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Development of a controlled release formulation based on a starch matrix system

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Abstract

Controlled release formulation (CRF) of the insecticide acetamiprid was made using tapioca starch, urea and sodium borate. The data show the recovery of this CRF process is >95.43%, there is no obvious difference with increase of sodium borate added, however, with the increase of urea in the mixture, the formulation has a decrease recovery. In stability test, the decomposition rate of acetamiprid CRF was less one tenth than that of the acetamiprid emulsifiable concentrate (EC) under UV radiation. The release kinetics of acetamiprid from granules with variation content of urea, sodium borate and granule sizes were evaluated in water under laboratory condition. The release data were fitted to the generalized model $M_t/M_z = kt^n$, where M_t/M_z is the percentage of insecticide released at time t, k and n are constants, and n is constant that indicates the mechanism of release. The results indicated that the release of acetamiprid was diffusion-controlled. The time taken for 50% of the active ingredient to be released into water, T_{50}, was also calculated for the comparison of formulations. The results showed that the formulation with the increasing urea in formulation had the higher value of T_{50}, which means a slower release of the active ingredient, while that the formulation with the increasing sodium borate in formulation had the lower value of T_{50}, which means a faster release of the active ingredient. It was also found that as the size of this formulation decreased, the release of the active ingredient was faster.
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Keywords: Acetamiprid; Controlled release formulation; Tapioca starch; Stability; Kinetics

1. Introduction

Pesticides are employed in agriculture to improve crop yields by controlling pests such as weeds, insects, nematodes and fungi that attack plants and transmit diseases. Pesticides, however, require repeated application at targeted sites during the growing season to replace losses due to volatilization, leaching and degradation. Repeated pesticide application, it is undesirable because of high costs and possible phytotoxicity, and because certain pesticides are well known environmental pollutants. Various pesticide compositions and meth-

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ods for preparing them have been developed in attempt to enhance pesticide efficacy so that less pesticide may be used and to reduce the need for repeated application. Exemplary of such compositions include controlled release formulations (CRFs) which have become increasingly popular due to safe handling and ease of application.

CRFs have the potential to reduce the environmental problems associated with the application of pesticides. The use of CRFs can, in many cases, supply the active ingredient (a.i.) at the required rate for pest control while decreasing the total amount of chemical needed, thereby decreasing the risk to the environment, savings in manpower and energy by reducing the number of applications required in comparison to conventional formulations, increased safety for the farmer or pesticide applicator, and a general decrease in nontarget effects (Schreiber et al., 1993). The use of biodegradable polymers in CRFs is one area which is expected to grow in the future (Wilkins, 1990). Much of the work carried out to date on agricultural CRFs has concentrated on devices using substrates such as starch, bentonite, kraft lignin, and alginate. Mehltretter et al. (1974) studied the release of 2,4-D from several starch formulations and found them to exhibit desirable release rates. Boydston (1992) found reduced leaching of norflurazon and simazine in soil columns when they were applied in starch-based granules as compared to the other commercial products. Gish et al. (1994) and Schreiber et al. (1993) have also shown that these formulations are beneficial in that they significantly reduce atrazine leaching, and the greenhouse and field test of starch-based CRFs have been summarized by Schreiber et al. Starch is a naturally occurring biodegradable material, which is readily available, is inexpensive, and has shown promise in the area of pesticide formulations (Shasha et al., 1976, 1981, 1984; Trimnell and Shasha, 1990). Urea was used as one of additives in these study, additives not only improve the properties of the formulations but also affect the release kinetics. Urea is also a good fertilizer, inexpensive, and environmentally safe. The starch and urea can form urea-starch polymer in the presence of sodium borate (Yun, 1990; Wang and Wu, 2003), this polymer as matrix of formulation provide timed release of the active ingredient.

