STUDY OF ABSORPTION AND DESORPTION OF WATER IN SUPERABSORBENT POLYMER

[a]M.A. Suryawanshi*, [b]V.B. Tidke , [c]N.B. Khairnar, [d]R.D. Patil

[a]Department of Chemical Engineering, Bharati Vidyapeeth college of Engineering,MH,India
E-mail: * masuryawanshi@gmail.com, contact no: 8108802233
[b]Department of Chemical Engineering, Institute of Chemical Technology(UDCT), MH,India
[c,d,] Department of Chemical Engineering, Bharati Vidyapeeth college of Engineering,MH,India

Abstract: The objective of our project is to study the kinetics of absorption and desorption of water in SAP. SAP's are able to absorb water up to 300 times of its own weight. The basic property of the water absorption has suggested the use of SAP in many fields such as Agriculture, Horticulture, Disposable baby diapers, sanitary goods and Medicine. The ability of swollen SAP's to release the water to surrounding as vapor has also been used in various ways for example Humidity Controlling or Soil Conditioner. The SAP's used for experiment were poly-acrylic based. The swelling tests carried out at 20, 30 and 60 ^{0}C temperatures to study the thermal stability of SAP. The results have shown that the swelling rate increases with increase in surrounding water temperature. The kinetics were fitted to different models namely Peleg, First order absorption kinetic and Exponential association equation models. Out of all models Peleg model provides a good agreement with experimental data with high value of R^2, slope and intercept, it is concluded that the Peleg's model represent swelling characteristics better than other models.

*Keywords***:** SAP, absorption, desorption, agriculture, models etc.

INTRODUCTION

Superabsorbent polymers (SAP's) are materials that have the ability to absorb and retain large volumes of water and aqueous solutions. This makes them ideal for use in water absorbing applications such as baby nappies and adults incontinence pads to absorbent medical dressings and controlled release medium. Early superabsorbent were made from chemically modified starch and cellulose and other polymers like poly (vinyl alcohol) PVA, poly (ethylene oxide) PEO all of which are hydrophilic and have a high affinity for water. When lightly cross-linked, chemically or physically, these polymers became water-swellable but not water-soluble [Francesco F.M. *et.al.*].

Today's superabsorbent polymers are made from partially neutralized, lightly cross-linked poly (acrylic acid), which has been proven to give the best performance versus cost ratio. The polymers are manufacture at low solids levels for both quality and economic reasons, and are dried and milled in to granular white solids. In water, they swell to a rubbery gel that in some cases can be up to 99% wt water.

Superabsorbent hydrogels are a particular class of gels, obtained by chemical stabilization of hydrophilic polymers in a Three-dimensional network. Most of the traditional hydrogels on the market are acrylate-based products, thus not biodegradable. Due to the increase inattention for environmental protection issues, biodegradable hydrogels arise lively interest for potential commercial application in agriculture. It is a polymer where the long chains are cross-link to one another. A polymer can absorb water many times its volume therefore earning the term superabsorbent. After it absorbs the water, it forms a stiff gel.

Cross-links between polymer chains form a three-dimensional network and prevent the polymer swelling to infinity i.e. dissolving. This is due to the elastic retraction forces of the network, and accompanied by a decrease in entropy of the chains, as they become stiffer from their originally coiled state. There is a balance now between the forces of retraction and the tendency for the chains to swell to infinite dilution. The degree of cross-linking has a direct effect on the level of swelling of the polymer and the strength of the network i.e. Increased cross-link density = decreased swelling capacity = increased gel strength.

MATERIALS AND METHODS

Raw Materials
The polymeric material used in this study was purchased from local market, Matunga, Mumbai. The material is locally known as magic balls. We have performed two sets of experiments to study the kinetics for absorption and desorption phenomenon of water in SAP. The material used is shown in Figure 1.

Method used for swelling of SAP
Swelling tests were carried out at different temperatures of 20, 30 and 60 ^{0}C of water. Starting water content of SAP balls were considered as zero (g water/g dry SAP). Sample of SAP balls was weighted and put inside the beaker filled

with water for swelling. The constant temperatures were observed throughout the experiment by using digital temperature indicator. The experimental set up is shown in Figure 2. The swelling content and diameter of SAP were measured at specific time interval. While taking readings sample were removed from water and surface water wiped by using tissue paper. Then using this weight and diameter data the swelling kinetics were investigated. The experiments were carried out till equilibrium weight of SAP was observed.

