

# Application of superabsorbent polymers (SAP) as desiccants to dry maize and reduce aflatoxin contamination

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**Abstract** The ability of superabsorbent polymers (SAP) in drying maize and controlling aflatoxin contamination was studied under different temperatures, drying times and SAP-to-maize ratios. Temperature and drying time showed significant influence on the aflatoxin formation. SAP-to-maize ratios between 1:1 and 1:5 showed little or no aflatoxin contamination after drying to the optimal moisture content (MC) of 13 %, while for ratios 1:10 and 1:20, aflatoxin contamination was not well controlled due to the overall higher MC and drying time, which made these ratios unsuitable for the drying process. Results clearly show that temperature, frequency of SAP change, drying time and SAP-to-maize ratio influenced the drying rate and

aflatoxin contamination. Furthermore, it was shown that SAP had good potential for grain drying and can be used iteratively, which can make this system an optimal solution to reduce aflatoxin contamination in maize, particular for developing countries and resource-lacking areas.

**Keywords** Aflatoxin · Maize · Hydrogel · Postharvest · Superabsorbent polymers · Water sorption

## Introduction

It is by now well recognized by the scientific community that microorganisms naturally growing on foods, in particular grains and nuts, can produce toxins that have serious effects on health. Among these toxins, aflatoxin, a highly toxic secondary metabolite produced by *Aspergillus flavus*, is estimated to cause up to 28 % of the total worldwide cases of hepatocellular carcinoma (HCC), the most

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common form of liver cancer, 55 % of which occur in developing countries (Wu 2014; Wu et al. 2014; Knipstein et al. 2015; Wagacha and Muthomi 2008). There are different types of aflatoxins, including AFB1, AFB2, AFG1, AFG2, AFM1 and AFM2, contributing to the aflatoxin contamination in food, and the total cumulative contamination becomes dangerous for human consumption after exceeding certain levels. These levels, which are normally specified for aflatoxin contamination of type B1 (AFB1) are regulated by the European Union to a maximum acceptable standard of 4 ng/g (Rahmani et al. 2010; Azziz-Baumgartner et al. 2005). Aflatoxin contamination in Kenya is particularly severe, the acceptable level was regulated to be 10 ng/g (Muthomi et al. 2012).

Grain losses have been reported to be mainly due to post-harvest aflatoxin contamination of maize (Wagacha and Muthomi 2008), which in developing countries, reached to about half of the harvested grain (Magan and Aldred 2007; Wagacha et al. 2013; Mrema et al. 2011; Dwivedi and Singh 2011; Shephard 2008; Muthomi et al. 2009; Okoth and Kola 2012).

In general, this problem can be prevented by improving drying methods and storage conditions employing natural, chemical agents and irradiation techniques (Hassan and Aziz 1998; Womack et al. 2014), since the main causes of the contamination are high temperature, relative humidity of the surrounding air and moisture content of the grain (Mrema et al. 2011; Hassan and Aziz 1998). However, the problem of post-harvest aflatoxin contamination becomes even more serious in developing countries where farmers are not able to dry their grain adequately and store in recommended conditions for two main reasons. Firstly, farmers in developing countries depend on open air-drying of maize using natural sunlight. In recent years, the weather has become increasingly unpredictable and often, the rainy season occurs when the maize is ready for harvest but not adequately dry for storage. As a result, the maize remains with high moisture content long enough for aflatoxin contamination to occur. The second reason is the restricted accessibility and affordability of most farmers to electric power. However, where energy for drying is not available, it is not possible to dry maize timely and effectively to preclude the aflatoxin contamination (Magan and Aldred 2007; Wagacha et al. 2013; Mrema et al. 2011; Dwivedi and Singh 2011; Shephard 2008; Muthomi et al. 2009; Okoth and Kola 2012; Womack et al. 2014).

One particularly interesting aspect to tackle is to prevent aflatoxin contamination in seeds, which are planted. This is because the infection may persist through the growth life of the plant and contaminate the harvest. It is well documented that seed is very sensitive to temperature and moisture during drying and storage (Kunusoth et al. 2012; Hettiarachchi et al. 2001). 1 % increase in moisture would

reduce by half the longevity of the seed and decrease the seed germination, viability and vigor. Likewise, an increase in temperature by 5 °C also reduce seed longevity by half (Kunusoth et al. 2012; Hettiarachchi et al. 2001). For these reasons, it is generally recommended to dry and store seeds using desiccants as this would keep both the temperature and moisture content low enough to preserve seed viability and vigor.