Acetamiprid ((E)-*N*-[(6-chloro-3-pyridinyl)methyl]-*N*-cyano-*N*-methylethanimidamide $C_{10}H_{11}ClN_4$) is a new insecticide. Besides contact, stomach poisoning, it has strong osmotic and systemic action. With the special active mechanism, it can kill those insects which have resistance to organphosphorus and other insecticides. It can be used on vegetables, melon plants, fruit trees, wheat, tobacco, murphy, tea, cotton, etc. to control sucking insects including aphids, leafhoppers, leafminer moth, fruit moth, thrips, whiteflies, termites, and some beetle species, such as colorado potato beetle. It is used as seed dressing, soil treatment, and foliar treatment in different crops (Tomlin, 1999). This insecticide is widely applied in China, normally used as emulsifiable concentrates (EC), seed treatments and wettable powders.

The present study provides an improved CRF comprising a pesticide which is alkali-sensitive or high temperature-sensitive encapsulated in a polymer matrix of starch–borate–urea, and also provides a method for preparing the CRF so that pesticide release rate and release period can be adjustable. The objective of the work was to gain a better understanding of the release mechanism of the acetamiprid CRF. The effect on the release rates of acetamiprid with the addition of urea, sodium borate and different granules size were investigated.

2. Materials and methods

2.1. Chemicals

The starch was a commercially available tapioca starch (85.5%, Zhongshan food factory, Guangxi, China). Urea, sodium borate were lab reagent grade. Methanol was chromatograph reagent (Shanghai experiment reagent Co. Ltd., China). Technical grade acetamiprid (98.5%) and its standard (99.6%) were friendly supplied by Sanonda Zhengzhou Pesticide Co. Ltd. (Henan, China). Acetamiprid molecular formula and selected properties are as follows (Tomlin, 1999): molecular formula, $C_{10}H_{11}ClN_4$; molecular weight, 222.68; melting point, 98.9 °C; vapor pressure (20 °C), 1×10^{-8} mmHg; water solubility (25 °C), distilled Water, pH 5, 7, 9 are, respectively, 4.25, 3.48, 2.95, 3.96 gL^{-1}; octanol/water partition coefficient, $K_{ow} = 6.27$; the structure is shown in Fig. 1.

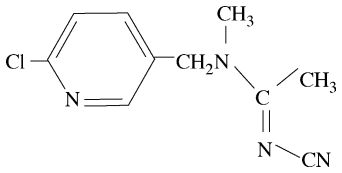

Fig. 1. The structure of acetamiprid.

2.2. Instrument

Model JB-10 high-speed blender (Chongqing degold science and technology Co. Ltd., China); Model 1200 ultrasonic bath, Model CHM hammer mill (Shanghai machinery and instruments Co. Ltd., China); Model SY serials wire mesh sieve (Anping county wire and wire mesh factory, Hebei, China); High performance liquid chromatograph LC-10A (Shimadzu, Japan). BH-2 Olympus microscope with digital camera (Olympus, USA); 36W UV germicidal lamp (Philips lighting company, USA).

2.3. Preparations process

The controlled release pesticide formulation are manufactured by admixing tapioca starch powder, acetamiprid, urea and water in suitable ratios and dispersing the mixture with high-speed (1200 rpm) blender at a temperature ranging between 60 and 80 °C, for about 10–15 min to gelatinize the starch and to thoroughly and uniformly disperse the pesticide in the gelatinized starch. Sodium borate is then mixed into the gelatinized mixture to convert the mixture into a rubbery mass. The rubbery mass is then ground, under high-speed blender or hammer mill and in the presence of additional starch powder, into small starch-coated granules. The resultant starch-coated particles have a particle size ranging between about 0 and 2.83 mm. These particles are subsequently dried at a temperature about 40–50 °C, the drying process is performed for a period of time about 20 h to reduce the water content of the particles to less than 10 wt.%.