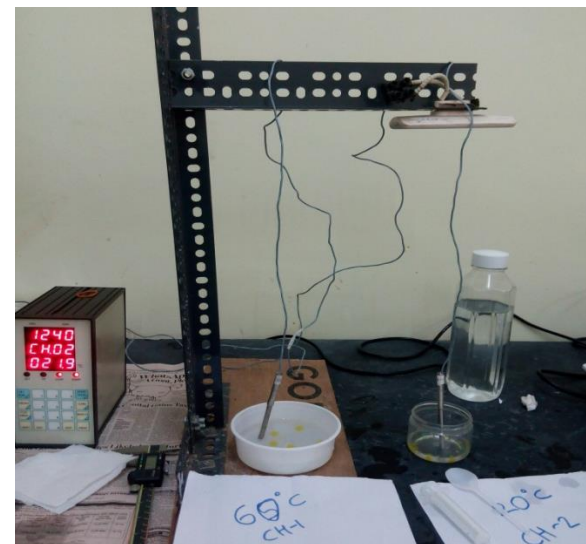**Figure 1**: SAP balls used for experiments

Figure 2: Experimental Set up for Absorption.

Method used for desorption of SAP

Desorption i.e. drying test was carried out at room temperature of 30 ^{0}C as shown in Figure 3. SAP sample used for experiment was completely saturated with water. The starting weight of SAP balls were measured after wiping surface water by tissue paper. The reduction in

water content and diameter were measured after specific time interval continuously till constant weights were observed.

Figure 3: Desorption of SAP balls

Swelling content

The swelling contents were calculated as follows:

$$S = \frac{w_s - w_d}{w_d}, \qquad (1)$$

Where,
S is the swelling content (g of water/g of dry balls), w_s is the weight of swollen SAP at time t and w_d is the weight of original dry SAP.

Swelling rate

Change in swelling content per unit of time in SAP is called "swelling rate" of SAP and is calculated using,

$$S_R = \frac{S_{t+\Delta t} - S_t}{\Delta t}, \qquad (2)$$

Where,
S_t is swelling content at any time (g/g of dry balls) and $S_{t+\Delta t}$ is the swelling at "$t + \Delta t$."

Diffusion of water

The Ficks law is used for the calculation of the swelling kinetics and diffusion of SAP structure. Swelling kinetics of polymers can be given by Peppas *et al*.

$$F = \frac{S_t}{S_e} = kt^n, \qquad (3)$$

Where,
F represents the swelling fraction, S_e is the equilibrium swelling content of the SAP, n is the diffusion exponential of water and k is the constant that changes according to the SAP structure. To identify the type of diffusion, the parameter "n" must be known. And it can be estimated from slope of a line obtained from lnF-lnt graph data. The diffusion coefficient "D" can be found by equation

obtained from the arrangement of Fick's II law and given as [R. Dengre *et.al.*]

$$D = \pi r^2 \left(\frac{k}{4}\right)^{1/n}, \qquad (4)$$

Where,

D represent coefficient of diffusion as m2/s and r represents the swollen SAP balls radius as m.

Activation Energy

The dependence of the diffusivity coefficient on temperature is often given by an Arrhenius type equation [M. Bohning *et.al.*]

$$D = D_0 \exp\left(\frac{-E_a}{R(T+273.15)}\right), \qquad (5)$$

Where,

D_0 is the pre-exponential factor of Arrhenius equation (m2/s), E_a is the activation energy (kJ/mol), T is temperature of water (K-1) and R is the universal gas constant of 8.314×10^{-3} (kJ/mol.K).

Mathematical Modeling of Absorption Kinetics

In this study, the methods that are developed from different researchers were used. Namely Peleg's model (6), First order absorption kinetics model (7) and Exponential association equation (8) [M. Peleg, D.K. Apar, M. Noshad]

Peleg proposed a two parameter model to describe water absorption by grains [M. Peleg]

$$S = S_0 \pm \frac{t}{k_1 + k_2 t}, \qquad (6)$$

Where S_0 is swelling content at t=0 (g of water /g of dry balls), S is the swelling content at any time (g/ g of d.b.), t is the swelling time in (s), k_1 is kinetic constant of the model (h(g.d.b)/g), and k_2 is characteristics constant of the model (g d.b./g). In equation (6) "$\pm$" becomes "$+$" if the process is absorption or adsorption and "$-$" if the process is drying or desorption.

