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Decomposition of selected carbamate herbicides in a constructed wetland system supported by a biopreparation

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ABSTRACT

The study aimed to evaluate the effectiveness of a constructed wetland system (CWS) in degrading specific herbicides present in wastewater. To enhance process efficiency, accelerate degradation rates, and reduce the compounds' half-lives in wastewater, a biopreparation was introduced. Conducted on a semi-technical scale, the research compared two CWS systems: one with the biopreparation and one without. The findings demonstrated a high overall efficiency of 96.2%. On the first day, herbicide removal efficiency was 26% in the standard CWS, whereas the system with the biopreparation achieved 41%. By the tenth day, removal efficiency exceeded 90%. The study also determined the DT50 half-life parameters of the herbicides in wastewater and calculated the theoretical time required to reach a concentration of 0.01 mg/dm^3. The application of the biopreparation reduced the degradation time of the carbamate herbicide by up to seven days.

Keywords: pesticide, herbicide, constructed wetland system, pesticide degradation.

INTRODUCTION

Pesticide contamination of surface and groundwater is one of the key challenges of modern water and wastewater management [1–4]. The intensive use of chemical pesticides in agriculture leads to their discharge into the aquatic environment, where they can have harmful effects on ecosystems and human health [5–8]. Traditional wastewater treatment methods, such as physicochemical and biological processes, are not always effective in removing pesticide compounds, and their use is often associated with high costs and the generation of additional waste [9–11]. Various methods are currently being used to treat sewage containing compounds, but these are often technologies dedicated to single pesticides [12–17]. In response to these challenges, there is growing interest in solutions based on natural biological processes that combine efficiency with minimized environmental impact. One such method is a constructed CWS based on aquatic plants, microorganisms and a properly selected substrate that together create an effective mechanism for wastewater treatment [7, 18, 19]. To increase the efficiency of these systems, researchers are experimenting with the use of biopreparations - specially formulated mixtures of microorganisms and enzymes that accelerate the degradation of organic pollutants, including pesticides.

The purpose of this study was to determine the applicability of constructed wetland system for the degradation of selected herbicides from wastewater and to evaluate their removal efficiency. In addition, microorganisms was used to increase the efficiency of the process.

STUDY METHODOLOGY

Technology methodology

The study was conducted on a model that included two hydrophytic beds with the common reed *Phragmites australis*. The design of the CWS was done according to the guidelines given in the literature [18, 19]. The operating parameters of the beds are given in Table 1. The deposit structure is shown in Figure 1. The hydrophytic beds were constructed in a subsurface vertical CWS. The CWS had three layers of filling with varying granulometric parameters (Figure 1).

During the period of bed introduction, in accordance with the guidelines of literature [18, 19] in order to acclimatize the plants well, the bed was fed with treated wastewater. During this period, the microorganisms was added to the treated wastewater. The biopreparation BIO AQUA PUR KOD 106 from EKOB-TBA was dosed into the treated domestic wastewater during this period. It enriched biological beds with microorganisms to improve their biodegradation properties. This preparation is formed by selected microorganisms immobilized on mineral supports, particularly active against compounds resistant to natural biological degradation in wastewater treatment plants. The biopreparation was applied once a week. The biopreparation must be administered in a systematic manner on a weekly basis to ensure the maintenance of its efficacy. Wastewater was fed to hydrophytic beds maintaining a bed load of 0.1 m^3/m^2/day.

The most commonly used herbicide in agriculture from the carbamate group was selected for the study. The structural formulas and characteristics of the active ingredient are shown in Table 2. As a thiocarbamate herbicide, prosulfocarb (PSC, $(C_3H_7)_2NC(O)SCH_2C_6H_5$), S-benzyl-di-propylcarbamothioate) is mainly used on winter crops [20–22].

After the beds were introduced, the wastewater mixture containing carbamate was fed into the tank. The sewage was then dosed to each bed in a volume of 20 dm^3 once a day. In addition, the microorganisms was further dosed every 7 days.