In this study, the granules were formed by mixing the tapioca starch, acetamiprid, urea, water and sodium borate in different ratios (Table 1). On cooling, the glassy matrixes were crushed in a hammer mill or blended and then sieved to obtain same size granules (1.0–1.68 mm). A code for the formulations was used, ASBU[M] where A represents the active ingredient (acetamiprid), B is the mount of sodium borate, S is the tapioca starch, U is the urea added in the formulation (w/w), and M represents the size range (mm). In order to examine how does the granules size affect the release rate of the CRF, formulation ASB_5U_{20} was crushed in a hammer mill and sieved to obtain different granules of size: 0–0.50, 0.50–1.00, 1.00–1.68, 1.68–2.83 mm.

2.4. Analysis of acetamiprid in the granules

Granules (100 mg) were treated with methanol (25 mL) in an ultrasonic bath for 10 min. This led to the complete disintegration of the granules. After standing for 24 h at room temperature, the mixture was sonicated for a further 10 min and then filtered quantitatively through a syringe filter (0.2 μm). The volume was then made up to 50 mL with methanol, and the resulting solution was then diluted 1:4 with methanol and analyzed for the acetamiprid using HPLC. Three replicates were carried out for each formulation.

Table 1
Different composition of acetamiprid CRF

Component (g)	Acetamiprid	Water	Urea	The first starch for gelatinization	Sodium borate	The second starch for grinding
ASB_5U_0	12	70	0	50	5	60
ASB_5U_{10}	12	70	10	50	5	50
ASB_5U_{15}	12	70	15	50	5	50
ASB_5U_{20}	12	70	20	50	5	50
ASB_5U_{25}	12	70	25	50	5	50
ASB_0U_{20}	12	70	20	50	0	60
$ASB_{2.5}U_{20}$	12	70	20	50	2.5	50
$ASB_{7.5}U_{20}$	12	70	20	50	7.5	50
$ASB_{10}U_{20}$	12	70	20	50	10	50

2.5. HPLC analysis

The aqueous samples from the static immersion tests and the methanol extracts of the pesticide matrices were analyzed using a reverse phase column (Spherisorb ODS, 220 mm × 4.6 mm, 5 μm packing) and detection on a variable wavelength UV detector at 254 nm. A flow rate of 1 mL min^{-1} was used, with a mobile phase composition of methanol and water (60:40), injecting volume 10 μL.

2.6. Stability test

CRF granules (50 g) were packed in glass tube and stored at 40, 50, 60 °C for a period of 60 d, then analyze the active ingredient changes; stability against UV radiation was assayed by exposing samples to a 36 W germicidal lamp (254 nm) at a distance of 20 cm about 48 h, then analyze the active ingredient changes, the 3% acetamiprid emulsifiable concentrates was tested as a control in the same time.

2.7. CRF structure under microscope

The acetamiprid CRF granules were carefully cut to expose the crosssection without deformation of the granules, the structure of the granules were observed with various magnification under Olympus BH-2 microscope.

2.8. Static immersion tests

Granules (1 g) were immersed in double-distilled water (300 mL, pH 5.5–6.5) at room temperature, with three replicates for each formulation. Samples were taken for analysis by HPLC every day for the first week, after 7 d, and then every week thereafter. After each sampling time the water was replaced with fresh water to maintain sink conditions.

2.9. Treatment of data from release studies

The release data was analyzed by applying the empirical equation proposed by Ritger and Peppas (1987).

$$\frac{M_t}{M_z} = kt^n$$

where M_t/M_z is the percentage of active ingredient released at time t; k, the constant that incorporates characteristics of the macromolecular network system and the active ingredient; and n, the diffusion parameter that is indicative of the transport mechanism. All the experiments were done in triplicate plates.