In the first order absorption kinetic model, the equation used is of the following form, [K.G. Kaptso, K. Gomicki]

$$S = S_e + (S_0 - S_e)\exp(-k_{R1}t), \qquad (7)$$

Where,

k_{R1} is the swelling kinetic constant (h-1). Consider

$$S = S_e[1 - \exp(-k_{R2}t)], \qquad (8)$$

RESULTS AND DISCUSSION

Swelling Curves

From the results obtained the SAP swelling came to equilibrium at value at different time for different temperature of water and diameter of balls. The swelling equilibrium values for SAP were found as 84.5, 86.5 and 92.57 g water/g SAP balls for temperatures of 20, 30 and

60 0C, respectively for diameter of 3mm and similarly 26.8, 46 and 32.1 for 1mm diameter. Swelling content S is calculated by (1). The *S-t* graph was drowning from these values and swelling isotherms were constructed, shown in Figure 4 and 5 for 3mm and 1mm diameter respectively.
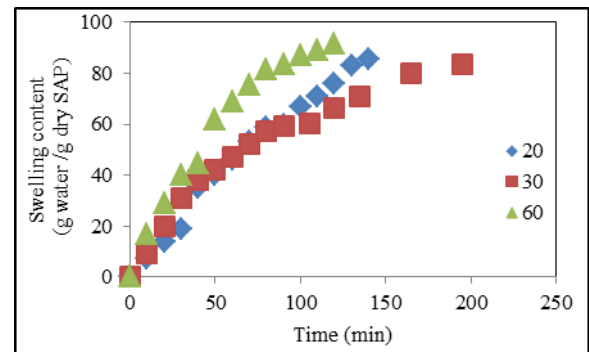

Figure 4: Swelling of SAP balls as a function of time at different temperatures for 3mm diameter of balls.
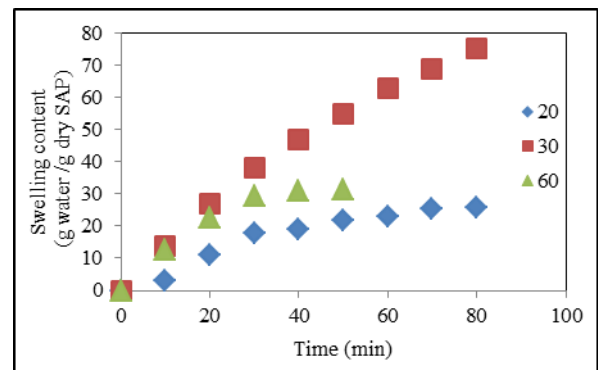

Figure 5: Swelling of the SAP balls as a function of time at different temperatures for 1mm diameter of balls.

The hydrogels swelling increases with increase in temperatures as seen in Figure 4 and 5. Figure 6 shows the change in SAP swelling rate with respect to swelling content for 3mm diameter of SAP balls.
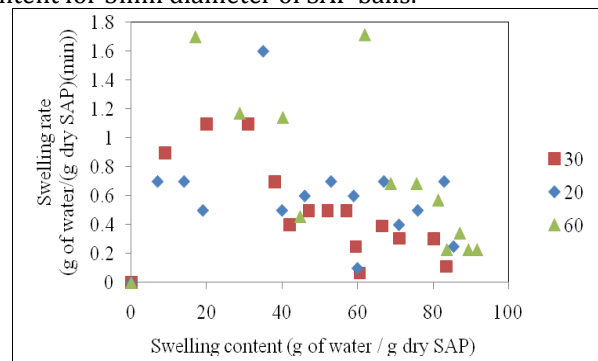

Figure 6: Swelling rate curve for SAP at different temperatures for 3mm diameter

As seen in Figure 7, the swelling rates and swelling content are increased with increasing temperatures. The maximum swelling content is found at 60^0C temperature of water, i.e. 92.57 g water/g dry SAP for 3mm diameter.
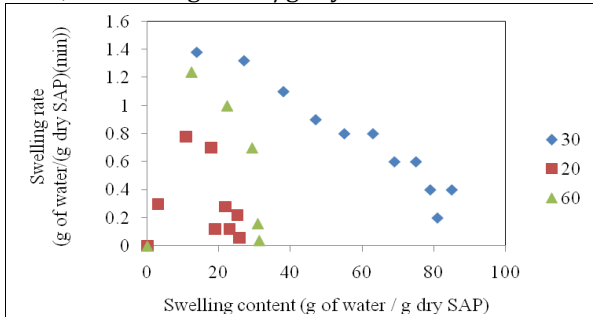

