

Original Research Paper

# Controlled Release Behaviors of Tribenuron Methyl Herbicide and Potassium Nitrate Fertilizer from Natural Polymer Blended Poly(Vinyl Alcohol) Hydrogel Microspheres

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**Abstract:** Polyvinyl Alcohol (PVA) hydrogel microspheres for controlled release of fertilizer ( $\text{KNO}_3$ ) and Tribenuron Methyl Herbicide (TBM) were prepared by blending the naturally occurring Alginate (AL) and Pectin (PE). The cross-linking in PVA hydrogel microspheres was carried out by varying the amount of glutaraldehyde from 0.5-1.0 wt%. To control the loading and release properties of PVA hydrogel microspheres, a small amount of NaCl (0.2 wt%) was also added in formulation of microspheres. The blending of PE and AL in PVA hydrogel microspheres was confirmed with FT-IR spectra and by increased thermal stability PVA hydrogel as determined by Differential Scanning Calorimetry (DSC) and Thermogravimetric (TGA) analysis. The PVA hydrogel microspheres were characterized for degree of swelling and for loading and cumulative release of fertilizer ( $\text{KNO}_3$ ) and herbicide (TBM), which were carried out in solutions of different pH and at different temperatures. The Scanning Electron Micrographs (SEM) of PVA hydrogel microspheres were recorded before and after the release of loaded agrochemicals and used to confirm the shape and homogeneous blending of PE/AL in PVA hydrogels. The enhanced brittle morphology from SEM images of PVA hydrogel microspheres after the release of loaded agrochemicals has suggested the controlled release of agrochemicals through a mechanism of degradation of polymer chains. Thus natural polymer blended PVA hydrogel microspheres are found to be a potential candidate for the formulation of controlled release systems for the application of agrochemicals in soils and to overcome the environmental problem, which usually encountered on applications of fertilizers and herbicides in agricultural fields by conventional methods.

**Keywords:** Agrochemicals, Controlled Release, Polyvinyl Alcohol, Hydrogels, Pectin and Alginate

## Introduction

Synthetic polymers blended with natural polysaccharides offer a number of potential advantages such as chemical and thermal stability, film-forming ability, biocompatibility (Cifci and Kaya) and high hydrophilicity (Xu *et al.*, 2016; Rogovina *et al.*, 2013). Generally, polymers are of great significance in various stages and dimensions of human lives (Bortolin *et al.*, 2012; Cespedes *et al.*, 2013; Yang *et al.*, 2014) such as in the field of delivery formulations for drugs

(Fernandez-Perez *et al.*, 2011; Perez *et al.*, 2011), herbicides (Grillo *et al.*, 2012) and pesticides, (Kumar *et al.*, 2014) but often polymers in these applications remain as inert materials (Bortolin *et al.*, 2012). The inert polymers in controlled-release devices are mostly used to protect the loaded ingredients (Chowdhury, 2014; Roy *et al.*, 2014) but in catalysis they are used as support and provide a suitable microenvironment (Idris *et al.*, 2008; Mendes *et al.*, 2013; Zhu *et al.*, 2015). Unfortunately, conventional methods of application of fertilizers are inefficient to meet out the target due to the excessive loss

of fertilizers. Studies have indicated that only 20-30% of applied fertilizers is adsorbed by the plants and remaining is lost through volatilization, nitrification and leaching (Purnomo *et al.*, 2017), which causes environmental problem (Naz and Sulaiman, 2016). In comparison to Quick Release Fertilizer (QRF) formulation, the technique of Controlled Release Fertilizer (CRF) formulation is found to be quite suitable to increase the efficacy of fertilizers and to solve the environmental problems. Thus polymers found to be useful materials in application of fertilizers to agricultural fields to optimize the intake of nutrients by the plant and to increase the crop productivity. The polymer based controlled release systems are found to be helpful in releasing an optimum amount of agrochemicals for a sustained period of time. This helped in minimizing the contamination of water system and in reducing undesirable emissions of hazardous chemicals such as; ammonia that are usually emitted on application of urea coated fertilizers or on application of conventional form delivery of fertilizers (Azeem *et al.*, 2014; Naz and Sulaiman, 2016; Purnomo *et al.*, 2017). Recently in various studies, attempts are made to develop controlled release systems for the application of fertilizers that would enhance the efficacy of fertilizers and minimize the loss of fertilizers to the environment by slow release of loaded fertilizers to the soils (Pourjavadi *et al.*, 2011). The application of agrochemical controlled release systems helps in developing disease resistance and to the growth of plants, which seems to be an ideal way for the protection of crops and to enhance the crops productivity (Kumar *et al.*, 2014). Though different type of carriers have been use for the development of control release systems for drugs, fertilizers and agrochemicals but polymer hydrogels are found to be a better choice. The polymer hydrogels are able to imbibe a large amount of water that helps in slow release of loaded agrochemicals and in wetting the soil for a sufficient period of time. The hydrogels have been developed using natural (Melaj and Daraio, 2013) as well as synthetic polymers. In comparison to biodegradable polymer based controlled release systems, the controlled release fertilizer formulations of nondegradable polymers are found to be quite harmful in reducing the soil fertility due to the presence of residual nondegradable polymers in the soils after the release of loaded agrochemicals (Raut *et al.*, 2013; Poratkar and Raut, 2013; Naz and Sulaiman, 2016; Paul *et al.*, 2019). Thus controlled release formulations for fertilizers based on degradable polymers are found to be useful in overcoming the environmental problem (Chien *et al.*, 2009; Fereydun *et al.*, 2018) and in maintaining an optimum amount of agrochemicals in the soil (Azeem *et al.*, 2014; Pourjavadi *et al.*, 2011). To fulfill these objectives, the control release formulations for agrochemicals (Quinones *et al.*, 2010; Raafat *et al.*, 2012) or drugs are developed based on either polyvinyl alcohol (Kulkani *et al.*, 2010) or

polyacrylamide alone or in combination with naturally occurring biodegradable polymers such as; guar gum (Saruchi *et al.*, 2019), starch (Jo *et al.*, 1992), alginate (Bidarra *et al.*, 2014; Dalmoro *et al.*, 2012; Samanta and Ray, 2014; Zhang *et al.*, 2015; Idris *et al.*, 2008), cellulose derivatives (Hou *et al.*, 2019) and chitosan (Yang *et al.*, 2014; Choudhary *et al.*, 2016; Rakhshaei *et al.*, 2019). The methylcellulose (MC) based hydrogels are found to be potentially useful in developing controlled delivery systems for fertilizers ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, KH<sub>2</sub>PO<sub>4</sub>), herbicides and pesticides (Chen and Chen, 2019). Hydrogels based on combination of methylcellulose-polyacrylamide (Bortolin *et al.*, 2012), starch-alginates (Singh *et al.*, 2009), carboxy methylcellulose-polyvinyl pyrrolidone (Raafat *et al.*, 2012) and matrices of cross-linked chitosan (Quinones *et al.*, 2010), polylactic acid (Zhao and Wilkins, 2005), polycaprolactone (Grillo *et al.*, 2012) are also used in formulations of delivery systems for fertilizers ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, KH<sub>2</sub>PO<sub>4</sub>), triazine herbicides and bromacil pesticide. To overcome the physical and bead forming problem of PVA, the naturally occurring polymers such as; chitosan (França *et al.*, 2018) and alginates (Idris *et al.*, 2008) were mixed with PVA to develop controlled release formulations (Zain *et al.*, 2011; Paipitak *et al.*, 2011). The hydrophilicity of PVA (Xu *et al.*, 2016) is found to be useful in formulation of controlled released systems as it helped in controlled release of loaded agrochemicals due to sufficient degree of swelling in presence of water (Idris *et al.*, 2008). However, this hydrophilic nature of PVA is found to be a drawback in developing a controlled a release system that is insoluble in presence of water. Therefore, PVA is used after blended with other polymers (Paipitak *et al.*, 2011; Shukla *et al.*, 2008) and after cross-linking (Zain *et al.*, 2011). The blending of natural polymers with PVA increases the intermolecular interactions, which improves thermal and mechanical strength of PVA. Thus PVA has been used after blending with chitosan (Yang *et al.*, 2014), starch (Han *et al.*, 2009) and alginates (Zain *et al.*, 2011). The blending of alginates in PVA hydrogels has increased the bead forming ability of PVA (Paipitak *et al.*, 2011) as well as it also increased the biocompatibility (Cifci and Kaya) and non-toxicity of PVA (Kelly *et al.*, 2003). Thus considering the potential properties of PVA (Wang and Hsieh, 2016; Han *et al.*, 2009), an attempt has been made to prepare cross-linked hydrogel microspheres by blending PVA with naturally occurring Alginate (AL) or Pectin (PE) and crosslinking with suitable amount of glutaraldehyde. The resultant PVA hydrogel microspheres were used as control release formulations for fertilizer (KNO<sub>3</sub>) and herbicide (TBM). The thermal and spectral techniques were used to confirm the blending of natural polymers and their interactions with PVA. The morphological analysis of PVA hydrogels by scanning electron microscopy is used to confirm the homogeneous mixing of added polymers (PE or AL)

and to confirm the release mechanism of loaded agrochemicals. The cumulative controlled release properties of PVA hydrogel microspheres for loaded agrochemicals was evaluated as a function of type of loaded agrochemicals, degree of cross-linking and solution pH to optimize the composition and formulations of polymer blended PVA hydrogel microspheres to achieve optimum control release of loaded fertilizer ( $\text{KNO}_3$ ) or herbicide (TBM) in the soil.

## Experimental

### Materials

Granular Polyvinyl Alcohol (PVA) ( $\bar{M}_v = 101,000 \text{ g mol}^{-1}$ ) was purchased from Aldrich Chemical Company, USA and was used without further purification. Ammonium Alginate (AL) was procured from Hobkin, UK. Pectin (PE) and potassium nitrate ( $\text{KNO}_3$ ) were obtained from BDH Chemical Company, UK. The Tribenuron Methyl (TBM) was obtained commercially from WE Young Industrial and Trading Company LTD, China. Glutaraldehyde solution (50 wt%) and other chemicals were of analytical grade reagents and received from Fluka.