3. Results and discussion

3.1. The acetamiprid recovery of the process

A suspension of tapioca starch powder, acetamiprid and urea in water was formed and gelatinized by high-speed agitating blender at a temperature ranging between 60 and 80 °C for 10 min, with the addition of sodium borate, the gelatinized mixture was convert into a rubbery mass, therefore acetamiprid was encapsulated into rubbery mass in the presence of additional starch powder. Table 2 shows the total of acetamiprid added in the initial mixture, extracted from granules and the recovery of the process. The data show the recovery of this CRF process is >95.43%, there is no obvious difference with increase of sodium borate added, and with the increase of urea in the mixture, the formulation has a decrease recovery. Table 2 shows that the losses of the acetamiprid on formulating with starch, urea, sodium borate and water were relatively low, between 1.18% and 4.57%. Losses of acetamiprid are ascribed to the evaporation, degradation, or hydrolysis of the acetamiprid on heating with other additives. It may be ascribed the encapsulated acetamiprid to be incompletely extracted.

Table 2
The acetamiprid recovery of the preparations process

Formulation	Added (g)	Extracted (g)	Recovery (%)
ASB_5U_0	11.82	11.68	98.82
ASB_5U_{10}	11.82	11.61	98.22
ASB_5U_{15}	11.82	11.55	97.71
ASB_5U_{20}	11.82	11.44	96.78
ASB_5U_{25}	11.82	11.28	95.43
ASB_0U_{20}	11.82	11.63	98.39
$ASB_{2.5}U_{20}$	11.82	11.36	96.11
$ASB_{7.5}U_{20}$	11.82	11.58	97.97
$ASB_{10}U_{20}$	11.82	11.46	96.95

The weight of extracted acetamiprid was a mean of three replicates.

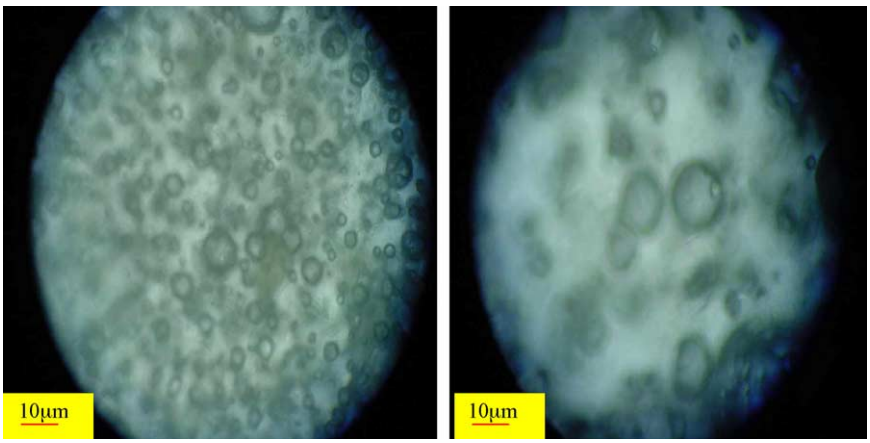

Fig. 2. Micrographs of the structure of acetamiprid CRF (100×, 200×).

3.2. Micrographs of the CRF structure

Fig. 2 presents micrographs of encapsulated acetamiprid in a polymer matrix of starch–borate–urea at different magnifications, the acetamiprid encapsulated in starch is of different diameters various between 2 and 20 μm.

3.3. Release kinetics

3.3.1. Effect of urea added in the mixture on the release of acetamiprid from CRF

The cumulative release of acetamiprid from granules with various content of urea, same size (1.0–1.68 mm), is shown in Fig. 3. In this study, technical acetamiprid was completely dissolved in 4 h, and the treatment ASB_5U_0[1.0–1.68] was completely dissolved in 14 h. In Fig. 3, the slowest release of acetamiprid is from treatment ASB_5U_{25}[1.0–1.68] granules. The other release data were analyzed by applying the generalized model $M_t/M_z = kt^n$. There is a good correlation of the release profiles of acetamiprid granules with the empirical equation. The correlation coefficients (r) were higher than 0.9947. The n values ranged from 0.47 for the ASB_5U_{10} [1.0–1.68] to 0.57 for the ASB_5U_{25} [1.0–1.68] (Table 3). The n values close to 0.5 indicate the release is diffusion-controlled (Ritger and Peppas, 1987). The T_{50} value was calculated for the formulations. These values are also shown in Table 3. The higher value of T_{50} corresponds to the ASB_5U_{25} [1.0–1.68] matrix, which means that this preparation produces the slowest acetamiprid release. The formulation with the same size can be ranked in order of increasing T_{50} values:

$$ASB_5U_0 < ASB_5U_{10} < ASB_5U_{15} < ASB_5U_{20} < ASB_5U_{25}$$

The possible mechanism may be described as Fig. 4a or b (Yun, 1990; Wang and Wu, 2003). Fig. 4a shows the tapioca starch could be modified into dialdehyde starch with sodium borate as catalyst, the dialdehyde starch prefer to react with urea and produce cross-linked starch. Fig. 4b shows the tapioca starch

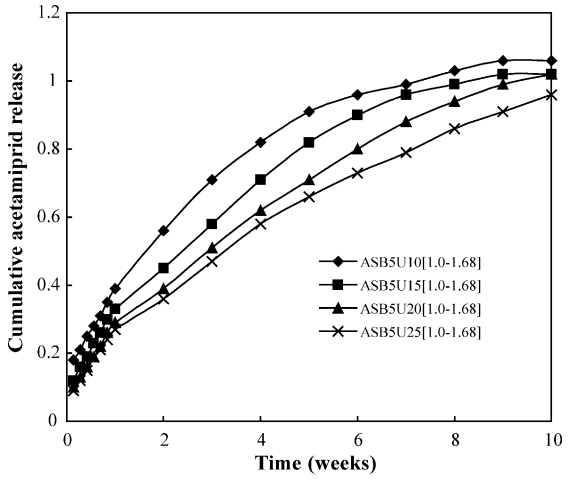

Fig. 3. Cumulative release of acetamiprid from granules into static water with various content of urea.

Table 3
Constants from fitting the generalized model, $M_t/M_z = kt^n$, to the release data of acetamiprid in water from granules with various content of urea, sodium borate and different granule sizes

Formulation	k (weeks)$^{-n} \times 10^{-2}$	n	r	T_{50} (weeks)
ASB_5U_{10}[1.0–1.68]	32.54	0.47	0.9947	1.65
ASB_5U_{15}[1.0–1.68]	32.34	0.54	0.9979	2.25
ASB_5U_{20}[1.0–1.68]	27.86	0.57	0.9984	2.77
ASB_5U_{25}[1.0–1.68]	25.94	0.57	0.9990	3.16
$ASB_{2.5}U_{20}$[1.0–1.68]	24.78	0.61	0.9986	3.18
$ASB_{7.5}U_{20}$[1.0–1.68]	31.57	0.55	0.9980	2.31
$ASB_{10}U_{20}$[1.0–1.68]	35.97	0.51	0.9983	1.90
ASB_5U_{20}[0–0.50]	45.55	0.46	0.9951	1.23
ASB_5U_{20}[0.50–1.0]	37.83	0.49	0.9968	1.77
ASB_5U_{20}[1.68–2.83]	24.38	0.59	0.9990	3.37

could be hydrolysed into D-(+)-glucose with sodium borate as catalyst, D-(+)-glucose can react with urea and produce urea-starch resin. Fig. 4a and b illustrate that urea was used as one monomer for synthesis polymer, with the increasing of urea, the urea-starch polymer molecule should be larger. The results also showed that the formulation with the increasing urea in formulation had the higher value of T_{50}, which means a slower release of the active ingredient.