Figure 7: Swelling rate curve for SAP at different temperatures for 1mm diameter

As seen in Figure 5, the swelling content content for higher temperature of 60^0C is lesser than at 30^0C temperature of water, this is because of smaller diameter of the SAP balls. It is possible to say the H-bonds inside the SAP balls were broken due to temperature rise, it also increases the thermal mobility of polymer molecules inside the hydrogels.[2]

Calculation of Diffusion Coefficients

The diffusion coefficients were calculated by using equation (4). The plot of $\ln F$ verses $\ln t$ were obtained through the logarithmic form of (3) and the graph is given in Figure 8 and 9 for 3mm and 1mm diameter respectively.
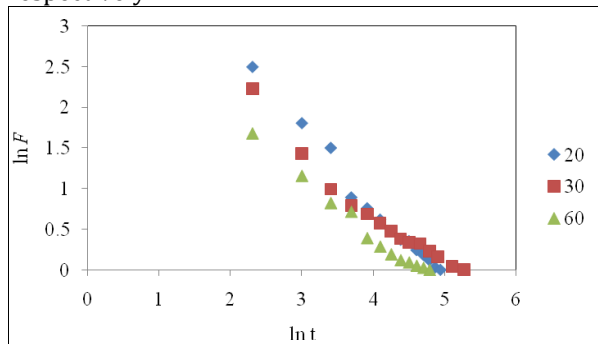

Figure 8: Swelling kinetics curves at different temperatures for 3mm diameter of SAP balls
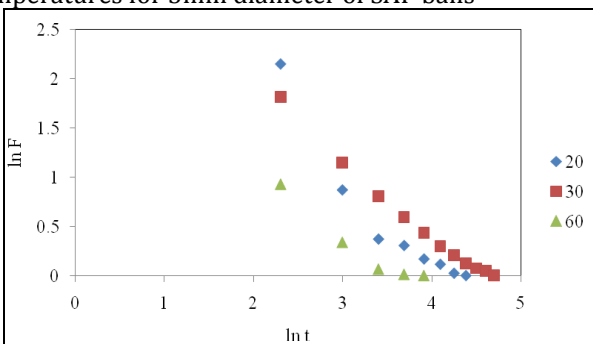

Figure 9: Swelling kinetics curves at different temperatures for 1mm diameter of SAP balls

Diffusion coefficient is one of the major parameters to determine the swelling characterisation of hydrogel, and it is calculated by using (4). The values of diffusion coefficient obtained for SAP are listed in Table 2.

Calculation of Activation Energy

The calculated diffusiveties Activation energy is calculated by using (5). The values of activation energies for 1mm and 3mm are given in Table 2.

Table 2: Values of swelling coefficients of SAP for 1mm and 3mm

Parameters	1mm			3mm		
Temperature (^0C)	20	30	60	20	30	60
Diffusion Coefficients (k × 10^{-5})	3.1	3.5	6.3	0.8	11.3	1.5
Activation Energy	22.43			49.73		

Evaluation of the Models

To describe swelling kinetics of the SAP balls at different temperatures (20, 30, and 60 ^0C), the three empirical models, namely, Peleg's, first order, and exponential association equation, are used and out of them the Peleg's model provide good agreement with experimental data. The kinetic rate constants k_1, k_2, R^2 values are given in Table 3 for different diameters at different temperatures. Where the constants k_1 and k_2 are the intercept and slope of the line obtained by the graph of x as shown in Figure 10.
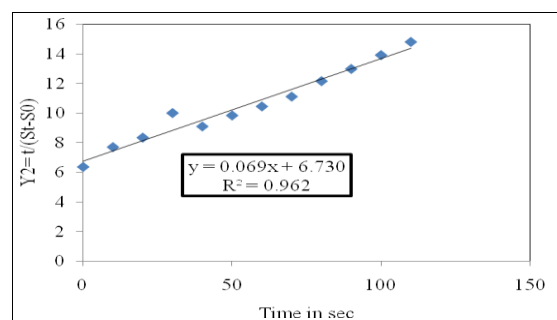

Figure 10: Change in swelling fraction with respect to time by applying Peleg's model at 60^0C for 3mm diameter of SAP balls

Table 3: Values of rate constants and R^2 for 1mm and 3mm at different temperatures

Parameters	1mm			3mm		
Temperature (^{0}C)	20	30	60	20	30	60
Intercept (k_1)	20.76	8.34	4.56	9.012	8.344	6.730
Slope (k_2)	0.488	0.16	0.53	0.057	0.087	0.069
R^2	0.576	0.79	0.90	0.431	0.976	0.962