In fact, different desiccants have generally been used in the past, but only for drying seed rather than grain. For example, the use of silica gel for drying seed of maize has previously been studied, indicating that silica gel:seed ratio between 1:1 and 1:2.5 in sealed containers with the maize and gel in contact maximized the storage life of the seeds (Daniel et al. 2009). Aluminium silicates—also called drying beads or zeolites—were reported to have a higher affinity for moisture than silica gel and were found to swell by 20–25 % of the original weight, upon moisture absorption. Desiccant:seed ratios between 3:2 and 1:4 were typically used, showing that saturated drying beads may be dried and reused (Sturton et al. 1983). Bentonite, a montmorillonite-based common clay desiccant, hydrated aluminium silicate with sodium and calcium as the common exchangeable cations, has been studied. A 1:1 corn to bentonite ratio was used, allowing the drying of 18 % MC in less than 24 h (Sturton et al. 1983). The same researchers reported that bentonite swelled up to 20 times its original volume in water; they also developed drying equations for the swelling of the desiccant and showed that the bentonite could be blown off the grain, leaving an ash content of 1.7 % (Sturton et al. 1983). Furthermore, the possibility of using a combination of desiccants such as bentonite and calcium chloride in addition to solar energy has also been explored, allowing the drying of maize from 38 to 15 % moisture content in 24 h (Thoruwa et al. 2000).

Superabsorbent polymers (SAP), also called hydrogels or Super Porous Hydrogels (SPH), represent another interesting family of desiccants. They are in fact polyelectrolyte networks known for their ability to absorb large amounts of water. One gram of hydrogel may absorb more than 4000 g of water in 200 min, with half of this water being absorbed within the first 12 min (Kuruwita-Mudiyanselage 2008; Delgado et al. 2009). Because of their moisture absorbing capabilities, it was hypothesized that SAP may serve as a possible solution to aflatoxin contamination, operating as drying agents for maize during the post-harvest stage.

SAP have not been applied as desiccants for drying grain. Indeed, their ability to absorb water can have immediate implications in reduction of aflatoxin contamination, because efficient water absorption is likely to slow down *Aspergillus* growth and sporulation, and thus aflatoxin contamination in wet maize. Therefore, the main motivation for

this work was to investigate potential role of SAP as drying means for both the seed industry as well as the grain industry.

One last consideration that applies to grain consumption is whether the drying agents, i.e. SAP are approved as food-grade compounds. SAP selected for grain drying would ideally have to conform with food safety requirements if used to dry grain for human consumption. There are many materials from which SAP are made, however the most commonly available SAP is sodium polyacrylate. This material is currently used in the manufacture of food grade products, such as Luquaflence<sup>®</sup> and Luquasorb<sup>®</sup>, which are applied in fish and meat packaging containers. Alternatively, SAP can be easily manufactured from natural products. For instance, a superabsorbent hydrogel has been processed from native cassava starch-poly[sodium acrylate-co-acrylamide], by alkaline hydrolysis of starch/PAN physical mixture. This is because graft copolymerization of vinyl monomers onto natural polymers is an efficient approach to achieve biopolymer-based super absorbing hydrogels. Because of their exceptional properties such as biocompatibility, biodegradability, renewability, and non-toxicity, these systems are ideal candidates for maize drying (Ekebafel et al. 2011).

By considering the findings available in literature, it can be expected that the use of SAP as desiccant for drying both seed and grain could be highly promising and deserves careful consideration. Compared to the other desiccants, SAP have a higher absorption capacity, absorption rate, can be re-used, all properties that make them particularly suitable as desiccants for drying maize. This motivates the present study and calls for a detailed analysis devoted to identify those drying conditions, which would minimize aflatoxin contamination in maize, with an immediate return measurable both in terms of economic investment and human lives.

## Materials and methods

### SAP preparation for assay

Super absorbent polymer (SAP) used in the drying and aflatoxin experiments is poly(acrylic acid) sodium salt, moderately cross-linked, and available from Sigma Aldrich (product number 43,636-4) as a powder with particle size <1000  $\mu\text{m}$  (99 %). Since the SAP forms a sticky gel and adheres to the maize when it absorbs moisture, it was kept in a porous tea bag membrane during all the experiments.

### Determination of the progression of *Aspergillus* contamination and the effect of SAP

A fresh sample of maize at a moisture content of 32.5 % (approximate moisture content of maize at harvest) that had been confirmed not to be contaminated with *Aspergillus* was prepared. The grain, stored in a sealed container, was mixed with SAP in teabags following SAP-to-maize ratios 1:1, 1:5, 1:10 and 1:20. Experiments were run in triplicates for each ratio. In each sample, the quantity of maize was set at 100 g, while the quantities of SAP used were 100, 20, 10, and 5 g to match the required SAP-to-maize ratios. The dry SAP was placed in 5 g teabags and the maize spread evenly around them in hermetically sealed containers. The mixtures of SAP and maize were placed at 20 °C, 30 °C and 40 °C in oven after 216 h. The effect of SAP on drying and aflatoxin contamination was further tested by varying the frequency at which the SAP was changed as follows:

- No change of SAP throughout the experimental period (216 h)
- Change of SAP every 48 h
- Change of SAP every 24 h

The maize samples were crushed using a Retsch rotor mill (model SK 1, Germany). Samples were then drawn at the end of the experiment for quantification of *Aspergillus* metabolites.