### Preparation of PVA Hydrogel Microspheres

The Pectin (PE) or Alginate (AL) blended polyvinyl hydrogel microspheres were prepared by blending natural polymers (PE or AL) in 1.0 wt% solution of PVA in distilled water as reported in literature (Cifci and Kaya, 2010; Han *et al.*, 2009). The PVA solution was heated at  $70^\circ\text{C}$  under constant stirring for about 30 min and then 1.0 g powder of Pectin (PE) or ammonium Alginate (AL) was added. The resultant mixture was heated continuously at  $50^\circ\text{C}$  for about 20 min and then poured separately in 500 mL round bottomed flask, which was subsequently refluxed at  $60^\circ\text{C}$ . To evaluate the effect of addition of salt on properties of PVA hydrogel microspheres, the polymer blended PVA hydrogel microspheres containing 0.2 wt% of NaCl was also prepared. To control the degree of cross-linking in polymer blended PVA hydrogel microspheres, the polymer blended solutions of PVA were added drop-wise with the help of a syringe within a period of 30 min in a flask containing either 0.5 or 1.0 wt% solution of glutaraldehyde. The flasks containing glutaraldehyde solution and resultant PVA hydrogel microspheres were magnetically stirred continuously for another 30 min to complete the process of cross-linking with added glutaraldehyde. The PVA hydrogel microspheres so produced were left overnight under stirring at  $30^\circ\text{C}$ . Finally, the glutaraldehyde cross-linked PVA hydrogel microspheres were separated and dried in a vacuum oven at  $30^\circ\text{C}$  after washing with deionized water.

## Characterization of PVA Hydrogel Microspheres

### Molecular Weight Determination

The viscometric molecular weight  $\bar{M}_v$  of PVA and natural polymers were determined using Ubbelohde type of capillary viscometer. The dilute solutions of polymers were prepared in 5 wt% solution of acetic acid at  $25^\circ\text{C}$  within a concentration range of 0.05-0.2g/dL. The Mark-Houwink equation (Equation 1) was used to determine the viscometric average molecular weight ( $\bar{M}_v$ ) of tested polymers (Singh *et al.*, 2010):

$$[\eta]_{25^\circ\text{C}} = K\bar{M}_v^\alpha \quad (1)$$

Where:

- $[\eta]$  = The intrinsic viscosity
- $\bar{M}_v$  = Viscometric average molecular weight
- $K$  and  $\alpha$  = Constants and their values depend on type of solvent and temperature

### Ft-IR and Thermal Characterization

FT-IR spectra of pure PVA hydrogel and of polymer blended PVA hydrogel microspheres were recorded by spectrophotometer (Tensor Company Bruker, 2003, Germany) before and after the loading of studied agrochemicals ( $\text{KNO}_3$  and TBM) by using KBr pellets. The TGA and DSC analysis of pure PVA and polymer blended PVA hydrogel microspheres was carried out by recording their thermograms before and after the release of loaded agrochemicals ( $\text{KNO}_3$  and TBM) using Perken-Elmer Pyris, Diamond (TG/DTA 6300) thermal analyzer (USA) at a heating rate of  $10^\circ\text{C}/\text{min}$  in presence of nitrogen.

### Scanning Electron Micrographs

SEM images of pristine and agrochemical loaded polymer blended PVA hydrogel microspheres were recorded using scanning electron microscope (LEO 435 VP-England). The SEM images of polymer blended PVA hydrogel microspheres after the release of loaded agrochemical were also recorded. To record the SEM images, the polymer blended PVA hydrogel microspheres were mounted on aluminum studs using double adhesive tape and then coated under vacuum by exposing to a gold ion beam sputter (PELCO S.C.6) at a current of 25 mA for about 40 sec.

### Swelling Behavior

The degree of swelling ( $S_w$ ) in PVA hydrogel microspheres and its polymer blended microspheres was determined by gravimetric analysis after carrying out swelling under different experimental conditions. To study the swelling in PVA hydrogel microspheres, a known amount of PVA hydrogel microspheres (100 mg)

was kept in 20 mL solution of different pH at 25°C. The buffer solutions of 4, 7 and pH 9 were used to maintain the pH of swelling solution. After swelling of PVA hydrogel microspheres for fixed time interval, the separated PVA hydrogel microspheres were wiped with filter paper and their weights were recorded to determine the degree of swelling (Bortolin *et al.*, 2012) using following equation (Equation 2).

$$S_w = \frac{WW_t - W_0}{W} \times 100 \quad (2)$$

where,  $W_t$  is the weight of PVA hydrogel microspheres after swelling at different intervals of time and  $W_0$  is the initial weight of dry microspheres before swelling. To study the effect of temperature on degree of swelling, the degree of swelling in PVA and polymer blended PVA hydrogel microspheres was determined by keeping PVA hydrogel microspheres in a swelling solution maintained at different temperatures (11, 25 and 45°C). The effect of degree of cross-linking on swelling was studied by recording the degree of swelling in PVA hydrogel microspheres, which were prepared by varying the amount of glutaraldehyde from 0.5-1.0 wt%. The effect of addition of NaCl (0.2 wt%) on degree of swelling was also studied by recording the degree of swelling in PVA hydrogel microspheres prepared with and without NaCl.

#### Loading of Agrochemicals in Microspheres

The loading of agrochemicals in PVA hydrogel microspheres and polymer blended hydrogel microspheres was carried out at room temperature by keeping microspheres (100 mg) for a fixed time interval in solutions (20 mL) of different pH (4, 7 and 9) containing a fixed amount of agrochemicals (100 mg). The loading of agrochemicals was also carried out in pure PVA hydrogel microspheres, which were prepared with different amount of glutaraldehyde and with fixed amount of NaCl as additive. The loading of agrochemicals in polymer blended PVA hydrogel microspheres with different degree of cross-linking (0.5-1.0 wt% of glutaraldehyde) was carried out by keeping PVA hydrogel microspheres for different time intervals in loading solution. The maximum weight loading of agrochemicals ( $L_{max}$ ) was determined by analyzing the remaining amount of agrochemicals in loading medium. The solution pH, loading time and degree of cross-linking were optimized by analyzing the weight percent loading of agrochemicals in PVA hydrogel microspheres in solution of different pH, on different contact time and on using PVA hydrogel microspheres with different degree of cross-linking. The maximum weight percent loading of agrochemicals in PVA hydrogel microspheres was determined using (Chien *et al.*, 2009; Perez *et al.*, 2011) following equation (Equation 3):

$$L_{max}(\%) = \frac{\text{Loaded amount of agrochemicals}}{\text{Amount of microspheres used for loading}} \times 100 \quad (3)$$

The loaded amount of agrochemicals ( $KNO_3$  or TBM) in PVA hydrogel microspheres was determined by recording the absorbance of loading media after separating the agrochemical loaded PVA hydrogel microspheres and by using a calibration curve, which was drawn using a series of standard solutions of  $KNO_3$  or TBM within a concentration range of 0.5-5.0x10<sup>-2</sup>g/mL (5-50 ppm). The absorbance of  $KNO_3$  (210 nm) and TBM (238 nm) were recorded at their  $\lambda_{max}$ , which were determined on recording UV spectra of  $KNO_3$  and TBM using UV-VIS spectrophotometer (UV-1650pc SHIMADZU Spectrophotometer).

#### Release of Agrochemicals from PVA Hydrogel Microspheres

The release pattern of agrochemical from PVA hydrogel and polymer blended PVA hydrogel microspheres loaded with maximum amount of agrochemical was determined by keeping 100 mg of agrochemical loaded PVA hydrogel microspheres in a release medium (20 mL) and the released amount of agrochemical was determined at each time interval (5 h) by recording the absorbance of agrochemical in release medium at their  $\lambda_{max}$ . To record the absorbance of release medium at fixed time interval (5h), 0.5 mL of release media was withdrawn for the analysis and same volume was replaced with fresh buffer solution. The cumulative release (%  $R_{cum}$ ) of agrochemical as weight percent was determined at particular interval of time by using following equation (Equation 4) under different conditions (Singh *et al.*, 2009).

$$\text{Percent cumulative release}(\% R_{cum}) = \frac{W_t}{W_0} \times 100 \quad (4)$$

where,  $W_t$  is the amount of agrochemicals released at time (t) and  $W_0$  is total amount of agrochemical released finally. The release behavior of  $KNO_3$  or TBM from pure PVA hydrogel and polymer blended PVA hydrogel microspheres were studied under different conditions to optimize the release properties of PVA hydrogel microspheres. The release studies of PVA hydrogel microspheres were carried out in solution of different pH and at different temperature using PVA hydrogel microspheres, which were prepared at different degrees of cross-linking and on mixing different polymers and agrochemicals.

#### Statistical Analysis

All experimental data were collected in triplicates and presented as means  $\pm$  standard deviations. The statistical analyses were performed using student's two tailed test considering  $p < 0.05$ , as statistically significant.

## Results and Discussion

The natural polymer mixed synthetic hydrogels are widely used in industries to develop controlled release systems to enhance the efficacy of fertilizers and to overcome environmental problems of fertilizers, insecticides and herbicides (Cespedes *et al.*, 2007). The natural polymer based controlled release formulations are found to be more potential in delivering the loaded agrochemicals at a controlled rate for a prolonged time interval (Melaj and Daraio, 2013) without causing any toxic effect to the crops and environment (Kelly *et al.*, 2003). To design efficient control release formulations, natural polymer mixed PVA hydrogel microspheres with different properties were prepared and analyzed for their control release under different conditions. The PVA on mixing with hydrophilic natural polymers like AL or PE has produced insoluble blends (Paipitak *et al.*, 2011; Shukla *et al.*, 2008), which on cross-linking with glutaraldehyde have produced hydrogels with useful properties (Zain *et al.*, 2011). The polymer mixed PVA hydrogels were shaped as microspheres to enhance interfacial area for interactions with surrounding media. The swelling behavior of polymer blended PVA hydrogel microspheres was studied as a function of solution pH to optimize the loading and release behavior of PVA hydrogel microspheres for selected fertilizer (KNO<sub>3</sub>) and herbicide (TBM). The prepared polymer blended PVA hydrogel microspheres also seems to be able in controlling the water retention properties of soil and in reduction of death rate of plants due to dryness.

