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KINETICS OF RELEASING HERBICIDE METAZACHLOR FROM HYDROGEL MICROCAPSULES TO AQUATIC ENVIRONMENTS

KINETYKA UWALNIANIA HERBICYDU METAZACHLOR Z HYDROŻELOWYCH MIKROKAPSULEK DO ŚRODOWISKA WODNEGO

Abstract: Formulation of metazachlor in the form of hydrogel capsules was carried out in the Packaging and Biopolymers Center at the West Pomeranian University of Technology in Szczecin. To produce the hydrogel matrix sodium alginate was used in 1.5 % solution. Kinetics of releasing metazachlor from the matrix was carried out for various aquatic environments (distilled water Wd and two natural waters W1 and W2) at 4 ± 1 °C and 20 ± 1 °C under laboratory condition. The release data were fitted to the generalized model proposed by Ritger and Peppas. For all the combinations in study, the high values of the correlation coefficient R (from 0.9254 to 0.9997) show a very good adjustment between the experimental data and the model applied. It was found that amount of metazachlor released from the capsules to water increased exponentially in time and depended on type of the aquatic environment and temperature of storage. For metazachlor, the highest values of time T_{50} , were recorded for the distilled water. For the natural waters, time T_{50} is significantly shorter, and, comparing with the distilled water, it was decreased by 83–90 % at 20 °C and by 69–96 % at 4 °C.

Keywords: metazachlor, release, hydrogel microcapsules, alginate, water environment

Pesticides make for a group of pollutants quite frequent in surface and underground waters. Their highest concentration is observed during the runoff of thaw water and on application of agricultural chemistry procedures [1–4]. Due to the necessity to protect the natural environment, there is an objective set forth to reduce the amount of pesticides by application of micro-doses or adjuvants, or by modification of the usable forms [5, 6].

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Formulas based on technologies of controlled release help to maintain the active substance on a constant, pre-defined level. This way it is possible to reduce the amount of the necessary pesticides and, at the same time, to minimize such negative environmental phenomena, as surface runoff, leaching or evaporation [7–10].

Parameters having an impact on quality of *controlled release* formulation (CR formulation) include structure and characteristics of the used polymers. Polymers, which are most frequently used in agriculture for CR formulation, are the natural polymers, ie starch, ethyl cellulose, lignin, bentonite, kaolin, chitosan or alginate, which, contrarily to the synthetic ones, feature the lack of toxicity, low price, availability, and, first of all, biodegradability [11, 12].

To obtain matrixes for controlled release of soil-applied herbicides the encapsulation method is used, as based on setting some emulsion containing the active substance through polymer cross-linking. This consists in binding the matrix components with a cross-linking polymer, at presence of multivalent metal cations (eg: Ca^{2+}). These conditions are met by the algae-originated biopolymer belonging to the polysaccharides – the biodegradable sodium alginate. This compound is used both for production of medicine controlled release carriers and for pesticides. Thanks to its specific chemical structure and the spatial configuration of its monomers, ie D-mannuric acid and L-guluronic acid, it has strong gelling qualities in aquatic environment. Additionally, application of such CR modifiers as natural clays, active carbon, humic acids, linseed acid for production of alginate formulations has an influence on the immobilization process, as well as ensures a better control of the process of releasing the active substance from the matrix [13–17].

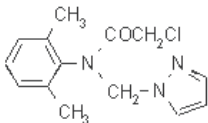
Therefore, our research was conducted in order to determine the kinetics of releasing herbicide metazachlor from hydrogel capsules to aquatic environments.

Material and methods

In the course of research, metazachlor herbicide of the chloroacetanilid group were used. Metazachlor is a selective herbicide, a sprout inhibitor, penetrating the roots and hypocotyl. It is applied to such plants as winter or spring rape. The active substance was made available by company FEINCHEMIE SCHWEBDA GMBH of Germany. Selected physical and chemical characteristics are presented in Table 1.

Table 1

Selected physical and chemical characteristics for metazachlor [17]

Molecular structure	Chemical name	2-chloro- <i>N</i> -(pyrazol-1-ylmethyl)acet- -2',6'-xylylidide
	Form Molecular formula: Molecular mass: Solubility in water: Octanol / water partition coefficient:	Yellowish crystals; (tech., beige solid) $\text{C}_{14}\text{H}_{16}\text{ClN}_3\text{O}$ 277.8 g/mol 430 mg/dm ³ (20 °C). $\log P_{ow} = 2.49$