### Extraction and purification of aflatoxins

Maize flour (10 g) was transferred into 100 mL falcon tubes. A mixture of acetonitrile:water 84:16 (40 mL) was added and vortexed for 5 min. An internal standard griseofulvin 5 mg/mL (40  $\mu\text{L}$ ) was added to the mixture and vortexed for 30 min and left to settle for another 30 min. The supernatant (6  $\mu\text{L}$ ) was drawn and filtered through multistep 228 AflaPat column. The filtrate (4 mL) was evaporated in the hood and re-constituted in methanol:water (20:80) (400  $\mu\text{L}$ ), vortexed for 5 min, centrifuged at 10,000 rpm for 3 min and the supernatant analyzed using LC/MS as described below.

### LC–MS analysis

LC–MS analysis was used to determine the amount of aflatoxin in the samples. LC–MS consisted of a quaternary LC pump (Model 1200) coupled to Agilent MSD 6120-Single quadruple MS with electrospray (Palo Alto, CA, USA) equipped with ChemStation<sup>®</sup> software (Hewlett-Packard). LC was performed on Agilent technologies

1200 infinite series with a Zorbax SB C18 column,  $2.1 \times 50$  mm,  $1.8 \mu\text{m}$  (Phenomenex, Torrance, CA, USA).

Samples were dissolved in 100 % MeOH (B) (LC–MS grade, Sigma, St. Louis, MO, USA), vortexed and centrifuged at 10,000 rpm to remove insoluble material before analysis by LC–MS. The mobile phase used a gradient program: initially 80:20 (A:B) (where A consists of 5 % formic acid in ultra-pure  $\text{H}_2\text{O}$ , Sigma, St. Louis, MO) to 0:100 (A:B) at 10 min and maintained at this solvent proportion for 15 min, 80:20 at 26 min up to 30 min which was the run time. The flow rate was  $0.7 \text{ mL min}^{-1}$ . Injection volume was  $10 \mu\text{L}$  and data were acquired in a full-scan positive-ion mode using a 100–800  $m/z$  scan range. The dwell time for each ion was 50 min. Other parameters of the mass spectrometer were as follows: capillary voltage, 3.0 kV; cone voltage, 70 V; extract voltage, 5 V; RF voltage, 0.5 V; source temperature,  $110 \text{ }^\circ\text{C}$ ; nitrogen gas temperature for dissolution,  $380 \text{ }^\circ\text{C}$ ; nitrogen gas flow for dissolution, 400 L/h.

### Quantification of aflatoxin

Standards of B1, B2, G1, and G2 each of  $3 \text{ ng}/\mu\text{L}$  concentration were purchased from Sigma-Aldrich (California, USA). Various concentrations of aflatoxin (3, 30, 60 and  $90 \text{ ng}/\mu\text{L}$ ) were prepared and were used to generate the standard curves, which allowed for external quantification of each targeted aflatoxin.

An internal standard griseofulvin was used to calculate the response factor. The internal standard calibration curve was developed by preparing various concentrations: 20, 40, 60, 80 and  $100 \text{ ng}/\mu\text{L}$ , each concentration analyzed in triplicates.

Peak areas of the excitation curves were used for quantification. Using the calibration curves the area obtained was converted to the concentration of aflatoxin contamination in  $\text{ng/g}$ . The results were compared with the standard recommended levels of aflatoxin in maize for human and livestock consumption.

### Diffusion vapor sorption analysis (DVS)

The sorption isotherm of SAP was determined using Dynamic Vapor Sorption equipment (VTI-SA, TA Instruments, Eschborn, Germany). The polymer powder was placed in the sample holder, which was hung in the thermostatically controlled cabinet where the pre-set relative humidity (RH) was increased from 0 to 90 % in steps of 10 % in a pre-programmed sequence. The mass of polymer was set at 35 mg and the sorption process was run at a constant temperature of  $40 \text{ }^\circ\text{C}$  over the full RH range. The running time, isotherm temperature, target RH, actual RH, and sample weight were recorded throughout the isotherm run (data not shown).

