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AN INVESTIGATION ON PESTICIDE ENCAPSULATION IN BINDING COMPONENTS

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Abstract: The encapsulation of the pesticides Perozin E and Ridomil Gold was studied and their content in aqueous emissions was determined during the storage of the capsules obtained. The epoxy resins "Epoxal II" and "Versamid" and cement were used as binders. Capsules containing 5, 10, 15 and 20 g Perozin E and Ridomil Gold in epoxy resins, and 2, 4, 6, 8 and 10 g pesticides in cement were prepared. The capsules were kept in water and the emissions of pesticides were periodically analyzed by HPLC. The results showed that the emission levels from epoxy capsules were low enough in the aqueous phase and reached 2.5-3.3 mg l^{-1}. The emission levels from cement capsules were quite higher (up to 15 mg l^{-1}) and concentration equilibrium was not observed for the whole period of the investigation.

Keyword: pesticides, encapsulation, HPLC.

1. INTRODUCTION

The use of various methods for detoxication of pesticides and other environmentally hazardous wastes has been reported in the literature. One of these methods is vitrification process at temperatures 1200-1400°C which provides opportunity for full decomposition of toxic organic substances and their safe deposition in the environment (Krau, 1996; Ito et al., 1996; Sobolev et al., 1996). The main problem of the vitrification process is its considerable energy consumption and the great variety of pesticides, which suggests insufficient data on their behaviour under heating and melting. Another method for utilization of pesticides and another solid waste is their encapsulation in polymer compositions, including polyethylene (Lageraaen et al., 1996; Kalb et al., 1996), epoxy resins (Faucette, 1996), etc. Some authors suggested urea-formaldehyde crosslinked starch and guar gum matrices for encapsulation of liquid pesticides (Kulkami et al., 1999). A different approach to the problem of pesticide detoxication is the synthesis of immunosorbents for selective solid phase extraction of pesticides from natural waters on the basis of polyclonal antibodies (Pichon et al., 1995). For extraction of pesticides from natural waters and various matrices, the methods of solid phase extraction using polymer sorbents are quite often used (Masque et al.,1997; Sheng and Nau,1998), as well as supercritical fluid extraction using CO_2 modified with 10% MeOH (Aschraf-Khorassami,1996). On the other hand, the problem of the analysis of the extracted pesticides is to be solved. Data on application of gas chromatography with different detectors – flame-ionization or flame-photometric ones have been published (Specht et al., 1995; Pihlström et al., 1997). The concentration of pesticides extracted by solid phase extraction with immunosorbents or polymer sorbents was determined by HPLC (Pichon et al.,1995; Sheng and Nau,1998). Rapid separation of environmentally important pesticides has been carried out by using diol-bonded, polyethylenimine-coated stationary phase (Wu et al.,1999).

The aim of the present study is to use various binding components to encapsulate the pesticides Perozin E and Ridomil Gold used in Bulgaria in order to prevent their emission from the capsules obtained. The concentration of pesticides emissions in water was determined by HPLC.

2. METHODS

The pesticides Perozin E (Zn-ethylen-bis-(dithiocarbamat)) from Agrochim, Bulgaria and Ridomil Gold (methyl (2,6-dimethyl-phenyl-N-methoxiacetyl) alaninat) from BASF AG, Ludwigshafen, Germany, were used for the experiments. They are system products of wide range of application. The epoxy resins - "Epoxal II" and "Versamid", with their hardeners diamine and triethylamine (Plastchem, Bulgaria), and cement 250 (Devnya, Bulgaria) were used as binding agents. The capsules were prepared in a rectangular matrix with dimensions 3x2x2 cm. The matrix was filled with 30 g epoxy resin or cement, then certain amounts of the pesticides were placed in it (5, 10, 15 or 20 g for epoxy resin and 2, 4, 6, 8 or 10 g for cement) and the mixture was homogenized. After solidification for 24 h, the cubes were taken out of the matrix.

Further, the cement containing cubes were treated in an 50 % - aqueous solution of sodium silicate (Silimex Ltd - Ruse, Bulgaria) and sintered in an oven at temperatures from 20 to 110 °C which was raised step-wise at steps of 20 °Ñ in order to glassify the surface. Then, the cubes were immersed in 500 ml distilled water from which samples were taken at certain intervals to determine the emission of extracted pesticides.