3.3.2. Effect of sodium borate added on the release of acetamiprid from CRF

The cumulative release of acetamiprid from granules with various content of sodium borate, same size (1.0–1.68 mm), is shown in Fig. 5. The study carried out with treatment ASB_0U_{20}[1.0–1.68] as control showed that, in this case, granules were completely dissolved in 1 d (17.8 h). The other release data were also analyzed by applying the generalized model $M_t/M_z = kt^n$ (Table 3). There is a good correlation of the release profiles of acetamiprid granules with the empirical equation. The n values ranged from 0.51 for the $ASB_{10}U_{20}$[1.0–1.68] to 0.61 for the $ASB_{2.5}U_{20}$[1.0–1.68]. The n values close to 0.5 indicate the release is diffusion-controlled. The T_{50} value was also calculated for the formulations. The formulations with the same size can be ranked in order of increasing T_{50}

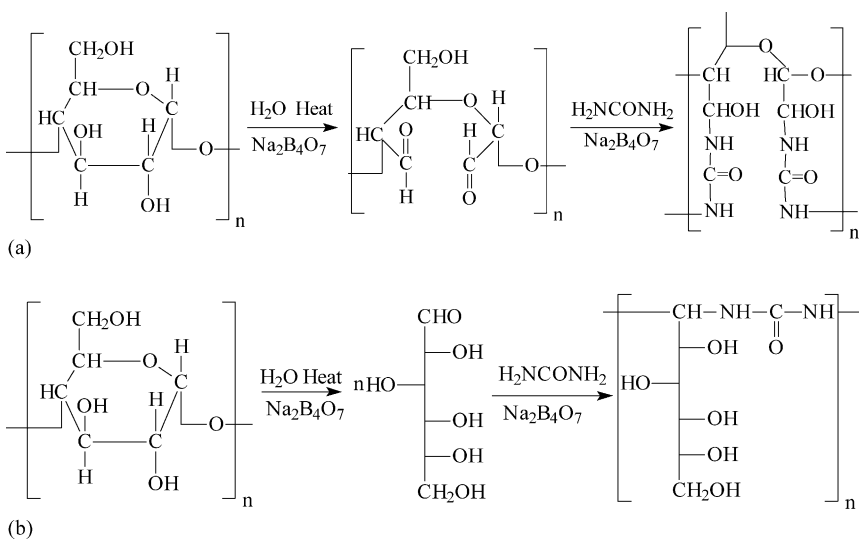

Fig. 4. The possible mechanisms of development a polymer matrix of starch–borate–urea.

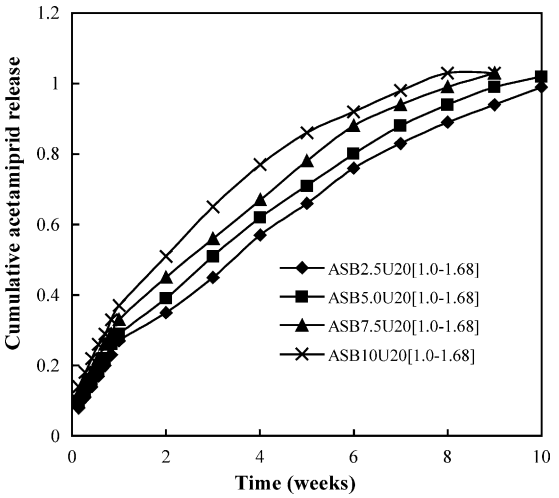

Fig. 5. Cumulative release of acetamiprid from granules into static water with various content of sodium borate.

values:

$$ASB_0U_{20} < ASB_{10}U_{20} < ASB_{7.5}U_{20} < ASB_5U_{20} < ASB_{2.5}U_{20}$$

The possible mechanism may be described in Fig. 4a or 4b (Yun, 1990; Wang and Wu, 2003), which show the sodium borate was used as catalyst in forming urea-starch polymer, an optimal rang of sodium borate content should be selected. The optimal molecular weight couldn't be obtained with less sodium borate; on the other hand, sodium borate would be used as a carry materials when the content of sodium borate more than the maximal content. It is well known that the release rate from polymer matrix is found to increase with increasing amount of a water soluble, low molecular weight additive. In this study the optimal rang of sodium borate should be between 2.5 and 5.0 g. The results also showed that the formulation with the increasing sodium borate in formulation had the lower value of T_{50}, which means a faster release of the active ingredient.