### SAP sorption and desorption behavior

Sorption and desorption experiments were carried out at 20, 30 and  $40 \text{ }^\circ\text{C}$  using the same set-up employed for the determination of the progression of *Aspergillus* contamination. Only the SAP-to-maize ratio of 1:5 was chosen which was found to be the minimum promising ratio in order to avoid aflatoxin formation. All the experiments were run in triplicates.

## Results and discussions

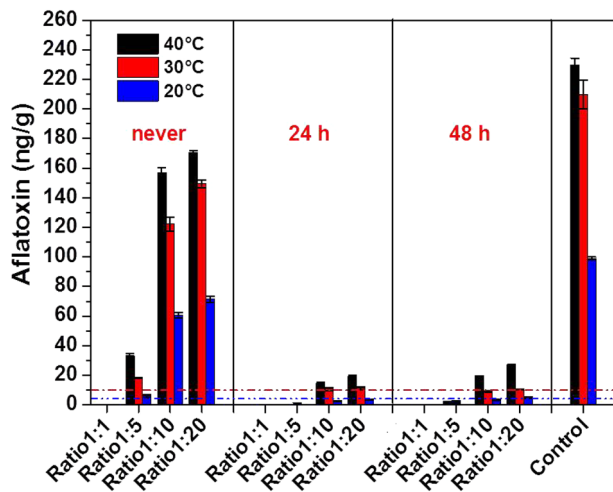
### Effect of SAP-to-maize ratio and temperature on aflatoxin contamination

Aflatoxin contamination in relation to the frequency of SAP change (never, every 24 h and every 48 h), SAP-to-maize ratios (1:1, 1:5, 1:10 and 1:20) and temperatures (20, 30 and  $40 \text{ }^\circ\text{C}$ ) are summarized in Table S1, S2 and S3 and shown in Fig. 1.

Maize samples sealed in container with no SAP were taken as control. The results showed that, maize samples that were not dried exhibited the highest aflatoxin contamination at all the temperatures investigated after 216 h of storage (Fig. 1). The other extreme was the SAP-to-maize ratio of 1:1, where no aflatoxin contamination was recorded at all the frequencies of SAP change and temperature levels. SAP-to-maize ratio of 1:5 showed very little or no aflatoxin contamination, except for the case when the SAP was not changed through the full duration of the experiment. Total aflatoxin content was  $33.17 \text{ ng/g}$  at  $40 \text{ }^\circ\text{C}$  (Table S1–S3). Because AFB1 accounts for the greatest portion of total aflatoxin contamination (see Table S1–S3), in the subsequent sections we take a conservative approach and used the Kenyan and European AFB1 limits as the limits for total aflatoxin contamination.

According to this conservative approach,  $33.17 \text{ ng/g}$  was recorded at  $40 \text{ }^\circ\text{C}$  which was above the Kenyan ( $10 \text{ ng/g}$ ) and the European Union (EU) standards ( $4 \text{ ng/g}$ ), respectively. However, when the SAP was changed every 24 and 48 h,  $<4 \text{ ng/g}$  of aflatoxin contamination was observed (Table S1–S3), close to the EU and Kenyan standards. Both SAP-to-maize ratios of 1:10 and 1:20 recorded high levels of aflatoxin contamination. However, these ratios met the Kenya standard and approached the EU standard at  $20 \text{ }^\circ\text{C}$  when SAP was changed every 24 and 48 h.

It can be concluded that the drying ability of SAP can be used as solution to reduce aflatoxin contamination in maize, and therefore be able to meet the EU and Kenyan standards when optimal conditions were employed. Furthermore, an increase in the amount of SAP resulted in less



**Fig. 1** Total aflatoxin content measured in different maize samples dried using different SAP frequency change (never, every 24 h and every 48 h), SAP-to-maize ratios (1:1, 1:5, 1:10 and 1:20) and temperatures (20 °C blue, 30 °C red, and 40 °C black). The dashed lines indicate, respectively the acceptable content of AFB1 aflatoxin for the EU standards (blue) and Kenyan standards (red), taken as a limit for total aflatoxin contamination (color figure online)

incidence of aflatoxin contamination in the system. For example, to be sure about the absolute absence of aflatoxin contamination at storage below 20 °C, a ratio SAP-to-maize of 1:5 or more was observed, lower ratios (such as 1:10 and 1:20) may prevent aflatoxin contamination at the same temperature if SAP was exchanged every 24 h. It should be noted that these results were obtained in a closed environment. Further work needs to be carried out to determine how to maximize the efficiency of SAP by incorporating natural ventilation and solar energy. However, in comparison to other desiccants, use of SAP was observed to be better than bentonite, silica gel and aluminum silicates (Sturton et al. 1983; Thoruwa et al. 2000).