### Molecular Weight Measurements

The viscometric average molecular weights ( $\bar{M}_v$ ) of PVA, PE, AL and their blends with PVA were determined by viscometric method (El-Sawy *et al.*, 2010; Singh *et al.*, 2010) using Equation 1. The

determined  $\bar{M}_v$  of PVA, PE, AL and polymer blended PVA in 1:1 weight ratio are shown in Table 1.

### FT-IR Characterization of PVA Hydrogels

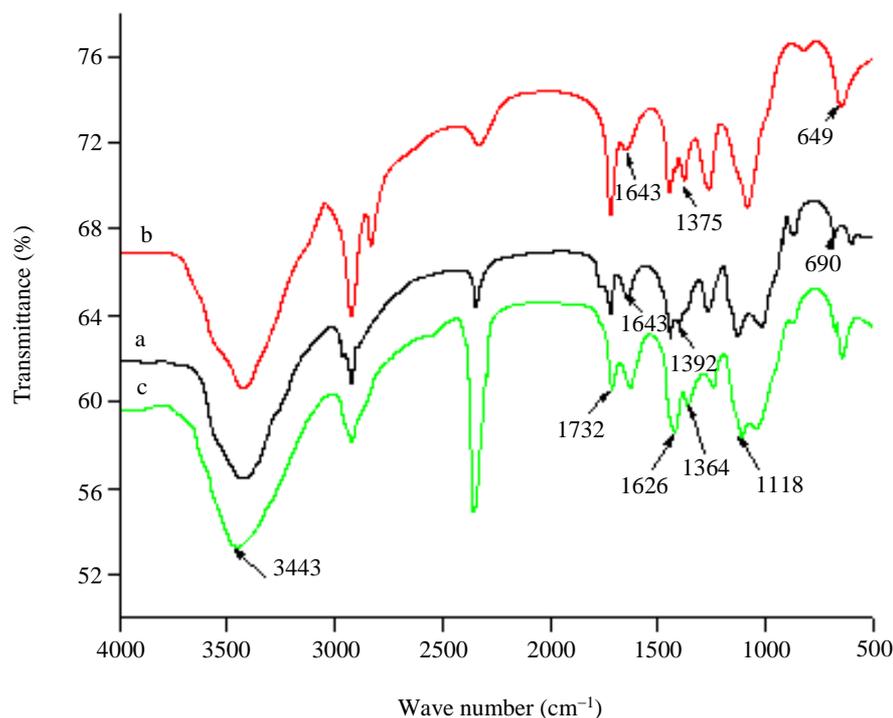
The FT-IR spectra of pure PVA hydrogels were compared with FT-IR spectra of polymer blended PVA hydrogels to confirm the blending of polymers with PVA and their interactions. The presence of characteristic absorption bands of PVA (Awada and Daneault, 2015) such as  $\nu$ (-OH),  $\nu$ (-CH) and  $\nu$  (-CO) and of blended polymers (PE or AL) were found useful to confirm the presence of polymers (PE or AL) in the blends of PVA. The appearance of characteristic absorption bands of AL at 1733cm<sup>-1</sup> (>C = O), 2925 and 2850cm<sup>-1</sup> (C-H<sub>str.</sub>), 1436 cm<sup>-1</sup> (C-H<sub>def.</sub>) and 1127cm<sup>-1</sup> (C-O<sub>str.</sub>) has confirmed the blending of AL in PVA (Table 2). Similarly, the presence of characteristic absorption bands of PE such as symmetrical and asymmetrical stretching bands of C ... O at 1389 and 1653cm<sup>-1</sup> and a band at 1260cm<sup>-1</sup> (C-O<sub>str.</sub>) has confirmed the blending of PE in PVA (Table 2). The small changes in position of characteristic absorption bands of PE and AL in PVA blends have suggested that PVA was interacting with functional groups of blended polymers (Table 2). The loading of agrochemicals in polymer blends of PVA was confirmed by comparing the FT-IR spectra of pure agrochemicals (KNO<sub>3</sub> and TBM) with FT-IR spectra of PVA hydrogels loaded with agrochemicals (Fig. 1).

**Table 1:** Viscometric molecular weights of PVA, AL, PE and polymer blends

Polymers and hydrogels	$\bar{M}_v$ /g mol <sup>-1</sup>
Polyvinyl alcohol (PVA)	101000
Alginate (AL)	2500
Pectin (PE)	20000
Polyvinyl alcohol-alginate blend (PVA-AL)	10300
Polyvinyl alcohol-pectin blend (PVA-AL)	120500

**Table 2:** Characteristic frequencies of PVA, TBM, KNO<sub>3</sub> and polymer blends

Sample code	Characteristic FT-IR frequencies of functional groups/ cm <sup>-1</sup>											
	N...O	-OH	-CH	-CO	-C = O	-NH	O-C-O	C-O	-SO <sub>2</sub> NH	-S = O	-C = N	-NO
PVA		3443	2924	1110								
PE			1435	1258	1736		1652	1388				
AL			1432	1127	1734							
PVA-AL		3455	2925	1116	1733							
			2850	1127								
			1436									
PVA-PE		3443	2924	1132	1735		1653	1389				
			2869	1260								
			1434									
TBM			2957	1136	1732	3431	1626	1388	1171	1358	1626	1633
									1348	1197		1384
										590		668
KNO <sub>3</sub>	1643											
	1392											
	690											



**Fig. 1:** FT-IR spectrum of (a) PVA-PE hydrogels loaded with KNO<sub>3</sub>, (b) PVA-AL hydrogels loaded with KNO<sub>3</sub> and (c) PVA-PE hydrogels loaded with TBM

The FT-IR spectrum of pure TBM was having a characteristic band (Fang *et al.*, 2010) at 3431cm<sup>-1</sup>(-NH<sub>str</sub>) and two bands at 1171 and 1348 cm<sup>-1</sup> corresponding to secondary -SO<sub>2</sub>NH group (Table 2). The sulfonate esteric bands appeared at 1398, 1197 and 590 cm<sup>-1</sup> due to -S = O<sub>str.</sub>. The imine absorption bands (>C = N) appeared at 1626 cm<sup>-1</sup>, whereas deformation (>C-H<sub>def</sub>) and stretching bands (>C-O<sub>str.</sub>) of methoxy group (-OCH<sub>3</sub>) appeared at 1434 and 1136 cm<sup>-1</sup> respectively. The FT-IR spectrum of TBM loaded in PE or AL blended PVA hydrogel microspheres has shown characteristics peaks of TBM (Fig. 1), which confirmed the loading of TBM in polymer blended PVA hydrogel microspheres. The FT-IR spectrum of TBM loaded PVA-BE hydrogel microspheres has shown characteristic bands of TBM (Fang *et al.*, 2010) at 3443, 1732, 1626, 1364 and 1113 cm<sup>-1</sup> respectively as shown in Fig. 1c.

However, the positions of absorption bands of TBM in PVA-PE hydrogel microspheres were found to be slightly different in comparison to PVA-AL hydrogel microspheres. This was due to the differences in interactions of TBM with PE and AL in PVA hydrogels. The FT-IR spectrum of pure KNO<sub>3</sub> has shown its characteristic bands (Luleva *et al.*, 2011; Bajpai and Giri, 2002) at 1633, 1384 and 668 cm<sup>-1</sup> corresponding to N=O group. The FT-IR spectrum of KNO<sub>3</sub> in PVA-PE hydrogel microspheres has shown characteristic bands

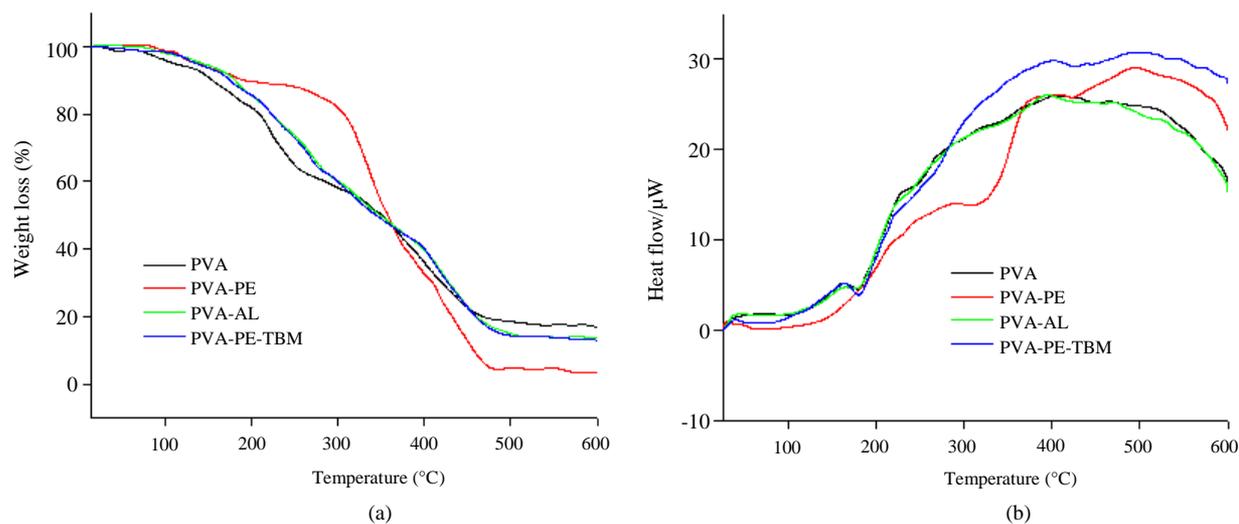
(Fig. 1a) at 1643, 1392 and 690 cm<sup>-1</sup> corresponding to nitro group (N=O), whereas PVA-AL hydrogel microspheres have shown these bands (Fig.1b) at 1643, 1375 and 649 cm<sup>-1</sup> corresponding to nitro group (N=O). This variation in position of absorption bands of nitro group was due to the difference in structures of AL in comparison to PE; hence the absorption bands of nitro group (N=O) have shown slight variation in their positions in PVA-AL hydrogel microspheres than PVA-PE hydrogel microspheres (Fig.1a and b).