Production of Metazachlor Hydrogel Capsules

Formulation of metazachlor in the form of hydrogel capsules was carried out in the Packaging and Biopolymers Center at the West Pomeranian University of Technology in Szczecin. To produce the hydrogel matrix sodium alginate was used in 1.5 % solution. To form microcapsules containing some immobilized active substance emulsion with concentration of the active substance equal to 18.55 % ($0.5 C_{\max}$, where $C_{\max} = 37.1$ %) was prepared in a mix of solvents: methyl acetate / vegetable oil (ratio 1:1). Metazachlor emulsion was prepared at the ambient temperature ($23 \text{ }^{\circ}\text{C} \pm 1$), with application of a homogenizer (Heidolph, Germany), at the constant speed of 12 thousand rpm. After 3-minute homogenizing, the metazachlor emulsion was dropped into the cross-linking agent – calcium chloride solution – where spherical hydrogel capsules with diam. 0.30–0.35 mm were obtained. Time of the cross-linking reaction in the calcium chloride for creation of an internally stable microcapsule membrane was about 15 minutes.

Preparations process

Kinetics of releasing metazachlor from the matrix was carried out for various aquatic environments (distilled water Wd and two natural waters W1 and W2) at $4 \pm 1 \text{ }^{\circ}\text{C}$ and $20 \pm 1 \text{ }^{\circ}\text{C}$. Table 2 presents selected physical and chemical qualities of the waters used in the experiment. Weighed amounts (5 g each) of metazachlor in the form of hydrogel capsules were placed in 200 cm^3 of appropriate water in polished-surface-closed Erlenmeyer flasks with capacity of 500 cm^3 and mixed with a magnetic agitator at 100 rpm (for each water three cycles were made). Solution samples of 5 cm^3 were collected after 60, 120, 240, 480 minutes and after 24 and 48 hours. In order to avoid saturation effect, the collected amount was re-filled with the appropriate water. The collected water samples were made subject to extraction process with dichloromethane, according to the general methods proposed by Ambrus et al [19].

Table 2

Chemical indicators of waters

Water	pH	N-NH ₄ [mgN · dm ⁻³]	N-NO ₂ [mgN · dm ⁻³]	N-NO ₃ [mgN · dm ⁻³]	P-PO ₄ [mgP · dm ⁻³]
W1	7.93	0.72	0.001	0.21	0.09
W2	7.61	0.58	0.004	0.17	0.02

Analysis of metazachlor in the microcapsules

With laboratory scales, in five cycles, 0.1 g portions of the microcapsules were weighed, containing immobilized metazachlor. These were transferred to conical flasks of capacity 100 cm^3 and underwent extraction process with acetone (50 cm^3). All the flasks were agitated by a rotary shaker for 8 hours. After 24 hours spent in ambient

temperature, all samples were percolated, separating the alginate matrix from the acetone layer, which contained the determined active substance. The acetone was evaporated dry with a vacuum evaporator made by Büchii, and dichloromethane and waterless Na₂SO₄ were added to the remnant. After the drying, all samples were filtered again and concentrated up to the volume of 2 cm³ with the vacuum evaporator. In the samples thus prepared, concentration of metazachlor was determined with the GC/MS method.

GC/MS analysis

Determination of metazachlor released from the hydrogel matrix to the water was carried out by gaseous chromatography. In order to do so, a gaseous chromatograph provided with an MS detector made by Perlan Technologis was used, making use of an Elite 5MS column (30 m × 0.25 mm × 0.5 μm). Helium was used as the carrying gas at a flow of 1.0 cm³/min. For the analysis, a programmed temperature of the column was applied: 30 °C – 1 min, 25 °C/min to 290 °C – 10 min, detector temperature 320 °C. To determine metazachlor in the tests, the method of electronic ionization type EI+ was used. Quantitative analysis was carried out according to the surface area.

Results and discussion

Results of tests on kinetics of releasing the metazachlor herbicide from hydrogel capsules at 4 °C and 20 °C are presented on Fig. 1. It was found that amount of metazachlor released from the capsules to water increased exponentially in time and depended on type of the aquatic environment and temperature of storage. After 48 hours, the highest concentrations of the herbicide were recorded for the natural waters at 20 °C, where 84 % of metazachlor got released from the hydrogel matrix. In the case of the distilled water, the release kinetics of the substance in question proceeded very efficiently too. After 48 hours, 78.7 % of metazachlor got released. Storage of the metazachlor microcapsules at low temperatures affected its release kinetics strongly. At 4 °C, its lowest concentration was observed also in the distilled water, where within 48 hours 56.4 % of metazachlor immobilized in the gel matrix got released. At the same time, at low temperatures, for the natural waters, impact of their physical and chemical qualities on the process in study was recorded. Within 48 hours, between 56.8 % (W2) and 66 % (W1) of the active substance were released.