**Effect of the final moisture content (MC) on aflatoxin contamination**

The Aflatoxin contamination measured in maize at different moisture and temperature levels is shown in Fig. 2.

From Fig. 2 it was determined that the higher the MC, the higher the aflatoxin contamination, with their relationship following a typical sigmoidal curve:

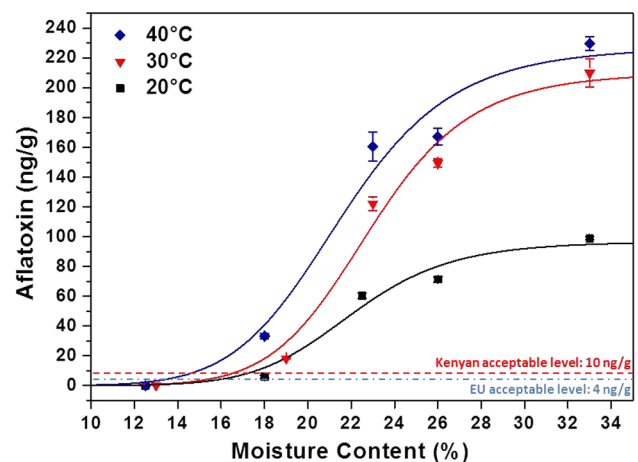
$$AF(ng/g) = \frac{AF_{MAX}}{1 + e^{-(MC-MC_{50\%})/\tau}} \quad (1)$$

where  $AF_{MAX}$  is the maximum observed content of aflatoxin,  $MC$  is the moisture content (%),  $MC_{50\%}$  is the moisture content at half aflatoxin contamination (%), and  $\tau$  is a characteristic moisture content relaxation value in the sigmoidal growth. Fitting parameters for the three temperatures are given in the SI (Table S4). The aflatoxin level

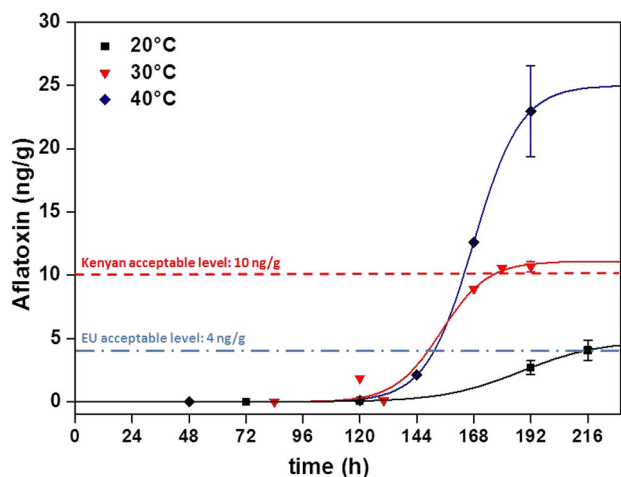
increased slowly at low moisture content, reached a maximum growth rate at around 21–23 % MC for all the temperatures considered. This was followed by reduction in growth rate, and eventually plateaus off. The major result emerging from Fig. 2 was the short range of moisture contents where aflatoxin contamination can be prevented in fact, in order to meet the requirements of Kenyan standards, the final MC should be less than a critical value of 17 % at 20 °C, 16 % at 30 °C and even <13 % at 40 °C, which was in agreement with previous results (Wicklow 1994). Given that maize is hygroscopic and absorbs moisture that presents the challenge of storage. Maize has to be dried below the critical value and stored under hermetic conditions preventing absorption of moisture.

**Effect of the drying time on aflatoxin contamination**

As shown in Fig. 1, the aflatoxin contamination is also influenced by the drying time. In order to find a relation between the drying time and the aflatoxin formation, the drying duration was associated to the time required to reduce the grain moisture content (MC) to the safe value of less than 13 % (Table S1–S3). All SAP-to-maize ratios except 1:1 ratio did not dry maize to the required 13 % MC. A relationship was established between time taken to dry a sample to 13 % MC and the level of aflatoxin contamination by considering only samples that actually dried to 13 % by the time the experiments were terminated at 216 h. All the data for samples that did not dry to 13 % MC were left out in this particular analysis. The data obtained are plotted in Fig. 3.