#### Thermal Characterization of PVA Hydrogels

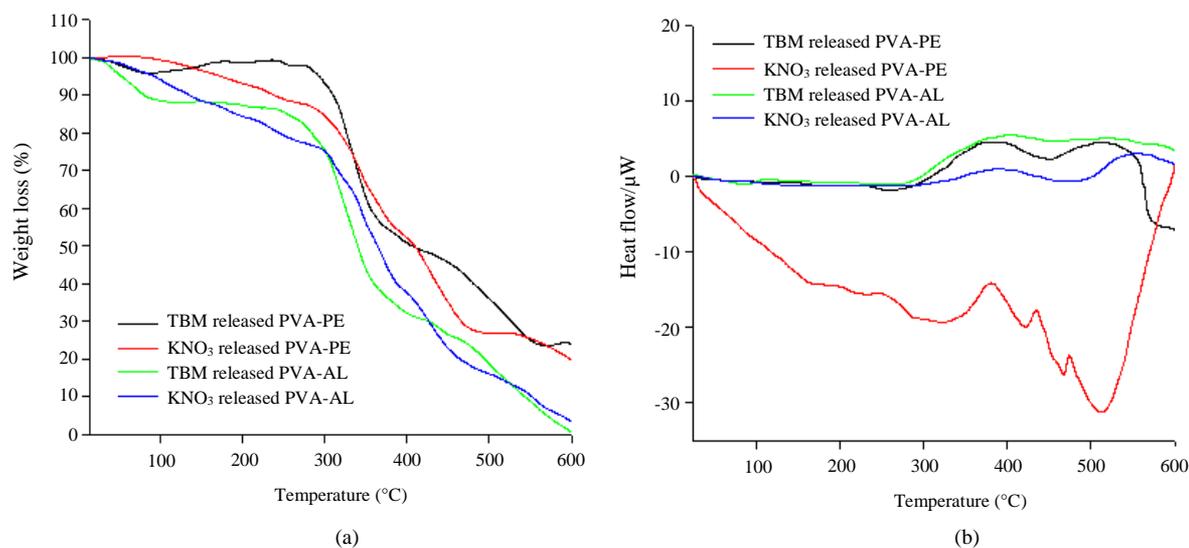
To confirm the effect of blending of polymers (AL or PE) and loading of agrochemicals in PVA hydrogel microspheres, the samples of PVA hydrogel microspheres were analyzed using TGA and DSC techniques. The data of pure PVA hydrogel, polymer blended PVA hydrogels and PVA-PE hydrogel microspheres loaded with agrochemical (TBM) are shown in Fig. 2 and Table 3, whereas thermal analysis polymer blended PVA hydrogel microspheres after the release of loaded agrochemical (TBM and KNO<sub>3</sub>) are shown in Fig. 3 and Table 3. The TGA and DSC analysis of PVA hydrogel microspheres have indicated that the blending of polymers in PVA hydrogels (Fig. 2) has increased the thermal stability of PVA (Escobar *et al.*, 2015; Wanyika, 2013).

**Table 3:** Thermogravimetric (TGA) and Differential Scanning Calorimetric (DSC) analysis of pure PVA hydrogels, polymer blended PVA hydrogels, and of polymer blended PVA hydrogels before and after the release of loaded agrochemicals

Samples code	Thermogravimetric analysis (TGA) data			DSC analysis data
	IDT/°C (% wt loss)	FDT/°C (% wt loss)	% wt loss at 400°C	$\Delta H_f / J\ mg^{-1}$ (Temp.range °C)
Pure PVA gel	163°C (11)	465 (80.0)	63.06	29.60 (160-600)
PVA-PEgel	280 (15)	465 (93.0)	66.69	37.20 (150-600)
PVA-ALgel	170 (8)	470 (84.2)	61.03	18.50 (125-600)
TBM loaded PVA-PE gel	210 (10)	575 (93.0)	68.45	10.20 (363-610)
PVA-PE gel after TBM release	250 (12)	560 (99.4)	65.51	12.50 (363-610)
PVA-PE gel after KNO <sub>3</sub> release	150 (9)	575 (90.0)	56.86	0.52 (378-470)
PVA-AL gel after TBM release	160 (12)	600 (99.5)	67.75	12.4 (397-580)
PVA-AL gel after KNO <sub>3</sub> release	150 (12)	600 (98.0)	61.56	0.82 (385-562)



**Fig. 2:** Thermogravimetric (a) and differential scanning calorimetric (b) analysis of PVA, PVA-PE, PVA-AL hydrogels and of TBM loaded hydrogels (PVA-PE-TBM)



**Fig. 3:** Thermogravimetric (a) and differential scanning calorimetric (b) analysis of PVA-PE, PVA-AL hydrogels after the release of loaded TBM or KNO<sub>3</sub>

The Initial Decomposition Temperature (IDT) of PVA-PE hydrogels has increased to 280°C in comparison to IDT of pure PVA hydrogels (163°C). However, PVA-AL hydrogels have shown a small increase in their IDT value (170°C). This might be due to low molecular weight of alginate in comparison to molecular weight of pectin (Fig. 2a and Table 3). The PVA-PE hydrogels have shown a substantial loss in their weights at Final Decomposition Temperature (FDT) in comparison to PVA-AL hydrogels or pure PVA hydrogels. This was attributed to a significant loss in degree of crystallinity in PVA on its blending with PE in comparison to its pure hydrogels or PVA-AL hydrogels (Fig. 2a and Table 3). The TBM loaded PVA-PE hydrogels have also shown less weight loss at FDT than PVA-PE hydrogels without TBM, which might be due to stronger interactions between TBM and PE in PVA-PE hydrogels (Fig. 2a and Table 3). This has been confirmed from the enhanced IDT (210°C) and FDT (575°C) for TBM loaded PVA-PE hydrogels. The DSC analysis of pure PVA hydrogels and polymer blended PVA hydrogels have shown significant variation in enthalpy of transition ( $\Delta H_f$ ), which was found to be maximum in PVA-PE hydrogels (-37.2 J mg<sup>-1</sup>) as shown in Table 3 and Fig. 2b. The blending of polymers (PE or AL) in PVA hydrogels has also shown a significant variation in glass transition temperatures (T<sub>g</sub>) of PVA hydrogels (Table 3).

The pure PVA hydrogels have shown two prominent weight losses in their thermograms (Fig. 2a and Table 3), one corresponding to decomposition in crystalline structure of PVA in hydrogels and other corresponding to the decomposition of methylenic groups in the backbone of PVA (Wanyika, 2013).

The polymer blended PVA have also shown two prominent weight losses (Fig. 2a and Table 3), first weight loss was corresponding to the decomposition of PVA and second weight loss was due to the decomposition of blended polymer (PE or AL). Polymer blended PVA hydrogels were having PVA in less crystalline state; hence PVA blended hydrogels did not show prominent weight losses maxima corresponding to the decomposition of crystalline state in PVA.

DSC thermograms of PVA hydrogels have shown phase transition with a change in enthalpy ( $\Delta H_f$ ) of -29.6 J mg<sup>-1</sup> within a temperature range of 160 to 600°C (Fig. 2b and Table 3) due to the decomposition of crystalline compact structures of PVA in hydrogels, which was due to the presence of hydrogen bonding. The observed increasing trend in change in enthalpy ( $\Delta H_f$ ) in PVA hydrogels blended with polymers has suggested for the presence of strong interactions between PVA and blended polymers (PE or AL). On blending PVA with PE, the phase transition enthalpy ( $\Delta H_f$ ) was 37.2 Jmg<sup>-1</sup> and temperature range was also found to be more than pure PVA hydrogels (Fig. 2b and Table 3).

This result has clearly indicated that blended PE in PVA hydrogels has interacted more strongly with PVA

and had produced compact structures (Grillo *et al.*, 2012; Quinones *et al.*, 2010), which required more energy to overcome the forces of interactions between PVA and blended PE. However, the enthalpy of phase transition ( $\Delta H_f$ ) in PVA-AL hydrogels is found to be lower (18.5 J mg<sup>-1</sup>), which suggested for the presence of weaker intra and inter interactions between PVA and blended AL (Fig. 2b and Table 3). The blending of AL in PVA hydrogels has destroyed the crystalline structures of PVA in hydrogels and at the same time it did not provide stronger interactions with PVA like PE. The loading of agrochemicals (TBM or KNO<sub>3</sub>) in polymer blended PVA hydrogels (PVA-PE or PVA-AL) has also shown significant variation in thermal behavior of PVA hydrogels (Quinones *et al.*, 2010) as indicated by their thermal analysis as shown in Fig. 2a and Table 3. The results have indicated a decreasing trend in IDT (210°C) on addition of TBM but FDT was found to be higher (575°C) in comparison to PVA-PE hydrogels (Table 3). However, PVA-PE hydrogels loaded with TBM have shown a slight increase in their weight losses at 300 and 400°C in comparison to PVA-PE hydrogels (Fig. 2a). Since the mixing of TBM did not provide additional interactions in PVA-PE hydrogels; hence enthalpy of phase transition ( $\Delta H_f$ ) of PVA-PE hydrogels loaded with TBM was found to be lower (10.2 J mg<sup>-1</sup>) than pure PVA hydrogels and PVA-PE hydrogels (Fig. 2b and Table 3).

The thermal behavior of polymer blended PVA hydrogels after the release of loaded agrochemicals (TBM or KNO<sub>3</sub>) was also recorded as shown in Fig. 3 and Table 3. The results have indicated that IDT and FDT temperatures did not vary significantly after the release of loaded agrochemicals (Fig. 3a and Table 3). However, the enthalpy of phase transition ( $\Delta H_f$ ) in PVA-AL hydrogels has shown a significant decreasing trend after the release of loaded (Singh *et al.*, 2009) agrochemicals (TBM or KNO<sub>3</sub>) in comparison to enthalpy of transition ( $\Delta H_f$ ) of PVA-PE hydrogels after the release of loaded agrochemicals (Fig. 3b and Table 3). This has clearly indicated that PVA-AL hydrogels were having ionic interactions with loaded agrochemicals but after the release of loaded agrochemicals, the structure of PVA hydrogels became relatively more weaker (Zhang *et al.*, 2014a) than the structure of PVA-PE hydrogels resulted after the release of loaded agrochemicals (TBM or KNO<sub>3</sub>). Thus thermal studies of polymer blended PVA hydrogels before and after the release of loaded agrochemicals are found to be useful in predicting a relative stability and shelf life of PVA hydrogels in soils to maintain a sustain release of loaded chemicals.