Effect of Initial Size and Water Temperature on Diameter of the SAP balls

The change in diameter of SAP balls were measured after specific time interval, for 1mm and 3mm diameter at different water temperature as shown in Figure 11 and 12.
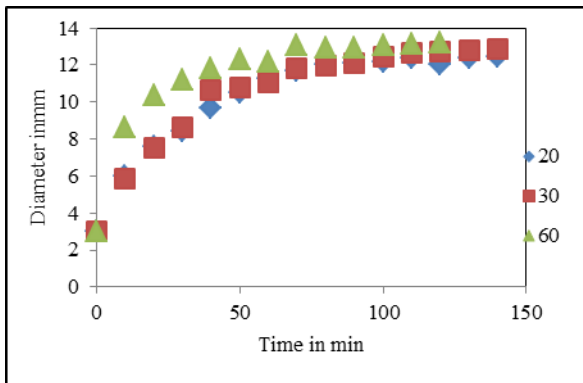
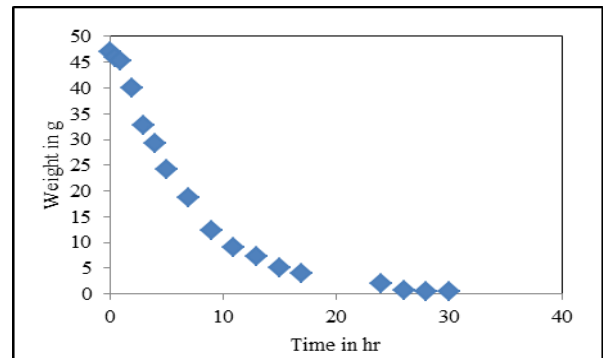**Figure 11:** Change in diameter of 3mm SAP balls at different temperatures
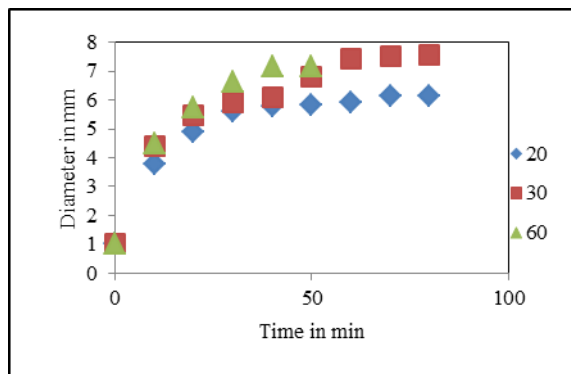
Figure 12: Change in diameter of 1mm SAP balls at different temperatures
Results of Desorption

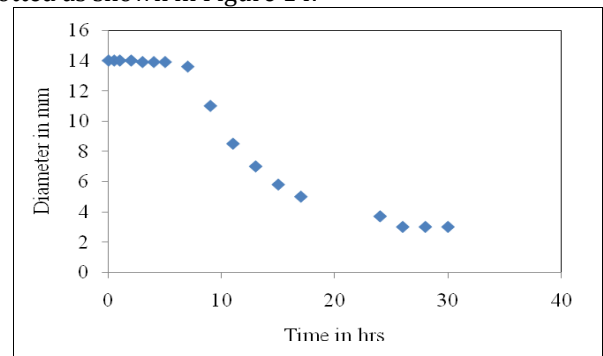***Change in Weight of SAP balls***

The change in weight of SAP during Desorption i.e. drying of SAP with respect to time is shown in Figure 13.

Figure 13: Desorption of SAP with respect to time

Change in Diameter of SAP balls

The change in diameter of SAP balls were measured after specific time interval at atmospheric temperature and it is plotted as shown in Figure 14.

Figure 14: Change in Diameter with respect to time

CONCLUSIONS

From the study, it is concluded that SAP is smart material. It has a very high water absorption capacity by its own weight, which helps in improving soil moisture capacity and hence reduces the water stress on the plant during irrigation intervals. SAP is also employed in hygienic uses for diapers, napkins etc. According to the results shown the size and weight of the SAP material is increases with respect to time. The absorption is higher at higher temperature of water. After the temperature of 60 ^{0}C SAP's have shrunk by giving their absorbed water. The swelling rate and effective diffusivity increases with increase in water temperature. To obtain the water content uptake as a swelling time, three different models were studied, out of which Peleg model has provided good agreement with experimental data. Therefore, this model is chosen to represent the swelling kinetics of SAP balls.

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