**Fig. 2** Relationship between final moisture content (MC) and total aflatoxin contamination at different temperatures (20, 30 and 40 °C). The dashed lines indicate respectively the acceptable content of AFB1 aflatoxin for the EU standards (blue) and Kenyan standards (red), taken as a limit for total aflatoxin contamination (color figure online)

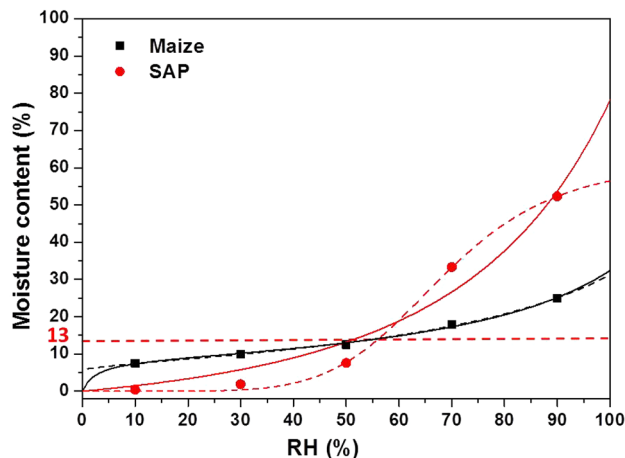


**Fig. 3** Relationship between time required to dry maize to  $\leq 13\%$  MC and total aflatoxin contamination at different temperatures (20–30 and 40 °C). The *dashed lines* indicate respectively the acceptable content of AFB1 aflatoxin for the EU standards (*blue*) and Kenyan standards (*red*), taken as a limit for total aflatoxin contamination (color figure online)

The increase in total aflatoxin contamination over time can be roughly approximated by the following logistic equation (Brzonkalik et al. 2011; Schaffner et al. 1998):

$$AF(\text{ng/g}) = AF_{MAX} + \frac{AF_0 - AF_{MAX}}{1 + \left(\frac{t}{t_m}\right)^p} \quad (2)$$

where  $AF_0$  is the initial aflatoxin concentration,  $AF_{MAX}$  is the maximum observed content of aflatoxin,  $t_m$  indicates the process time when half of the maximum toxin concentration is produced and  $p$  is the power parameter. This equation takes into account the finite amount of substrate available for the aflatoxin formation, which would otherwise follow the Malthus model. The equation employed here is the well-known logistic function usually employed for biological population growth and fitting parameters for the three temperatures are given in the SI (Table S5). Figure 3 shows the impact of temperature on the toxin formation. The increase in temperature resulted into increase in aflatoxin concentration while the time frame for the toxin formation decreases. The EU and Kenyan standards for aflatoxin contamination were superimposed on the curve to determine how much drying time would be sufficient to prevent aflatoxin contamination. From these results it can be concluded that the drying should be accomplished in  $\approx 150$  h at 40 and 30 °C and less than 213 h at 20 °C to prevent aflatoxin contamination beyond the prescribed EU standards. To meet the Kenyan standards, drying needed to be completed in less than 160 h and 180 h at 40 °C and 30 °C, respectively.



**Fig. 4** Moisture sorption isotherms of maize (*black curve*, from Chayjan and Esna-Ashari 2010) and SAP (*red curve*) at 40 °C. The *full lines* correspond to the GAB model while the *dashed lines* follow the SIPS model, respectively (color figure online)

### Optimal storage conditions: moisture content and relative humidity (RH)

In order to extract more information on the optimal storage conditions, such as the desired relative humidity (RH) corresponding to the optimal MC to avoid aflatoxin formation, it is a good practice to look at the moisture sorption isotherm of the system. Figure 4 shows the sorption isotherms of the Kenyan maize modeled by SIPS model alongside that obtained (Chayjan and Esna-Ashari 2010). These have been plotted on the same axes with the sorption isotherms for SAP measured by diffusion vapor sorption analysis (DVS) and modeled by GAB and SIPS models.

The relative humidity (RH) of the air at a given temperature is related to the water activity ( $a_w$ ) of the material in equilibrium with the surrounding atmosphere by the following equation:  $RVP = P/P_0 = a_w = RH/100$ , where  $P$  (Pa) is the pressure of the system,  $P_0$  (Pa) is the water vapor pressure,  $a_w$  is the water activity. The  $a_w$  is a parameter giving a measure of water mobility and accessibility in a certain material and its control has become the traditional approach for optimizing food quality and shelf-life of food products (e.g. the general findings that pathogenic bacteria do not grow below an  $a_w$  of 0.86 whereas yeasts and molds can grow at  $a_w$  values down to 0.60) (Labuza et al. 1972; Troller 1991). If different materials are in contact with each other in a hermetic environment and have different water activities, then moisture will migrate from the regions of high  $a_w$  to the regions of low  $a_w$ , at a rate depending on the difference in  $a_w$  between the regions. In the case of initially dry SAP and harvested maize, the maize, which initially contains 32 % moisture after being harvested, has a  $a_w$  close to 1 (saturating to nearly 100 %

RH the container filled with maize). When dry SAP was introduced in the container, the maize showed strong tendency to lose water which has an initial lower  $a_w$ . There was a drop in  $a_w$  of maize and increase in  $a_w$  of SAP.