Kinetics of releasing metazachlor to aquatic environments from the hydrogel capsules was studied based on a mathematical model proposed by Ritger and Peppas [19–21].

$$\frac{M_t}{M_0} = K \cdot t^n$$

where: M_t – represents quantities of the active substance released in time t ,
 M_0 – total amount of the active substance in the carrier,

- M_t/M_0 – refers to percentage of the active substance released in time t ,
K – a constant describing qualities of the component being released and qualities of the matrix that forms the carrier,
 n – a diffusion parameter helping to describe the transport mechanism.

For all the combinations in study, the high values of the correlation coefficient R (from 0.9254 to 0.9997) show a very good adjustment between the experimental data and the model applied. The constant values K and n were calculated with the Levenberg-Marquardt non-linear estimation method. For all the water combinations, low values of constant n were obtained, as below 0.5 ($n < 0.5$), which shows that the process of diffusion and release of metazachlor from the hydrogel matrix proceeds according to the Fick's laws of diffusion [12, 14, 21]. Regardless the temperature of the process, the highest values of n occurred for the distilled water and were as follows: for 20 °C = 0.1292, for 4 °C = 0.1382. At the same time it was established that the parameter in study, ie the process of release of the active substance from the matrix, was strongly affected by physical and chemical qualities of the natural waters and by the temperature. For the natural waters, n underwent a substantial decrease by 46–51 % at 20 °C and by 24–30 % at 4 °C.

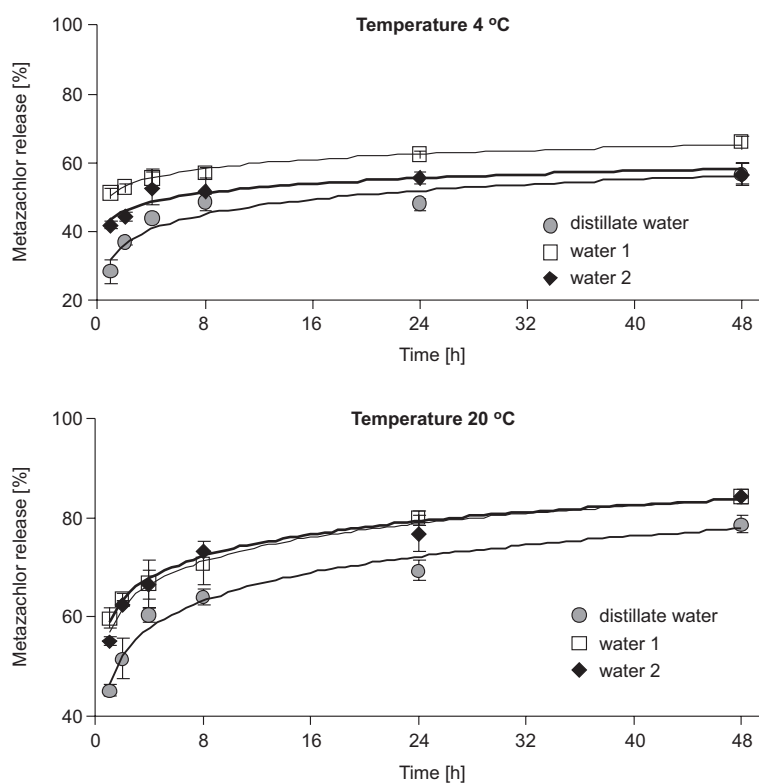


Fig. 1. Kinetics of releasing herbicide metazachlor from hydrogel microcapsules to water

Based on the constant K and n , for all the combinations, the time was calculated during which 50 % of the active substance was released from the hydrogel matrix (T_{50}) (Table 3). Obtained times T_{50} make it possible to state that the speed at which metazachlor is released depends both on the process temperature and the physical and chemical qualities of the water. For metazachlor, the highest values of time T_{50} , were recorded for the distilled water. For the natural waters, time T_{50} is significantly shorter, and, comparing with the distilled water, it was decreased by 83–90 % at 20 °C and by 69–96 % at 4 °C.

Table 3

Release parameters for metazachlor from hydrogel microcapsules

Metazachlor	Temperature 20 °C				Temperature 4 °C			
	R	K [h ⁻ⁿ]	<i>n</i>	Time T ₅₀	R	K [h ⁻ⁿ]	<i>n</i>	Time T ₅₀
Distillate water	0.9967	0.4760	0.1292	1.46	0.9843	0.3310	0.1382	19.78
Water 1	0.9997	0.5936	0.0906	0.15	0.9934	0.5045	0.0673	0.88
Water 2	0.9982	0.5748	0.0986	0.24	0.9254	0.4363	0.0747	6.20

Regardless the fact which water was analyzed, for the temperature of 4 °C higher values of metazachlor times T_{50} were observed. This dependence can be attributed to an increase of the diffusion barrier because of the growth of density of the oil used in the metazachlor microcapsules production process, as well as a decreased solubility of metazachlor.