The HPLC-analyses were carried out using a Series 4 liquid chromatograph (Perkin-Elmer Corporation, Norwalk, CT, USA), equipped with a UV-detector. The Chromatographics 2 Data System (Perkin-Elmer Corporation, Norwalk, CT, USA) was used for data handling. Separation was carried out using a LiChroCART® 250-4 Nucleosil 5 C18 column (250x4.5 mm i.d., 5 ì m particle size). A Super Pac Guard® Cartridge was used in order to protect the analytical main column. Sample introduction was made through a Reodyn 7010 injection valve (Perkin-Elmer Corporation, Norwalk, CT, USA) with a 20 ì l sample loop. The detection wavelength was 230 nm. The mobile phase was prepared from methanol and bidestilated water (60:40). The mobile phase flow was 1 ml min^{-1}. Methanol was HPLC-grade (LiChrosolv) from Merck (Darmstadt, Germany). Separation was carried out at temperature 36°C. The quantitative HPLC analysis was carried out by the method of internal standard-dichlorophene (Merck, Darmstadt, Germany).

3. RESULTS AND DISCUSSION

According to the aim of the study, several basic products were used for pesticide encapsulation. The use of epoxy resin “Versamid”, which has low molecular weight and high plasticity during hardening, did not give satisfactory results due to the specific properties of the hardener. The hardener triethylamine has a strong complex-forming ability to Cu^{2+} and the pesticides used contain more than 40% copper. Therefore, the effect of the hardener was inhibited and the process of hardening was disturbed. The capsules obtained were neither strong nor compact, so the experiments with “Versamit” were discontinued.

Diamine was used as a hardener in “Epoxal II” as it has a lower complex-forming ability. This allowed introducing up to 20 g pesticide in 30 g resin at concentration of the hardener three times higher than normal.

Fig. 1 shows the change of Perozin E concentration on time (days) determined from HPLC analysis data. The rate of pesticides emission in aqueous medium was proportional to their concentration in the capsules and depended probably only on the diffusion. Up to the tenth day a weak diffusion was observed, followed by an abrupt increase of diffusion between the tenth and the thirtieth day. After that, pesticide concentrations practically remained unchanged. This may be due to the equilibrium established between capsule surface and aqueous system. Maximal emissions of 0.7 to 1.6 mg l^{-1} were registered at Perozin E amounts up to 10 g while at amounts between 10 and 20 g the maximal emission was from 2.5 to 3.3 mg l^{-1}. The impeding of the process above these concentrations shows that the pesticides within the capsule had been blocked and the emission was only due to the active substance present at capsule surface.

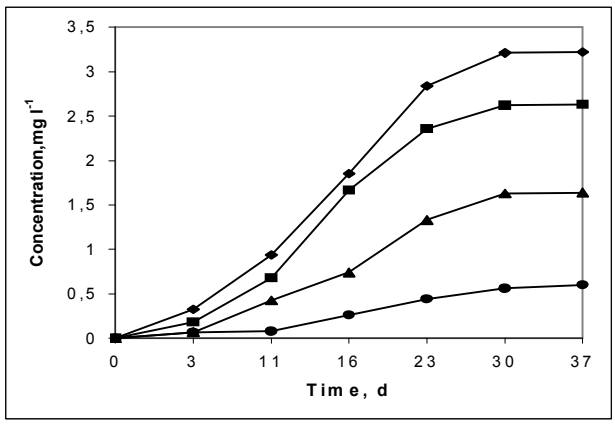

Fig. 1. Concentration variation of Perozin (encapsulated in epoxy resin) as a function of time.. Quantity of the encapsulated Perozin (g): ●-5; ▲-10; ■-15; ◆- 20.

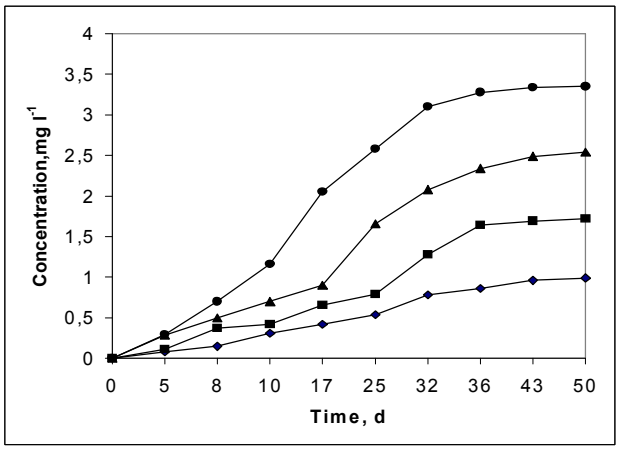

Fig. 2. Concentration variation of Ridomil Gold (encapsulated in epoxy resin) as a function of time. Quantity of the encapsulated Ridomil Gold (g): ◆-5; ■-10;▲-15; ● -20

The experimental conditions used with Ridomil Gold were the same. The results obtained are shown in Fig. 2. The results showed that, despite the pesticide concentration in the capsules, the emission was weak up to the eighth day. The emission measured between the eighth and the thirtieth day was found to be proportional to the Ridomil Gold concentration in the capsules. After that, the pesticide concentration in the aqueous medium remained constant, i.e. fresh amounts of pesticide were not released. The maximal emission was almost the same as for Perozin E: from 0.5 to 1.6 mg l^{-1} at 5-10 g pesticide in the capsules and from 2.5 to 3.3 mg l^{-1} at 10-20 g. The equal emissions of both products and their quite different solubility in water (0.01 g l^{-1} for Perozin E and 7.1 g l^{-1} for Ridomil Gold) showed that the extraction involves only the capsules surface.