#### *Degree of Swelling in PVA Hydrogel Microspheres*

The degree of swelling in hydrogels helps in controlling the loading and delivery of active components; hence evaluation of degree of swelling in polymer blended PVA hydrogel microspheres in solution of different pH was determined. The degree of swelling

of polymer blended PVA hydrogel microspheres was studied in buffer solutions at 4, 7 and 9 pH at room temperature. The solution pH was chosen corresponding to the soil pH of agricultural fields. The degree of swelling in polymer blended PVA hydrogel microspheres was determined at different time intervals using Equation 2 (Bortolin *et al.*, 2012; Grillo *et al.*, 2012). The PVA-PE hydrogel microspheres have shown maximum degree of swelling at pH 4 (Fig. 4). This was due to the formation of positive charge at the surface of hydrogel microspheres by the adsorption of protons, which caused more expansion of crystalline structures of PVA in favor of high degree of swelling (Quinones *et al.*, 2010).

The hydrogel microspheres on swelling have imbibed a large volume of water at pH 4 in comparison to hydrogel microspheres in neutral and alkaline media. Though prepared hydrogel microspheres have shown 200 %

degree of swelling within a period of 20 h at pH 4 but at pH 9 they were able to show maximum degree of swelling (100%) within a period of 48 h. In comparison to PVA-PE hydrogel microspheres, the degree of swelling was found to be more in PVA-AL hydrogel microspheres as shown in Fig. 5. The rate of swelling was also found to be more in PVA-AL hydrogel microspheres at all pH in comparison to PVA-PE hydrogel microspheres (Fig. 4 and 5).

Similarly, Both hydrogel microspheres never attained a maximum degree of swelling at pH 9 even if kept for a long time (Zhao and Wilkins, 2005). This was due to weaker interactions between AL and PVA and due to more hydrophilicity (Xu *et al.*, 2016) of AL in comparison to PE in PVA hydrogel microspheres. These factors helped in imbibing more amount of water within a short period in PVA-AL hydrogel microspheres than PVA-PE hydrogel microspheres within the studied range of solution pH.

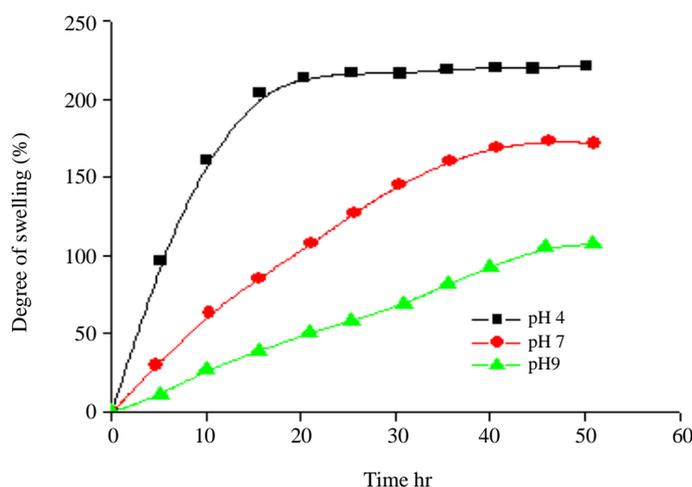


Fig. 4: Degree of swelling in PVA-PE hydrogel microspheres in solution of different pH

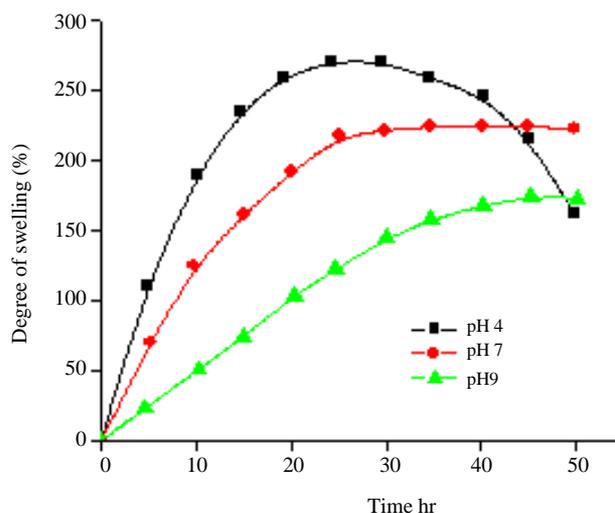


Fig. 5: Degree of swelling in PVA-AL hydrogel microspheres in solution of different pH

The PVA-AL hydrogel microspheres have shown maxima in degree of swelling after a contact time of 50 h at pH9. In comparison to PVA-PE hydrogel microspheres, the degree of swelling in PVA-AL hydrogel microspheres was relatively higher within the studied range of pH (Fig. 4 and 5). The degree of swelling in polymer blended PVA hydrogel microspheres was also studied at different temperatures at constant pH. To study the effect of temperature, the degree of swelling was studied in buffered solution maintained at 11, 25 and 45°C, which were selected according to the expected temperature of the seasons. The results have indicated that polymer blended PVA hydrogel microspheres have shown maximum degree of swelling at 45°C within a short time interval. However, polymer blended (PVA-AL or PVA-PE) hydrogel microspheres eroded on keeping for longer time at 45°C. The polymer blended (PVA-AL or PVA-PE) hydrogel microspheres have taken more time in showing maximum degree of swelling on keeping in buffered solution maintained at 11°C but were able to show maximum degree of swelling within a short time at 25°C on keeping in buffered solution. Thus PVA-AL hydrogel microspheres were found to be more suitable to use in low temperature control release applications whereas, PVA-PE hydrogel microspheres might be suitable to use at higher temperature without any variation in their structures. Since, the degree of swelling in PVA hydrogel microspheres has shown dependence on degree of cross-linking and on the presence of electrolytes in hydrogels (Hu *et al.*, 2016; Lu *et al.*, 2015); hence the degree of swelling in PVA hydrogel microspheres was also studied using PVA hydrogels prepared with different amount of glutaraldehyde and in PVA hydrogel microspheres prepared with fixed amount of NaCl (0.2 wt%) as additive. To study the effect of degree of cross-linking, the PVA hydrogel microspheres were prepared using 0.5 or 1.0 wt% of glutaraldehyde as cross-linker and blended polymers (AL or PE) were used as property modifier of PVA hydrogel microspheres. The PVA-PE hydrogel microspheres cross-linked with 0.5 wt% of glutaraldehyde were quite compact but shown swelling very slowly in comparison to PVA-AL hydrogel microspheres cross-linked with same amount of glutaraldehyde (0.5 wt%). This has indicated that 0.5 wt% of glutaraldehyde was optimum to prepare PVA-PE hydrogel microspheres with suitable degree of swelling but PVA-AL hydrogel microspheres needed high amount (1.0 wt %) of glutaraldehyde to produce hydrogel microspheres with suitable degree of swelling and cross-linking. The polymer (PE or AL) blended PVA hydrogel microspheres with small amount of NaCl (0.2 wt%) have shown significant variation in degree of swelling in comparison to polymer blended hydrogel microspheres without NaCl. The presence of NaCl in PVA hydrogel microspheres has controlled the degree of swelling due to the presence of osmotic pressure (Yan *et al.*, 2016) that allowed the transport of more amount of water in

PVA hydrogel microspheres from swelling media in comparison to hydrogel microspheres without NaCl.

### *Loading of Agrochemicals in PVA Hydrogel Microspheres*

The maximum percent loading capacity ( $L_{max}$ ) of prepared PVA hydrogel microspheres for agrochemical as a function of solution pH, loading time and degree of cross-linking was evaluated using Eqn. 3. The PVA-PE hydrogel microspheres cross-linked with 0.5 wt% of glutaraldehyde (Wanyika, 2013) have shown maximum loading capacity ( $L_{max}$ ) as 77 and 74% for KNO<sub>3</sub> and TBM respectively at pH 4 within a contact time of 30 h. However, PVA-PE hydrogel microspheres were able to show this maximum loading capacity (~77%) for KNO<sub>3</sub> within a contact time of 20 h at pH 7. This has indicated that swelling behavior of PVA-PE hydrogel microspheres and ionic state of KNO<sub>3</sub> have influenced the loading of KNO<sub>3</sub>. At pH 7, the diffusion of KNO<sub>3</sub> in PVA-PE hydrogel microspheres was high in comparison to pH 4; hence pH 7 was suitable to achieve maximum loading of KNO<sub>3</sub> in PVA-PE hydrogel microspheres within a time interval of 20 h. On the other hand, the maximum loading capacity for TBM was achieved in more than 30h at pH 4 in PVA-PE hydrogel microspheres cross-linked with 0.5 wt% of glutaraldehyde. This has indicated that TBM was able to form diffusible ionic species in acidic medium (pH 4) in contrast to KNO<sub>3</sub>, which was able to form diffusible ionic species at pH 7. The maximum loading behavior of PVA-AL hydrogel microspheres was found to be different than PVA-PE hydrogel microspheres. The PVA-AL hydrogel microspheres cross-linked with glutaraldehyde have shown maximum loading capacities (% $L_{max}$ ) for TBM and KNO<sub>3</sub> as 79 and 82% respectively. However, this maximum loading capacity for TBM (79%) was achieved when PVA-AL hydrogel microspheres were cross-linked with 0.5 wt% solution of glutaraldehyde and placed in a loading solution for 25 h at pH 4. Similarly, the maximum loading capacity for KNO<sub>3</sub> (82%) was achieved when PVA-AL hydrogel microspheres were cross-linked with 1.0 wt% solution of glutaraldehyde and placed in a loading solution for 15 h at pH 7. These variation in loading capacity has indicated that the nature of loaded agrochemical has a significant effects on the maximum loading capacity of PVA-PE hydrogel microspheres, where ionic nature of KNO<sub>3</sub> would help it to diffuse inside the swollen microspheres and easily hydrolyzed in neutral loading solution at pH 7 within a short time interval of 20 h. On the other hand, TBM needs acidic loading medium (pH 4) for hydrolysis and need a long time (30h) to reach a maximum loading capacity in PVA-PE hydrogel microspheres. Similarly, the type of delivery systems (Yang *et al.*, 2014) also have a significant effects on maximum loading capacity, where PVA-AL hydrogel microspheres have shown different optimized loading conditions for agrochemical

than PVA-PE hydrogel microspheres. Considering these trends, the contact time and solution pH were optimized for the loading and release of  $\text{KNO}_3$  and TBM in polymer blended PVA hydrogel microspheres having different degree of cross-linking.