Release of the herbicide from the matrix in an aquatic environment is a function of physical and chemical characteristics of the herbicide, as well as of contents of the controlled release matrix. The herbicide outflow rate is also correlated with its solubility in water and the higher solubility, the quicker release. This is confirmed by such studies as those by Cespedes et al [16], who, when studying kinetics of release of chloridazon (solubility in water 340 mg · dm⁻³) and metribuzin (1050 mg · dm⁻³) from alginate capsules, obtained much longer times T_{50} for substances with lower solubility. The experiments show that release of active substances depends strongly on the matrix porosity, and thus on its components. Addition of such modifiers as minerals, eg montmorillonite, bentonite, or linseed or soya bean oils slows the outflow of active substances from the matrix dramatically down. An additional parameter that impacts the pace of the active substance release is the size of the microcapsules. According to Yongsong and others' studies [11], the smaller the diameter of the CR granules is, the shorter the times T_{50} are. The time T_{50} values obtained for acetamipirid ranged from 1.65 week for the smallest granules to 3.16 week for large granules.

The available literature does not provide any information on formulation of metazachlor controlled release. According to our own research, a sufficient control on the release process was not achieved, which results from the short metazachlor T_{50} times. This might be attributed to the fact that for testing the release of the active substance from the hydrogel matrix wet capsules were used, and thus the capsule swelling process (absorption of water), which makes the release process slow down,

was overlooked. Simultaneously, studies on kinetics of the metazachlor release from hydrogel capsules were conducted on small-diameter capsules (0.25–0.3 mm).

Conclusions

1. Concentration of metazachlor released from the hydrogel capsules to the aquatic environment grows exponentially in time and depends on type and temperature of the aquatic environment.
2. After 48 hours, the highest concentrations of the herbicide were recorded for the natural waters at 20 °C, where 84 % of metazachlor underwent the release from the hydrogel matrix.
3. The mathematical model, as proposed by Ritger and Peppas, describes the process of metazachlor release from the hydrogel matrix very precisely.
4. The lowest values time T_{50} for metazachlor were obtained for the distilled water.

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KINETYKA UWALNIANIA HERBICYDU METAZACHLOR Z HYDROŻELOWYCH MIKROKAPSULEK DO ŚRODOWISKA WODNEGO

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Abstrakt: W badaniach wykorzystano hydrożelowe mikrokapsułki herbicydu metazachlor otrzymane w Zakładzie Opakowalnictwa i Biopolimerów Zachodniopomorskiego Uniwersytetu Technologicznego w Szczecinie. Badania kinetyki uwalniania przeprowadzono w warunkach laboratoryjnych, w różnych środowiskach wodnych (woda destylowana Wd, dwie wody powierzchniowe W1, W2) w temperaturze $4\text{ }^{\circ}\text{C} \pm 1$ i $20\text{ }^{\circ}\text{C} \pm 2$. Kinetykę uwalniania metazachloru do środowiska wodnego z hydrożelowych mikrokapsulek opracowano, wykorzystując model matematyczny zaproponowany przez Ritgera i Peppasa. Uzyskane dla wszystkich analizowanych kombinacji duże wartości współczynnika korelacji R od 0,9254 do 0,9997 wskazują na bardzo dobre dopasowanie danych eksperymentalnych z zastosowanym modelem. Stwierdzono, iż ilość uwolnionego metazachloru z hydrożelowych mikrokapsulek do środowiska wodnego wzrasta wykładniczo w czasie i zależy od rodzaju środowiska wodnego i temperatury przechowywania. Otrzymane czasy T_{50} pozwalają na stwierdzenie, iż szybkość uwalniania metazachloru zależy zarówno od temperatury procesu, jak i właściwości fizykochemicznych wód. Największe wartości czasu T_{50} metazachloru, w przypadku obu temperatur, uzyskano dla wody destylowanej. Uzyskany dla wód naturalnych czas T_{50} herbicydu jest znacznie niższy i uległ zmniejszeniu o 83–90 % w temp. $20\text{ }^{\circ}\text{C}$ i o 69–96 % w temp. $4\text{ }^{\circ}\text{C}$.

Słowa kluczowe: uwalnianie metazachloru, hydrożelowe mikrokapsułki, alginian sodu, środowisko wodne