Sorption isotherms were fitted by both the GAB and SIPS model which are given by Eqs. (3) and (4), respectively, and the parameters are reported in Table S6 and S7.

$$MC = \frac{M_0 \cdot K_G \cdot k \cdot a_w}{(1 - k \cdot a_w) \cdot [1 + (K_G - 1) \cdot k \cdot a_w]} \quad (3)$$

$$MC = K_S \cdot \frac{a_w^n}{1 + C \cdot a_w^n} \quad (4)$$

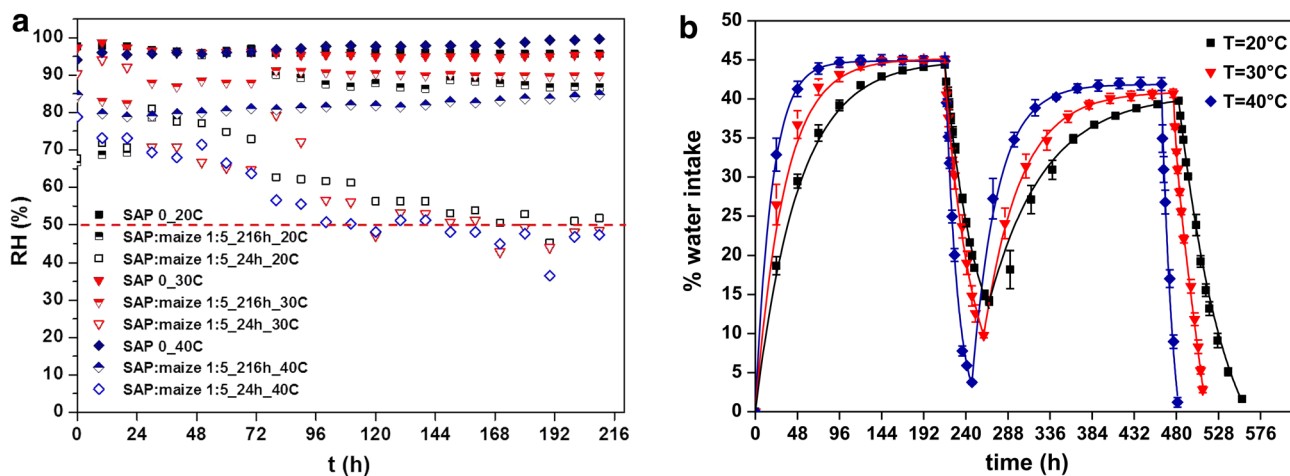
where  $MC$  (%) is the moisture content,  $a_w$  is the water activity,  $M_0$  (%) is the monolayer sorbent content on the internal surface,  $K_G$  is a dimensionless GAB parameter related to heat of sorption of the monolayer region,  $k$  is a dimensionless GAB parameter related to heat of sorption of the multilayer region,  $K_S$  is the SIPS sorption capacity,  $n$  is the sorption intensity and  $C$  is the energy of adsorption. The GAB equation is well established as a model for food and it was already employed to follow water sorption in maize (Chayjan and Esna-Ashari 2010; Andrade et al. 2011). Unfortunately the GAB model does not converge for the SAP data, for this reason the SIPS model has been introduced in order to fit better the SAP sorption isotherm. The SIPS isotherm is a combined form of Langmuir and Freundlich expressions deduced for modeling heterogeneous adsorption systems (Foo and Hameed 2010). In this case the model predicts very well the water sorption isotherms of both materials, in particular showing a better sorption power for SAP than maize, i.e. the sorption constant  $K_S$  is higher in the case of SAP than maize (see Table S7).

The results obtained from the sorption isotherms suggested that in order to maintain the MC in maize below the critical value of 13 %, the relative humidity (RH) of the system should be equal or below 50 %. These results were in agreement with the results obtained during the adsorption/desorption studies performed with the SAP to maize ratio of 1:5 and different SAP frequency changes (never, every 24 h) and temperatures (20, 30 and 40 °C) shown in Fig. 5a.

The system where SAP was changed every 24 h was showed the RH of 50 %. This value corresponds to a MC of 13 %, from the results obtained by the sorption isotherms. In this case therefore, aflatoxin levels fell below the maximum acceptable levels for Kenyan standards (Fig. 2). Furthermore, the optimal RH value obtained by drying upto 149 h was found to be an optimal drying time in order to achieve the European standards (Fig. 3). It is therefore possible to conclude that by using a SAP-to-maize ratio of 1:5 with a 24 h SAP frequency change, the aflatoxin formation was reduced to expected Kenyan standards, which agreed with the results obtained from the LC-MS analysis (Fig. 1).