#### *Controlled Release of Loaded Agrochemicals*

The release behavior of prepared PVA hydrogel microspheres was studied under different experimental conditions to determine the factors that played a significant role in release kinetics of loaded agrochemicals. To analyze the release behavior of PVA hydrogel microspheres (Equation 4), the released quantity of loaded agrochemicals was expressed (Roy *et al.*, 2014) as cumulative release ( $\%R_{cum}$ ) for a fixed time interval of 5h from a fixed quantity (100 mg) of PVA hydrogel microspheres loaded to their maximum capacities. The release behavior of PVA hydrogel microspheres was studied under different experimental conditions such as at different solution pH, temperature and by using PVA hydrogel microspheres with different degree of cross-linking.

#### *Effect of Solution pH on Controlled Release of Agrochemicals*

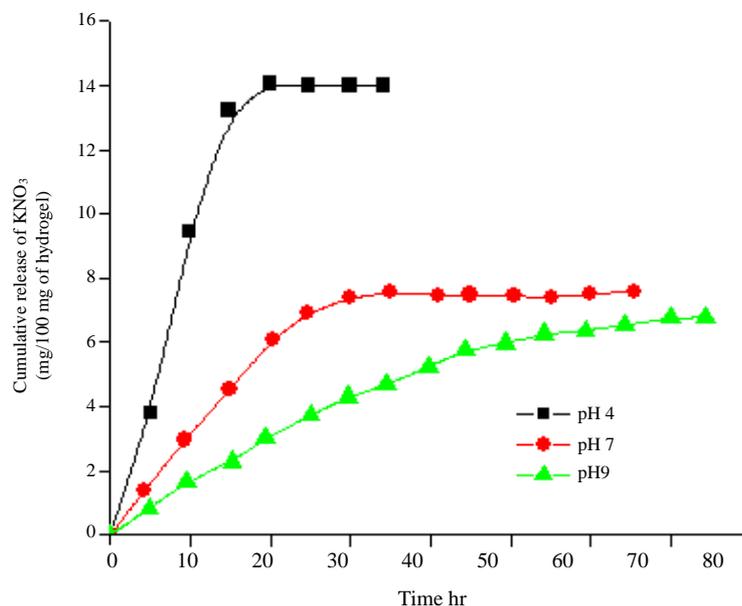
The pH of release solution has shown a significant effect on controlled release of loaded  $\text{KNO}_3$  or TBM from polymer blended PVA hydrogel microspheres. The polymer blended PVA hydrogel microspheres, which were having 0.2 wt% of NaCl and optimum amount of glutaraldehyde have shown improved release behavior of loaded agrochemicals in comparison to polymer blended PVA hydrogel microspheres without NaCl or cross-linked with different amount of glutaraldehyde. To analyze the release pattern of polymer blended PVA hydrogel microspheres, the polymer blended PVA hydrogel microspheres loaded with maximum amount of agrochemicals were used at fixed temperature of 25°C. Results have indicated that release pattern was influenced significantly with the type of PVA hydrogel microspheres and with the properties of loaded agrochemicals ( $\text{KNO}_3$  or TBM). The release behavior of  $\text{KNO}_3$  from PVA-AL hydrogel microspheres cross-linked with 1.0 wt% of glutaraldehyde has been studied as a function of solution pH as shown in Fig. 6.

The release of  $\text{KNO}_3$  from PVA-AL hydrogel microspheres within a initial period of 20 h was found to be a burst release at pH 4 but in solution at pH 7, the release of  $\text{KNO}_3$  from PVA-AL hydrogel microspheres was found to be a sustain release for a period of about 50 h without initial burst release of  $\text{KNO}_3$  as was found at pH 4 (Fig. 6). The PVA-AL hydrogel microspheres at pH 9 have shown a reduced and incremental release of loaded  $\text{KNO}_3$  but did not show noticeable controlled and sustained release of  $\text{KNO}_3$ . This trend was due to the enhanced degree of swelling and relaxation in polymer chains on surface protonation at pH 4, which caused a

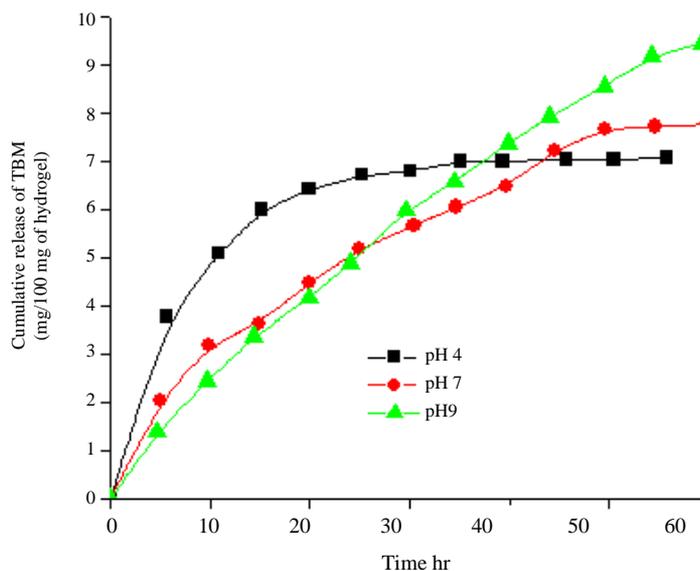
burst release of loaded  $\text{KNO}_3$ . On the other hand, the polymer chains were highly shrunk and compacted (Grillo *et al.*, 2012; Quinones *et al.*, 2010) in solution at pH 9, which retarded the release of loaded  $\text{KNO}_3$  from PVA-AL hydrogel microspheres, hence PVA-AL hydrogel microspheres at pH 9 have shown a slow and incremental increase in release of  $\text{KNO}_3$  without any sustain period of controlled release at pH 7 (Fig. 6). The release behavior is also found to be dependant on the type of loaded agrochemicals; hence the release of  $\text{KNO}_3$  was different in presence of NaCl than in PVA-AL hydrogel microspheres without added NaCl. The presence of NaCl has influenced the swelling in PVA-AL hydrogel microspheres and also controlled the ionization of  $\text{KNO}_3$ , which ultimately influenced the release rate of  $\text{KNO}_3$  from PVA-AL hydrogel microspheres at pH 7. However, the presence of NaCl in PVA-AL hydrogel microspheres has affected the release pattern for TBM due to enhanced hydrogen bonding between TBM and PVA-AL hydrogel in microspheres in presence of NaCl (Raafat *et al.*, 2012; Zhao and Wilkins, 2005). Thus the nature of loaded agrochemical (Bortolin *et al.*, 2012) has also played a significant role in controlling its release behavior from PVA-AL hydrogel microspheres at fixed pH.

To analyze the effect of type of polymer on controlled release of loaded agrochemicals, the release behavior of  $\text{KNO}_3$  or TBM from PVA-PE hydrogel microspheres was also studied in solution of different pH as shown in Fig. 7. The PVA-PE hydrogel microspheres have shown a significant sustained release of TBM at pH 4 in comparison to solution at pH 7 or pH 9.

This can be explained considering the compactness (Grillo *et al.*, 2012; Quinones *et al.*, 2010) in PVA-PE hydrogel microspheres, which were needing acidic medium to achieve sufficient swelling and relaxation in large sized pectin chains to show significant sustain release of loaded TBM as was shown by PVA-PE hydrogel microspheres. The PVA-PE hydrogel microspheres in solution of pH 7 or pH 9 have shown slow and uncontrolled release of loaded TBM without a significant period of sustained release as was observed in solution of pH 4 (Fig. 7). The PVA-PE hydrogel microspheres were able to show better sustained release of  $\text{KNO}_3$  than TBM because added NaCl was quite effective in controlling the degree of swelling in PVA-PE hydrogel microspheres as well as in controlling the degree of ionization of  $\text{KNO}_3$ . This has clearly suggested that the state and interactions of loaded agrochemicals in PVA hydrogel microspheres have also influenced their release behavior as was influenced by solution pH. The release rate of TBM from PVA-PE hydrogel microspheres was found to be slower as it was able to form more hydrogen bonding with PVA hydrogels in microspheres than  $\text{KNO}_3$ . However, the release rate of  $\text{KNO}_3$  from PVA-PE hydrogel microspheres was influenced by the added NaCl due to variation in degree of ionization of  $\text{KNO}_3$  in presence of NaCl.



