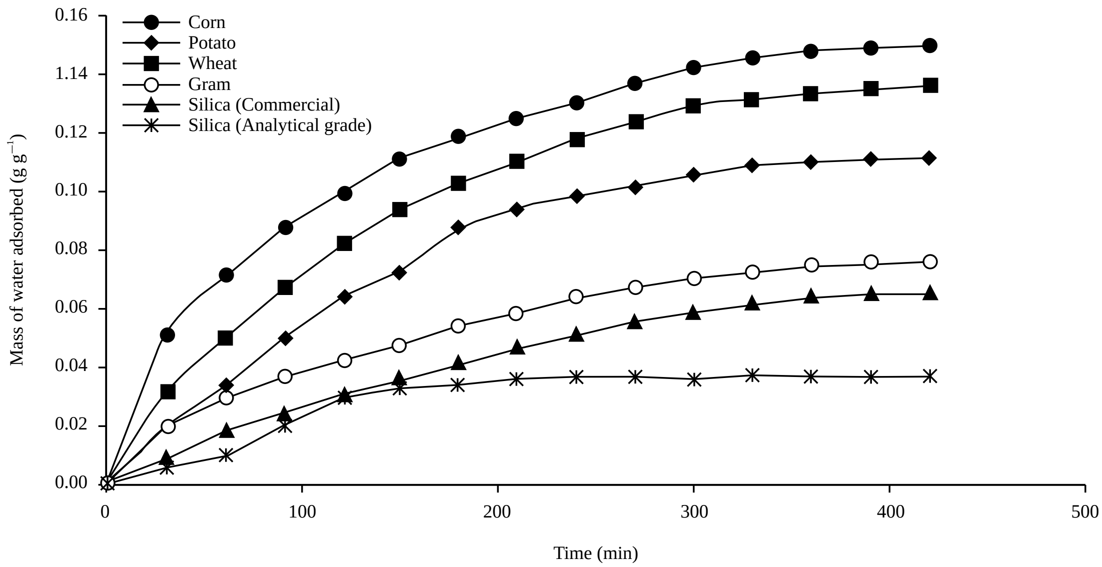

Fig. 7: Mass of water absorbed in per gram of sample within specific time

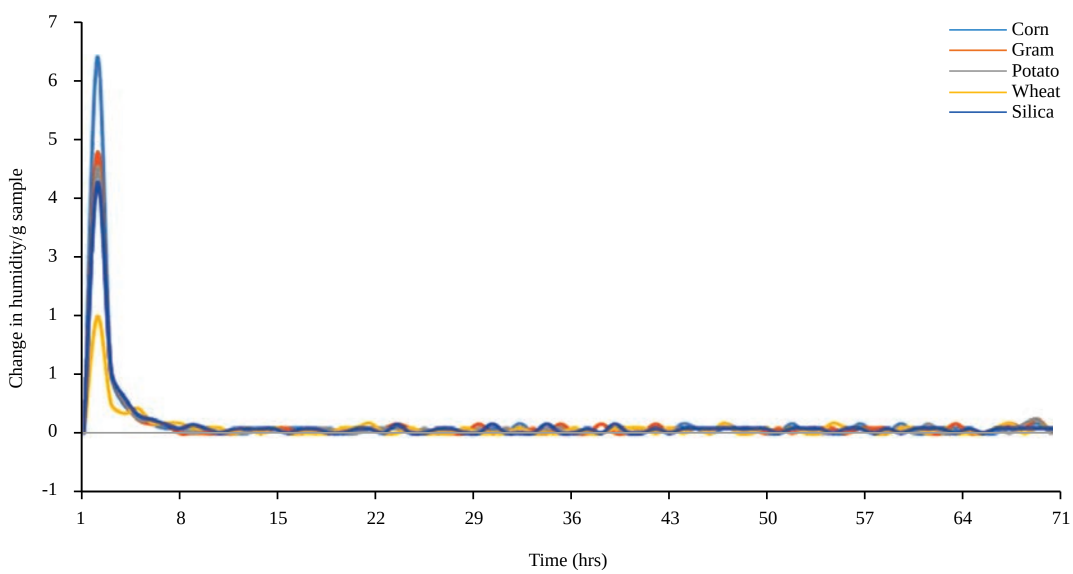

Fig. 8: Change in humidity per gram of sample for three days

Comparison with reference materials to identify peak positions of OH combination frequencies of water molecules hydrogen bonded to OH groups on glucose molecular units in wheat flour positions are in the same vicinity. Small shifts in the peak positions are normal and do not affect the results.