### SAP adsorption/desorption behavior and its reusability

The dynamic and equilibrium swelling properties of SAP are important parameters in order to better understand its drying ability and optimize the storage conditions with maize. SAP-to-maize ratio of 1:5 with a 24 h SAP frequency change and temperatures of 20, 30 and 40 °C, were chosen in order to study the effect of temperature on the swelling capacity of the polymer following the same conditions as used for evaluation of aflatoxin formation. The



**Fig. 5** SAP and maize: storage conditions and SAP reusability **a** relative humidity (RH) recorded during the different maize samples without SAP (*full symbols*) and dried using SAP-to-maize ratio of 1:5, different SAP frequency change (never, every 24 h) and temperatures

(20, 30 and 40 °C). **b** Adsorption and desorption kinetics of SAP using exchange intervals of 24 h, SAP-to-maize ratio of 1:5 at different temperatures (20, 30 and 40 °C). *Full lines* are fits to Eqs. 6 and 7

**Table 1** Swelling and deswelling cycle parameters of SAP using exchange intervals of 24 h, SAP to maize ratio of 1:5 at different temperatures (20, 30 and 40 °C)

	T = 20 °C			T = 30 °C			T = 40 °C		
	$M_{eq}$ (%)	$M_0$ (%)	$\tau_s/\tau_d$ (h)	$M_{eq}$ (%)	$M_0$ (%)	$\tau_s/\tau_d$ (h)	$M_{eq}$ (%)	$M_0$ (%)	$\tau_s/\tau_d$ (h)
1st swelling	44.7 ± 0.1	0.1 ± 0.1	44.9 ± 0.4	45.0 ± 0.1	0.1 ± 0.3	27.7 ± 0.4	44.9 ± 0.1	0.1 ± 0.2	18.5 ± 0.2
1st deswelling	4 ± 2	39 ± 2	35 ± 4	0 ± 3	41 ± 3	30 ± 4	0 ± 2	41 ± 2	12 ± 2
2nd swelling	40.1 ± 0.3	18.4 ± 0.4	52 ± 3	41.1 ± 0.2	24.1 ± 0.3	45 ± 2	42.2 ± 0.2	27.2 ± 0.2	33 ± 1
2nd deswelling	0 ± 2	39 ± 2	31 ± 4	0 ± 4	37 ± 4	18 ± 5	0 ± 6	41 ± 6	9 ± 3

swelling ratio of the networks was calculated by using the following equation:

$$\Delta m(\%) = \frac{m_s - m_d}{m_d} \cdot 100 \quad (5)$$

where  $m_d$  and  $m_s$  denote the mass of the dry and swollen polymer, respectively. Figure 5b shows the swelling and deswelling cycles of SAP at different temperatures.

In order to obtain additional information into the swelling kinetics and properties of the polymer, all the experiments were fitted using exponential models for vapor sorption and desorption, which are given by the following Voight-based equations (Omidian et al. 1998):

$$\Delta m = \Delta m_0 + \Delta m_{eq} \left(1 - e^{-\frac{t}{\tau_s}}\right) \quad (6)$$

$$\Delta m = \Delta m_{eq} + \Delta m_0 \cdot e^{-\frac{t}{\tau_d}} \quad (7)$$

where  $\Delta m$ ,  $\Delta m_0$ ,  $\Delta m_{eq}$  are the swelling ratio, the initial swelling ratio and the equilibrium swelling ratio, respectively, while, the two kinetic factors  $\tau_s$  and  $\tau_d$  are the relaxation times of the swelling and deswelling behavior, respectively. All calculated parameters are shown in Table 1.

The decrease trend found in the factors  $\tau_s/\tau_d$  with increasing the temperature was evidenced that SAP swelled and deswelled faster at higher temperatures. At all temperature the maximum swelling of the SAP was <50 %. These results show that the adsorption and desorption kinetics follow a clear trend with temperature and can be reused several times without losing its drying properties, a very interesting property in terms of the affordability of the proposed drying technology.

## Conclusion

A new solution to dry maize was proposed in this study by employing food grade super adsorbing polymers (SAP), as a cheap and reusable drying agent. The results show that aflatoxin formation can be reduced by employing SAP at different temperatures and conditions. The aflatoxin contamination below acceptable standards can be reduced in a

temperature range between 20 and 40 °C by using a SAP-to-maize ratio of 1:5 with a 24 h frequency change of the SAP. The kinetics of the swelling properties of SAP measured indicated an appropriate and affordable material to avoid aflatoxin contamination.

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