**Fig. 6:** Release behavior of KNO<sub>3</sub> from PVA-AL hydrogel microspheres having NaCl (0.2 wt%) as additive and cross-linked with 1.0 wt % of glutaraldehyde at 25°C in solution of different pH



**Fig. 7:** Release behavior of TBM from PVA-PE hydrogel microspheres having NaCl (0.2 wt%) as additive and cross-linked with 0.5 wt % of glutaraldehyde at 25°C in solution of different pH

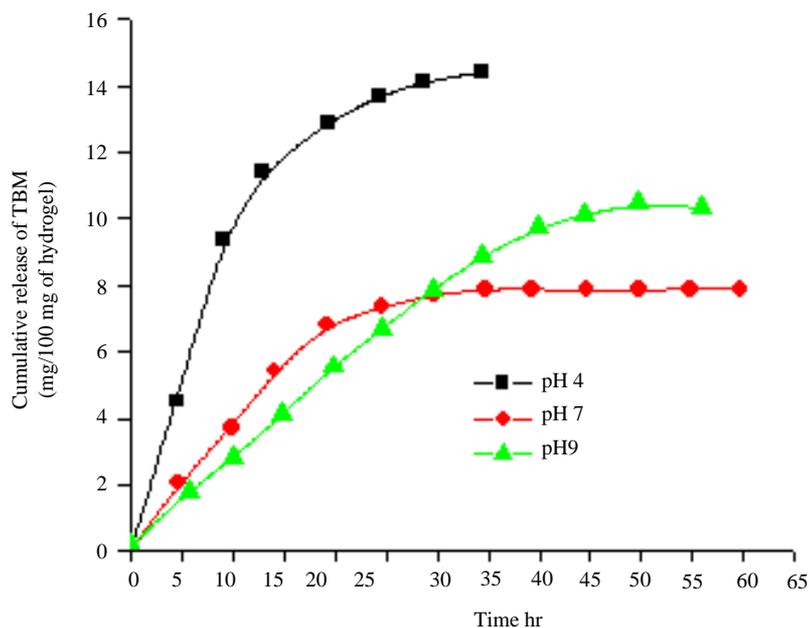
### Effect of Solution Temperature On Controlled Release of Agrochemicals

The release studies were also carried out by keeping agrochemicals (KNO<sub>3</sub> or TBM) loaded PVA hydrogel microspheres in solution maintained at different temperatures (11, 25 and 45°C). Results have indicated that the release of loaded agrochemicals was better in a medium at 25°C than at other temperatures (Bortolin *et al.*, 2012). This trend was found to be same irrespective

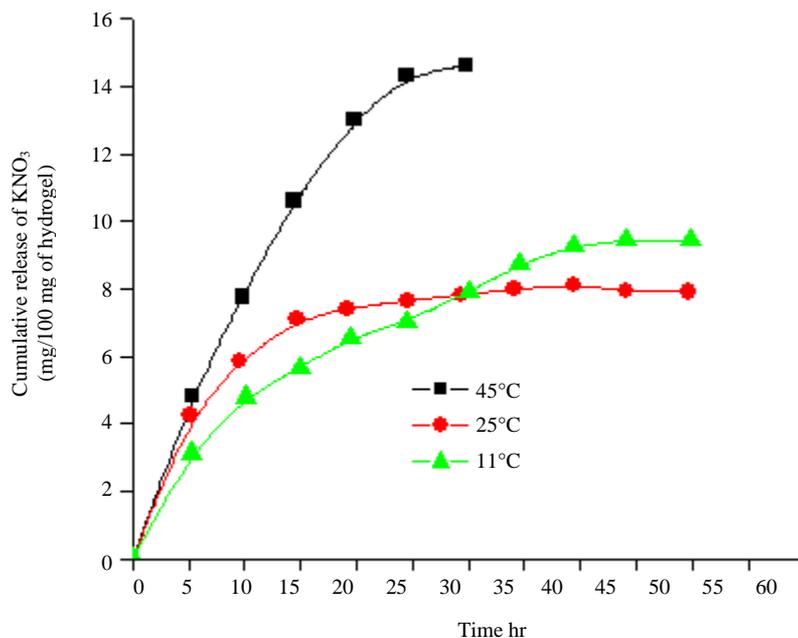
of the type of PVA hydrogels in microspheres (PVA-AL or PVA-PE) or the type of loaded agrochemicals (KNO<sub>3</sub> or TBM) as shown in Fig. 8 and 9. At high temperature (45°C), the enhanced degree of swelling in PVA hydrogel microspheres has caused a burst release of loaded agrochemicals within a period of 10-15 h without having a significant period of sustained release (Fig. 8). However, at low temperature (11°C), the degree of swelling in PVA hydrogel microspheres was low, which did not allow the release of loaded

agrochemicals in a controlled and sustained manner. But at 25°C, the degree of swelling in PVA hydrogel microspheres had become optimum within a period of 15 h and then remain constant, which supported a sustain release of loaded agrochemicals for a significant period of 50h from polymer blended PVA hydrogel microspheres (Fig. 8 and 9). At low temperature (11°C),

the PVA-PE hydrogel microspheres have shown relatively a lower cumulative release of agrochemicals (Fig. 9) than from PVA-AL hydrogel microspheres (Fig. 8). This variation in cumulative release of loaded agrochemicals might be due to the higher degree of swelling in PVA-AL hydrogel microspheres than PVA-PE hydrogel microspheres.



**Fig. 8:** Release behavior of TBM from PVA-AL hydrogel microspheres with NaCl (0.2 wt%) and cross-linked with 1.0 wt% glutaraldehyde at pH 7 and in release medium maintained at different temperatures



**Fig. 9:** Release behavior of KNO<sub>3</sub> from PVA-PE hydrogel microspheres with NaCl (0.2 wt%) and cross-linked with 0.5 wt% glutaraldehyde at pH 4 and in release medium maintained at different temperatures

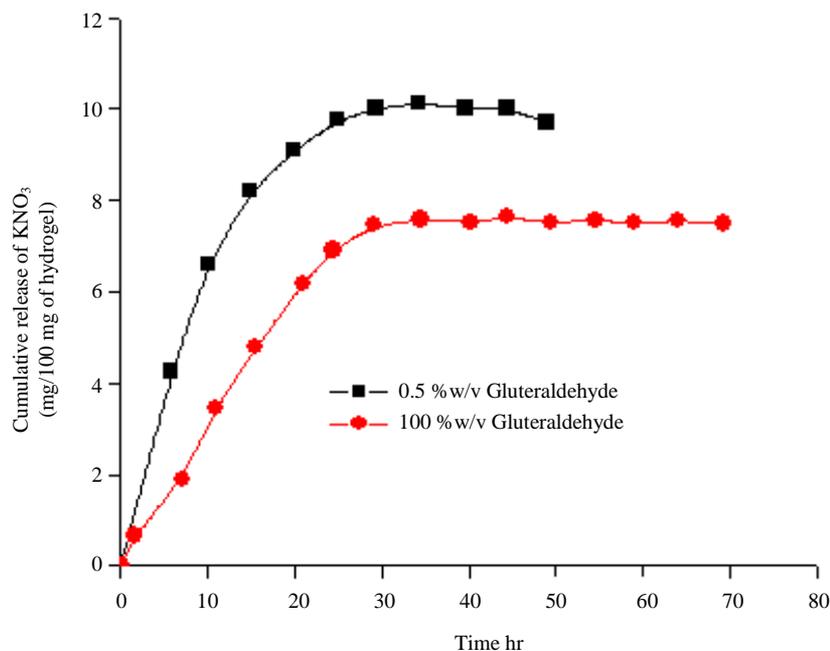
The temperature controlled release pattern of loaded agrochemicals from PVA hydrogel microspheres was found to be slightly dependant on the type of loaded agrochemicals (Bortolin *et al.*, 2012). The release behavior of  $\text{KNO}_3$  was found to be better (Zhang *et al.*, 2014b) in comparison to TBM at low temperature (Fig. 9) but at high temperature ( $45^\circ\text{C}$ ), the release of  $\text{KNO}_3$  was found to be more sustained in PVA-PE hydrogel microspheres (Fig. 9) than the release of TBM from PVA-AL hydrogel microspheres (Fig. 8). This was due to the difference in interactions of  $\text{KNO}_3$  with PE in PVA-PE hydrogel microspheres than the interactions of TBM with AL in PVA-AL hydrogel microspheres (Fig. 8) at  $45^\circ\text{C}$ . These studies have suggested that polymer-agrochemicals interactions may be optimized by controlling the temperature to enhance the period of sustain and controlled release of loaded agrochemicals.

#### *Effect of Cross-Linking on Controlled Release of Agrochemicals*

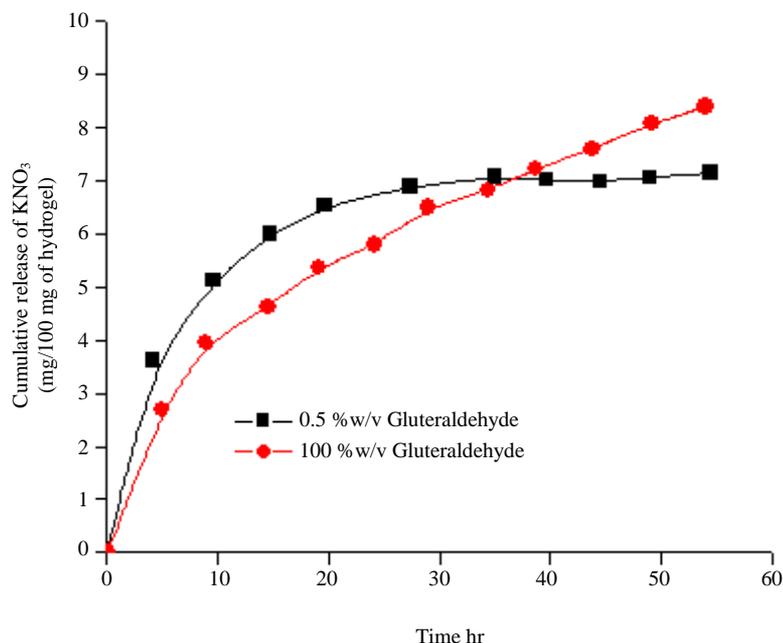
The effect of degree of cross-linking (Isiklan, 2007) on controlled release of loaded agrochemicals ( $\text{KNO}_3$  or TBM) was also studied by using maximum agrochemicals loaded polymer blended PVA hydrogel microspheres prepared using different amount of glutaraldehyde (0.5 and 1.0 wt%). The PVA-AL hydrogel microspheres cross-linked with 1.0 wt% of glutaraldehyde have shown enhanced period of

sustained release of agrochemicals ( $\text{KNO}_3$  or TBM) as indicated in Fig 10. The PVA-AL hydrogel microspheres prepared with 0.5 wt% of glutaraldehyde have shown high degree of swelling, which allowed a large proportion of loaded agrochemical ( $\text{KNO}_3$ ) to release in burst manner than sustained release manner (Fig. 10). The PVA-AL hydrogel microspheres cross-linked with 1.0 wt% of glutaraldehyde have shown better controlled release of  $\text{KNO}_3$  than TBM. This difference in controlled release of agrochemicals ( $\text{KNO}_3$  and TBM) was due to the difference in ionic state of  $\text{KNO}_3$  and hydrogen bonding of TBM with PVA hydrogels in microspheres (Roy *et al.*, 2014).