Further, the fourth derivative spectra of each flour sample obtained at different exposure times were investigated. The results showed that the intensities of all the resolved bands have increased with time in wheat and corn samples meaning that all the-OH groups on C2+C3, C4, C6 and C1 have adsorbed water molecules. The OH groups on C2+C3, C6 and C1 are responsible for the adsorption of water molecules in potato and gram flours.

The comparison of rates of adsorption of each OH group in the flour samples showed that the highest rate shown by different OH groups in the flour samples. Accordingly, C1-OH in wheat, C2+C3-OH in potato, C2+C3-OH and C1-OH (these have similar rates of adsorption) in gram and C2+C3-OH, C6-OH and C1-OH (these have similar rates of adsorption) in corn flour showed the highest rate of adsorption.

The mass of water adsorbed by a unit mass of flour was also plotted with the intensity of the fourth derivative band corresponding to C2+C3-OH and secondly with the time. The results indicated that the mass of water adsorbed per gram of dry flour is non-linear with both time and NIR absorbance (Log (1/R)'''' $\times 10^6$) in C2-OH+C3-OH band. This nonlinearity can be attributed to the water molecules adsorbed by other OH groups (C1, C4 and C6-OH) in flour samples.

From the gravimetric analysis, the mass of water adsorbed by different commercial flours during initial 7 hrs were plotted and it revealed that all the bio-polymers showed better adsorption than commercial silica desiccant and analytical grade silica (Fig. 7). Adsorption rate of flour has gradually decreased with time to attain a constant state towards the end. Highest adsorption rate was observed for corn flour while lowest adsorption rate was observed for gram flour. Thus, this confirms that natural bio-polymers are much more capable desiccants than the common silica gel desiccant which is the most widely used desiccant throughout the world.

In addition, the long-term efficacy testing carried out for flours also indicated similar trends in humidity variation of flours and commercial silica over the period of 3 consecutive days. Flour showed a deep drop of humidity in initial stage and showed a gradual increase towards the end. However, these variations are not effective in comparison work as the humidity drop is dependent on dry mass of the sample. Therefore, the change in humidity in each hour per dry mass of sample was derived for each sample and was plotted as shown in Fig. 8.

Accordingly, it is clear that the highest humidity drop is shown by corn flour with respect to other samples and at the same time supports the gravimetric data.

DISCUSSION

This study revealed that all bio-polymers are better absorbents compared to silica while the highest desiccant capacity lies with corn flour out of the tested bio-polymers and that different OH groups are involved in the sorption process in each type of bio-polymer. The increase in intensity of the OH combination frequency which occurred around 5300-5100 cm^{-1} happened in their natural state of the bio-polymers indicating that they can be utilized as desiccants without any special preparations or purifications. This OH combination peak that occurred around 5300-5100 cm^{-1} attributes to the OH combination frequencies from hydrogen bonded water molecules to carbohydrate OH groups and thus leave behind other possible NIR bands such as OH stretch 1st overtone, CH combination, CO stretch combination, CH 1st overtone and CH 2nd overtone[18,19]. This band was resolved into three to four peaks in their fourth derivative profiles indicating that there is more than one OH group of the monomer involved in adsorbing water. As mentioned under results, the identities of these OH groups in the samples were determined by comparing with the fourth derivative profiles of the NIR spectra of the standards. It is also noteworthy that the peak shapes and positions were similar to previously published study. Accordingly wheat and corn flour depicted four peaks attributing to water molecules on C1, C2+C3, C4 and C6-OH groups of the monomers while potato and gram flour showed only three peaks attributing to C1, C2+C3 and C6-OH. The involvement of more OH groups in the hydrogen bonding observed in corn and wheat is also confirmed by the gravimetric analysis. It is also noteworthy that the amount of carbohydrate present in its natural state also affects the desiccant capacity. The results of this study also correlate with the carbohydrate contents in the four tested flour samples in proximate analysis of previous studies. Accordingly, the maximum carbohydrate content is highest in corn flour which is 85.7 and 73.0% in wheat flour[20-23].