Analytical methodology

Analytical studies were carried out in an accredited laboratory at the Plant Protection Institute – National Research Institute using a Waters liquid chromatograph and AB SCIEX mass spectrometer following validated test procedures for the determination of herbicide in wastewater [5, 24]. The analytical procedure is described in an article by Ignatowicz et al. [24]. The optimization (DP – declustering potential; EP – entrance potential; CE – collision energy; CXP – collision cell exit potential) and validation parameters (U – extended measurement uncertainty, ME – matrix effect, R – recovery, RSD – relative standard deviation, R^2 – coefficient of determination) of the method are given in Tables 3 and 4.

A mathematical model of prosulfocarb degradation dynamics in wastewater was applied on the basis of European Union guidelines in the context of assessing the behavior of compounds in soil. Based on the obtained values of prosulfocarb concentrations in the effluent from the bed C_t [mg/dm^3] collected at different periods of time t [d], the partial degradation time DT_{50} [d] and the disappearance time of active substances in the form of $t_{0.05}$ [d] and $t_{0.01}$ [d] were calculated.

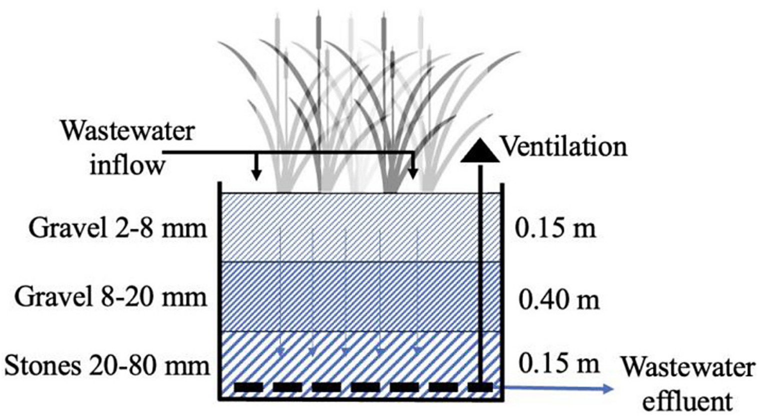


Figure 1. Construction of hydrophytic bed (CWS).

Table 1. Characteristics of research parameters of hydrophytic beds

No.	Index	Symbol	Unit	Value
1	Dimensions (radius/depth/surface area)	R/H/F	$m/m/m^2$	0.25/0.7/0.2
2	Hydraulic load	HL	$m^3/m^2/d$	0.10
3	Organic matter load	OML	g $BZT_5/m^2/d$	55–770

Table 2. Characteristics of the herbicide used in the study [23]

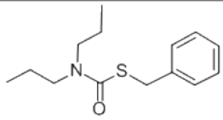
No.	Parameter	Characteristic
1	Active substance	Prosulfokarb
2	Chemical group	Karbabinianl
3	Structural formula	
4	Molecular weight(g/mol)	251.39
5	Lethal dose LD_{50} (mg/kg)	5000
6	Lethal Concentration LC (mg/dm^3) Fish	91
7	Dwell time DT_{50} (d)	38.4
8	Soil adsorption coefficient, Kfoc (cm^3/g)	1367–2339
9	Effective concentration EC_{50} (mg/ dm^3)	96
10	The depuration half-life CT_{50} (d)	1.7

Table 3. Optimized LC-MS/MS analyzed herbicide [24]

Herbicide	Retention time (min)	Quantitative/qualitative determination			Qualitative determination			DP (V)	EP (V)
		Fragmentation reaction (m/z)	CE (V)	CXP (V)	Fragmentation reaction (m/z)	CE (V)	CXP (V)		
Prosulfocarb	11.55	252.1 > 91	35	10	252.1 > 128.1	17	6	66	10

Table 4. Method validation characteristics [24]

Herbicide	R^2	0.001		0.05		0.5		10.0		100.0		U	ME
		mg/L											
		R	RSD	R	RSD	R	RSD	R	RSD	R	RSD		
		%											
Prosulfocarb	1.00	97	10	96	6	99	6	102	13	104	5	13	12