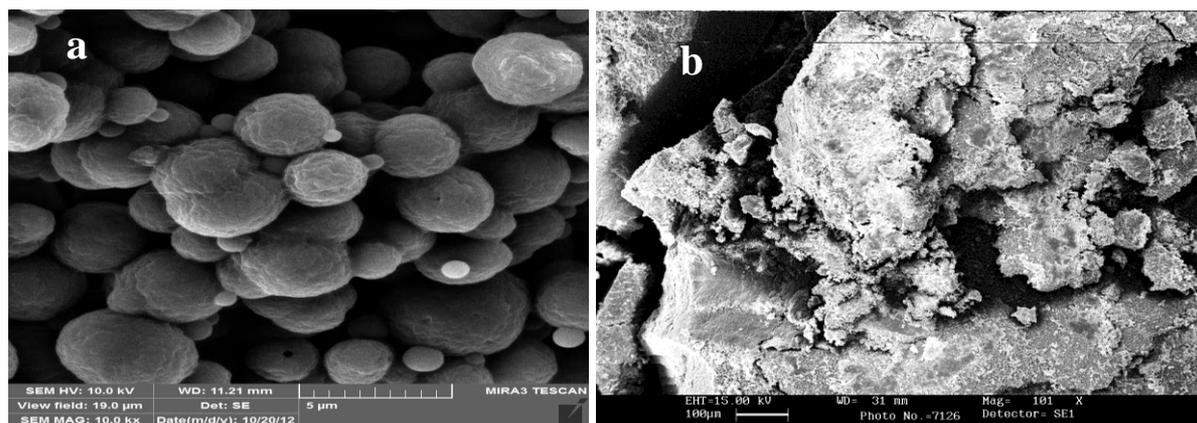
The effect of degree of cross-linking in PVA-PE hydrogel microspheres on control release of TBM was also studied to identify the effect of type of PVA hydrogel microspheres as well as on degree of cross-linking. Considering the properties of PVA-PE hydrogel microspheres, the release behavior of TBM was studied in solution at pH 4 and also using TBM loaded PVA-PE hydrogel microspheres with different degree of cross-linking (Fig. 11). The PVA-PE hydrogel microspheres, cross-linked with 0.5 wt% of glutaraldehyde have shown a large period of sustained release of TBM (Fig. 11) as similar to  $\text{KNO}_3$  in PVA-AL hydrogel microspheres (Fig. 10). However, PVA-PE hydrogel microspheres with 1.0 wt% cross-linking of glutaraldehyde did not show any remarkable period of sustain release of TBM.



**Fig. 10:** Release behavior of  $\text{KNO}_3$  from PVA-AL hydrogel microspheres with NaCl (0.2 wt%) and different degree of cross-linking when placed in solution at pH 7 at  $25^\circ\text{C}$



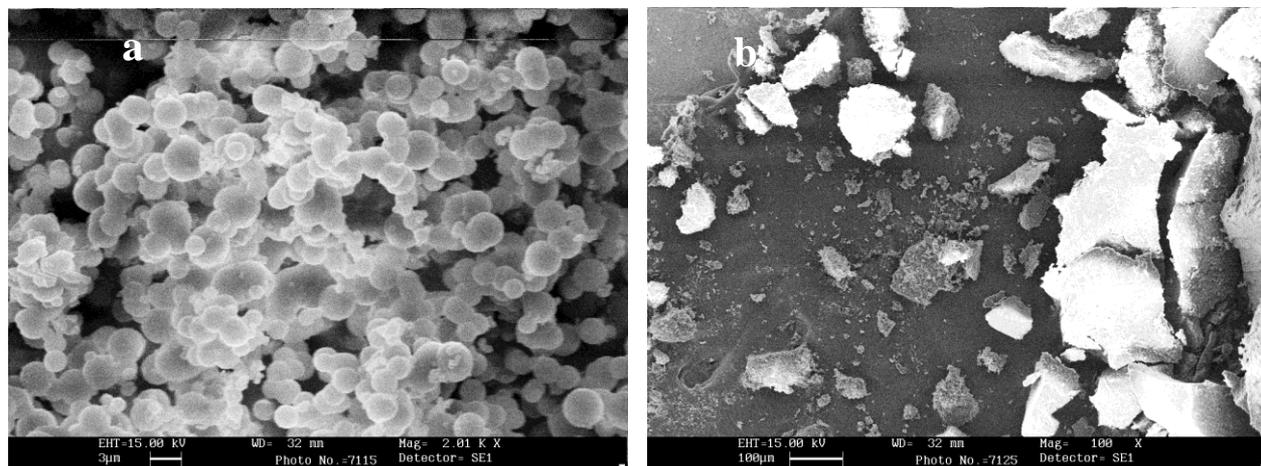
**Fig. 11:** Release behavior of TBM from PVA-PE hydrogel microspheres with NaCl (0.2 wt%) and different degree of cross-linking when placed in solution at pH 4 at 25°C



**Fig. 12:** SEM images of agrochemical loaded PVA-AL hydrogel microspheres (a) and after the release of loaded agrochemicals (b)

This was due to a slow and continuous increase in degree of swelling in PVA-PE hydrogel microspheres cross-linked with 1.0 wt% of glutaraldehyde (Fig. 11). This incremental increase in degree of swelling in PVA-PE hydrogel microspheres cross-linked with 1.0 wt% of glutaraldehyde has caused a uncontrolled release of loaded TBM (Fig.11). These studies have clearly indicated that PVA-AL hydrogel microspheres cross-linked with 1.0 wt% of glutaraldehyde, were able to release loaded  $\text{KNO}_3$  in a sustained manner (Fig. 10), whereas PVA-PE hydrogel microspheres cross-linked with 0.5 wt% of glutaraldehyde were able to show better sustained release of TBM. This variation in degree of cross-linking in PVA hydrogel microspheres was found useful to optimize the properties of PVA hydrogel microspheres to achieve a better sustain release of loaded agrochemicals.

The porous and folded morphology of PVA-AL hydrogel microspheres (Fig.12a) have helped in maximum loading of agrochemicals within the core and at their surfaces (Kamoun *et al.*, 2015). The cracked morphology of dried PVA-AL hydrogel microspheres after the release of loaded agrochemicals has suggested for polymer degradation during the release process (Fig.12b). This has indicated that the release of loaded agrochemicals was also supported by the degradation of PVA hydrogels in release medium. The SEM images of agrochemicals loaded PVA-PE hydrogel microspheres have indicated that PVA-PE hydrogel microspheres were also in spherical shape with an average diameter of 1  $\mu\text{m}$  and with smooth morphology (Fig.13a).



**Fig. 13:** SEM images of agrochemical loaded PVA-PE hydrogel microspheres (a) and after the release of loaded agrochemicals (b)

In comparison to PVA-AL hydrogel microspheres, the PVA-PE hydrogel microspheres were found to be clustered and aggregated due to having more interfacial area for adhesion than PVA-AL hydrogel microspheres. In contrast to PVA-AL hydrogel microspheres, the surface morphology of PV-PEA hydrogel microspheres was quite smooth without prominent folding and porous structures. This difference in surface morphology of PVA-PE hydrogel microspheres was largely due to the formation of compact and smaller sized microspheres by the blended PE in PVA. The SEM images of dried PVA-PE hydrogel microspheres after the release of loaded agrochemicals have shown enhanced brittleness, which was due to formation of residual empty reservoirs at their surfaces (Fig.13b). The enhanced brittleness in PVA-PE hydrogel microspheres after the release of loaded agrochemicals has further indicated that polymer degradation had taken place in PVA hydrogels during the release of loaded agrochemicals.

## Conclusion

The PVA based hydrogels were prepared successfully by blending a suitable amount of naturally occurring Pectin (PE) or Alginate (AL) polymers. The cross-linking in PVA hydrogels was controlled by adding difference amount of glutaraldehyde. The prepared hydrogels were characterized for thermal stability by TGA and DSC analysis and structural information of polymer blended PVA hydrogels was obtained by recording their FT-IR spectra. To evaluate the properties of polymer blended PVA hydrogels as a carrier for controlled release of agrochemicals, the prepared polymer blended PVA hydrogels were loaded with two model agrochemicals ( $\text{KNO}_3$  or TBM), which are commonly used by farmers in agricultural applications.

The loading and release behavior of these model agrochemicals was explained on the basis of variation in degree of swelling in polymer blended PVA hydrogels in solution of different pH and on the basis of ionic state of  $\text{KNO}_3$  in presence of added NaCl (0.2 wt%). The role of hydrogen bonding between TBM and PVA was also discussed to explain the maximum loading and release profile of TBM from PVA-PE hydrogel microspheres. The PVA-AL hydrogel microspheres have shown better sustained release at pH 7, whereas PE blended PVA hydrogel microspheres have shown better sustained release of TBM at pH 4. The PVA-AL hydrogel microspheres were slightly larger in size in comparison to PVA-PE hydrogel microspheres. The release behavior of loaded agrochemicals has also shown dependence on the properties of loaded agrochemicals. Thus present studies were found to be useful to prepare controlled release formulations for the application of fertilizers, herbicides and insecticides in agricultural fields to enhance the productivity of the crops without wasting chemicals and causing environmental pollution.

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## Author's Contributions

**Fawzi Habeeb Jabrail:** Contributed in analysis, discussing and interpreting of the data. He also participated in writing and checking of final review of the draft.

**Wajeih Mohammed Jamil:** Contributed in collection of literature and for carrying out experimental work.

**Maher Zeki Elsabee:** Contributed in checking of write up and reorganization of the draft.

**Kailash Chandra Gupta:** Contributed in collection of thermal data and in improving the discussion of the results.

## Ethics

This article is original and contains unpublished material. The corresponding author confirms that all of the other authors have read and approved the manuscript and no ethical issues involved.

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