As far as these bio-polymers with the glucose monomers are considered, it is clear that a single OH group is capable of forming a maximum of three hydrogen bonds by acting as a hydrogen bond donor and an acceptor. Further in terms of enthalpy, water adsorption is an exothermic process and thus supports the idea of forming saturated hydrogen bonds. The saturation process is greatly supported by the number of water molecules present in its immediate surrounding either within the polymer molecule or in its environment. But on the other hand, the number of hydrogen bonds formed by each OH group will depend upon the number of intermolecular and intermolecular hydrogen bonds formed by that particular OH group[18]. In contrast, some of the siloxane groups present on the surface transform in to hydroxyl groups which are polarized and thus are capable of forming hydrogen bonds with the nearby water molecules in silica. Accordingly, several layers of water get adsorbed around silica where the first layer is due to the hydrogen bonding between silanol groups and water molecules and the next layers arise due to the intermolecular hydrogen bonding[5].

When the rates of adsorption on to the specific OH groups were compared, it was observed that in corn highest and similar rates are shown by C1, C2+C3 and C6-OH groups while the lowest was shown by C4-OH. In wheat, gram and potato flours the highest rates were shown by either C1 or C2+C3-OH combination or by C2+C3-OH groups. In wheat flour the lowest rate was observed for C4-OH while for gram and potato flours the lowest rate was indicated by C6-OH. This lowest rate shown by C6-OH is in general attributed to the unfavorable energetic position in the glucose unit[24,25]. This study also presents a significant contrast between the adsorption rates of C1-OH in the tested bio-polymers at natural state and analytical grade amylose which shows that C1-OH has the lowest rate.

When the mass of water adsorbed per gram of dry flour was plotted against the NIR absorbance (Log $(1/R)'''' \times 10^6$) of the C2+C3-OH peak and time, both the plots appeared to be non-linear signaling that the surface coverage by water molecules keep increasing on a background where there is a specific amount of spots available and the number of spots available for the incoming water molecules to bind keep decreasing.

In the gravimetric study each flour clearly indicates that the adsorption of water is nonlinear with time and the adsorption rate of each flour has gradually decreased with time and has attained a constant state towards the end. In the comparison study where the flour samples were compared with silica gel sachets obtained from pharmaceuticals and food packages and analytical grade silica it was observed that the rates of adsorption of all the flours were greater than that of both types of silica and corn flour showed the highest rate while the analytical grade silica showed the lowest rate. Meanwhile it was also observed that all plot shapes do agree with previous literature findings[5,18].

In the long term efficacy testing where the humidity drop per gram of sample was considered for the purpose of comparison, corn flour again showed the highest activity even though the order of the wheat and gram samples varied a little than what was observed in the gravimetric analysis. But this variation could be attributed to the different amounts of air which were trapped in the sealed packages. Thus, this study also confirms that biopolymers are good desiccants than commercial silica, which is the most widely used desiccant throughout the world for long-term processes where corn flour can be graded at the top as the best out of the tested samples.

Furthermore, it is noteworthy that these results may slightly be deviated if a constant amount of air was present within the packages the amount of water vapor directly depends on the amount of air inside the package.

CONCLUSION

All flour samples studied using Near-Infrared (NIR) spectroscopy and gravimetric analysis exhibit the evolution of the-OH combination peak at around 5200 cm^{-1} over time which in turn consisted of three to four peaks in the fourth derivative profile signaling about the specific-OH groups onto which water was hydrogen-bonded. In conclusion, out of the tested flours, corn flour can be regarded as the best bio-desiccant with a promising desiccant efficacy.

SIGNIFICANCE STATEMENT

This study revealed that corn flour has a feasibility of replacing commercially used silica gel as one of the best bio-desiccant with a promising desiccant efficacy. This study can be a background for researchers and packaging engineers for exploring the desiccant properties of natural bio-polymers.

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