3.3.3. *Effect of granules size on the release of acetamiprid from CRF*

To analyze the influence of the granule size on the release rate, the ASB_5U_{20} formulation was used. The results are shown in Fig. 6. The smaller granule size (ASB_5U_{20}[0–0.50]) results in a faster release of acetamiprid. This was as expected due to a higher surface area of the matrix being exposed to water, along a smaller distance over which the acetamiprid must diffuse from the center of the granule. Similar results were obtained for the release of diuron and imidacloprid from granules based on a lignin matrix system (Cotterill et al., 1996; Fernández-Pérez et al., 1998). The data were fitted to the generalized model; the constants obtained from this model and T_{50} values are given in Table 3. The n values ranged from 0.46 for the ASB_5U_{20} [0–0.50] to 0.59 for the ASB_5U_{20} [1.68–2.83]. The T_{50} values ranged from 1.65 weeks for the smaller granule size (0–0.50 mm) to 3.16 weeks for the larger granule size (1.68–2.83 mm).

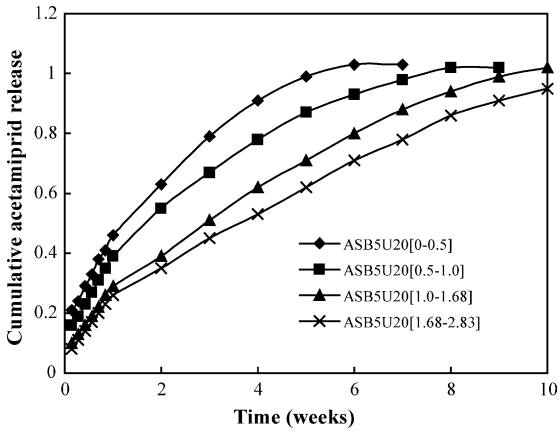

Fig. 6. Cumulative release of acetamiprid from ASB_5U_{20} with different granules sizes.

3.4. *Stability of CRF*

To determine the effect of temperature variations and stability against UV radiation, acetamiprid CRF and EC were stored at 40, 50, 60 °C for a period of 60 d, and the results of the active ingredient changes were determined by HPLC described as above. Table 4 showed that acetamiprid CRF was more stable than the acetamiprid EC under high temperature. The decomposition rate of acetamiprid EC was more ten times than that of the acetamiprid CRF, the later had no more than 3% decomposition rate under UV radiation test. A formulation with good stability against UV radiation and temperature has many advantages in preparation, storage, transportation and application. Acetamiprid CRF can have a number of advantages over acetamiprid EC: have longer residual biological activity; may reduce

Table 4
CRF stability effected by temperature and UV radiation

Tests	Content of acetamiprid	Acetamiprid CRF (%)	Acetamiprid EC (%)
Storage at 40 °C for 60 d	Initial	8.24	3.16
	After storage	8.18	3.12
	Decomposition rate	0.73	1.27
Storage at 50 °C for 60 d	Initial	8.22	3.18
	After storage	8.08	3.06
	Decomposition rate	1.70	3.77
Storage at 60 °C for 60 d	Initial	8.28	3.14
	After storage	8.02	2.86
	Decomposition rate	3.14	8.92
Irradiation at 254 nm for 48 h	Initial	8.26	3.16
	After irradiation	8.04	2.08
	Decomposition rate	2.66	34.18

Data are the means of triplicate samples.

mammalian toxicity; control or reduce evaporation of pesticide; may reduce phytotoxicity to the crop; reduce fish toxicity; reduce groundwater leaching; reduce solvent usage in the formulation; reduce the pesticide application rate.