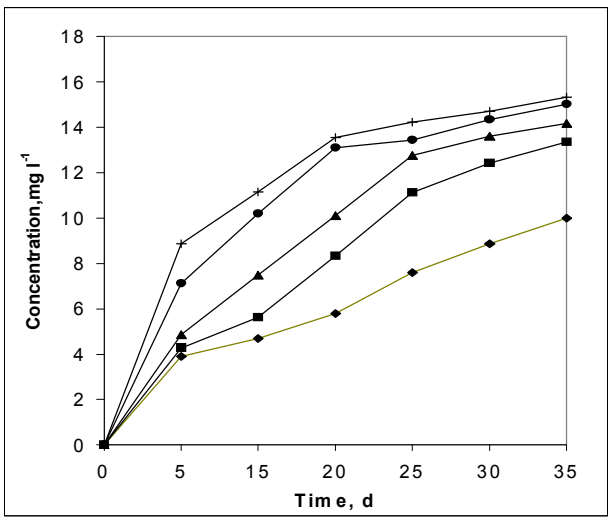

Fig. 3. Concentration variation of Perozin (encapsulated in cement) as a function of time. Quantity of the encapsulated Perozin (g): ◆-2; ■-4; ▲-6; ●-8; +-10.

The capsules prepared with cement and water glass were found to be quite fragile. This confirmed the well known fact that salt components impede the binding ability of cement clinker. Therefore, cement was used only for encapsulation of Perozin E. The results are presented in Fig. 3. As can be seen from the figure, the initial stage of the emission (until the fifth day) proceeded at a rate higher than that when epoxy resin was used. Dynamic equilibrium was not observed within the experimental period and the emissions were considerably higher (up to 15 mg l^{-1}) than these registered with epoxy resin.

4. CONCLUSIONS

The results obtained from the present study showed that, encapsulated in epoxy resins, pesticides give emission levels in aqueous medium up to 2.5-3.3 mg l-1 and were considered to be sufficiently low. It can be supposed that such capsules can successfully be stored in air or additionally isolated in polymer packing.

The use of cement for pesticide encapsulation is connected with impeding of the physic-chemical processes of cement binding, impossibility to introduce more than 10 g pesticide per capsule and presence of emissions higher than 15 mg l-1 of pesticide active substance.

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ÈÇÑËÄÄÂÀÍÅ ÊÀÏÑÓËÈÐÀÍÅÒÎ ÍÀ ÏÅÑÒÈÖÈÄÈ Â ÑÏ ÎÉÂÀÙÈ ÊÎ Ì Ï Î ÍÅÍÒÈ

Í. Äèìîâà, Ñ. Ïåòðîâ

Ðåçþìå. Â ðàáîòàòà ñå èçñëåäâà âëèÿíèåòî íà êàïñóëèðàíåòî íà ïåñòèöèäèòå Perozin E è Ridomil Gold íà îòäåëåíîòî è ìî êîëè÷åñòâî âúâ âîäíè ðàçòâîðè ïðå ñúõðàíÿâàíå. Êàòî ñïîéâàùè êî ì ïîíåíòè ñà èçïîëçâàíè åïîêñèäíèòå ãóì “Epoxal II” è “Versamit” è öåì åíò. Êîëè÷åñòâîòî íà ïåñòèöèäè â êàïñóëèòå îò åïîêñèäíè ãóì è å 5, 10, 15 è 20 g , à â öåì åíòîâèòå – 2, 4, 6, 8 è 10 g. Êàïñóëèòå ñå ñúõðàíÿâàò âúâ âîäà, à îòäåëåíîòî ïî âðåìå íà ñúõðàíÿâàíåòî êîëè÷åñòâî íà ïåñòèöèäà ñå îïðåäåëÿ ÷ðåç òå÷íîñòíà õðîìàòîãðàôèÿ – HPLC. Ðåçóëòàòèòå ïîêàçâàò, ÷å íèâîòî íà îòäåëåíîòî âåùåñòâî ïðèöèä ïðè öåëåíòîâèòå êàïñóëè å äîòà ïî-âèñîêî (íàä 15 mg/l), êàòî íå ñå äîòèãà ðàâíîâåñíà êîíöåíòðàöèÿ ïðåç öåëèÿ ïåðèîä íà èçñëåäâàíå.