4. Conclusions

The use of tapioca starch, urea, and sodium borate for the preparation of CRF was studied. The data showed the recovery of this CRF process is >95.43%, and the acetamiprid CRF was more stable than the acetamiprid EC against UV radiation and high temperature storage. In a series of laboratory experiments the release of the active ingredients into aqueous solution from the different preparations was determined. The release data were agreed to the generalized model $M_t/M_z = kt^n$. There was a good correlation of the release profiles of acetamiprid granules with the empirical equation. The n values close to 0.5 indicate the release is diffusion-controlled. It has been shown that there is a strong correlation between the T_{50} value and the urea, sodium borate content in the mixture and ground particles size. The release rate and release period of the formulations are adjustable by varying the urea, sodium borate content in the mixture and ground particles size. At increasing urea concentrations in the mixture, pesticide formulations having decreasing pesticide release rates and longer durations are obtainable. Urea serves to gelatinize and cross-link the starch in the mixture and is releasable from these particles, hence providing an added fertilizing effect for the pesticide formulations of the present study. The present study provides an improved CRF comprising a pesticide which is alkali-sensitive or high temperature-sensitive encapsulated in a polymer matrix of starch–borate–urea, and also provides a method for preparing the improved pesticide formulation so that pesticide release rate and release period can be adjustable.

Acknowledgment

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References

Boydston, R.A., 1992. Controlled release starch granule formulations reduce herbicide leaching in soil columns. Weed Technol. 6, 317–321.

Cotterill, J.V., Wilkins, R.M., da Silva, F.T., 1996. Controlled release of diuron from granules based on a lignin matrix system. J. Control. Release 40, 133–142.

Fernández-Pérez, M., González-Pradas, E., Ureña-Amate, M.D., Wilkins, R.M., Lindup, I., 1998. Controlled release of imidacloprid from a lignin matrix: water release kinetics and soil mobility study. J. Agric. Food Chem. 46, 3828–3834.

Gish, T.G., Shirmohammada, A., Wienhold, B.J., 1994. Field-scale mobility and persistence of commercial and starch-encapsulated atrazine and alachlor. J. Environ. Qual. 23, 355–359.

Mehltretter, C.L., Roth, W.B., Weakley, F.B., McGuire, T.A., Russell, C.R., 1974. Potential controlled-release herbicides from 2,4-D esters of starches. Weed Sci. 22, 415–418.

Ritger, P.L., Peppas, N.A., 1987. A simple equation for description of solute release. II. Fickian and anomalous release from swellable devices. J. Control. Release 5, 37–42.

Schreiber, M.M., Hickman, M.V., Vail, G.D., 1993. Starch encapsulated atrazine: efficacy and transport. J. Environ. Qual. 22, 443–453.

Shasha, B.S., Doane, W.M., Russell, C.R., 1976. Starch-encapsulated pesticides for slow release. J. Polym. Sci.: Polym. Lett. Ed. 14, 417–420.

Shasha, B.S., Trimnell, D., Otey, F.H., 1981. Encapsulation of pesticides in a starch–calcium adduct. J. Polym. Sci.: Polym. Chem. Ed. 19, 1891–1899.

Shasha, B.S., Trimnell, D., Otey, F.H., 1984. Starch-borate complexes for EPTC encapsulation. J. Appl. Polym. Sci. 29, 67–73.

Tomlin, C.D.S., 1999. The Electronic Pesticide Manual, 11th ed. Version 1.0, British Crop Protection Council, Surrey, UK.

Trimnell, D., Shasha, B.S., 1990. Controlled release formulations of atrazine in starch for potential reduction of groundwater pollution. J. Control. Release 12, 251–256.

Wang, X., Wu, Y., 2003. Preparation of urea–dialdehyde starch glue. Fine Special Chem. 13, 18–20.

Wilkins, R.M., 1990. Biodegradable Polymer Methods. Controlled Delivery of Crop-Protection Agents. Taylor & Francis, Bristol, PA, pp. 149–165.

Yun, K., 1990. Organic Chemistry, second ed. Advanced Education Press, Beijing, pp. 565–568.