The dynamics of prosulfocarb degradation in wastewater without biopreparation (PRO) and fed with biopreparation (PRO-MIK) were presented in the form of a single first-order (SFO) reaction kinetic equation by nonlinear estimation method (C_t – concentration in time t, (mg/dm^3), C_0 – initial concentration in time $t = 0$, (mg/dm^3), t – duration of the experiment (d), k – constant process rate (1/d)):

$$C_t = C_0 \cdot exp\ (-k \cdot t) \qquad (1)$$

Based on the value of the constant process rate k [1/d], DT_{50}, defined as the time required for 50% of the mass of the herbicide to disappear, was calculated. Values of DT_{50} [d] for experimental conditions were calculated using the formula:

$$DT_{50} = ln\ (2)/k \qquad (2)$$

Assuming the values of the final concentrations of C_t at 0.05 mg/dm^3 and 0.01 mg/dm^3, theoretical prosulfocarb disappearance times $t_{0.05}$ [d] and $t_{0.01}$ [d] were calculated based on the transformation of the mathematical Equation 1. Meanwhile, the change in prosulfocarb mass reduction efficiency values η_r [%] without addition of the

PRO and fed with the biopreparation (PRO/MIK) after flowing through the hydrophytic bed at different times t [d] was described by analytical-empirical mathematical equations of the form:

$$\eta_r = a_1 \cdot t/(1 + a_2 \cdot t) \tag{3}$$

where: a_1, a_2 – coefficients (–), t – duration of the experiment (d).

The quality of the obtained estimation and approximation equations is presented using the coefficient of determination R^2.

RESULTS AND DISCUSSION

Prosulfocarb was dosed at 53.3 mg/dm^3. Samples were then taken periodically and subjected to chromatographic analysis.

For the CWS bed without biopreparation addition, the prosulfocarb concentration in the treated wastewater after 24 hours was at 38.133 mg/dm^3. On the next day, the concentration decreased by 17 to 21.164 mg/dm^3 (Figure 2), and on the next day to 16.351 mg/dm^3. After one week the concentration of the prosulfocarb was 6.325 mg/dm^3, and after two weeks it was 2.165 mg/dm^3. After 24 days, the prosulfocarb amount reached 0.075 mg/dm^3. The herbicide was not detected after 42 days. The initial disappearance of the herbicide was slightly faster when the biopreparation was applied. On the first day, the prosulfocarb concentration decreased by 41% (30.487 mg/dm^3), while on the next day it decreased by 36 mg/dm^3, or as much as 70% (15.325 mg/dm^3). After one week the prosulfocarb concentration was 4.337 mg/dm^3, and after two weeks it was 0.778 mg/dm^3. After 24 days, the prosulfocarb amound was 0.024 mg/dm^3. The herbicide was no longer detected after 34 days. Prosulfocarb, an herbicide belonging to the thiocarbamate group, undergoes degradation processes upon entering the environment, resulting in the formation of various metabolites. Studies have indicated that the half-life (DT50) of prosulfocarb in soil ranges from 6.5 to 13 days under field conditions and from 6.3 to 40.3 days under laboratory conditions. This rapid degradation in soil is further confirmed by hydrophytic bed tests and the absence of Prosulfocarb metabolites in treated wastewater.

The mass reduction efficiency of prosulfocarb η_r [%] in treated wastewater without (PRO) and enriched with (PRO/MIK) biopreparation is shown in Figure 3. After the first day, there was a reduction in concentration in sewage without MIK and enriched with MIK by about 26% and 41%, and after the 2nd day by about 59% and 70%, respectively. By the 10th day, prosulfocarb concentration decreased by about 93% (without MIK) and 97% (with MIK). Complete degradation of prosulfocarb did not occur until after 42 days in wastewater without MIK and after 34 days in wastewater with MIK. The differences in biodegradation indicate

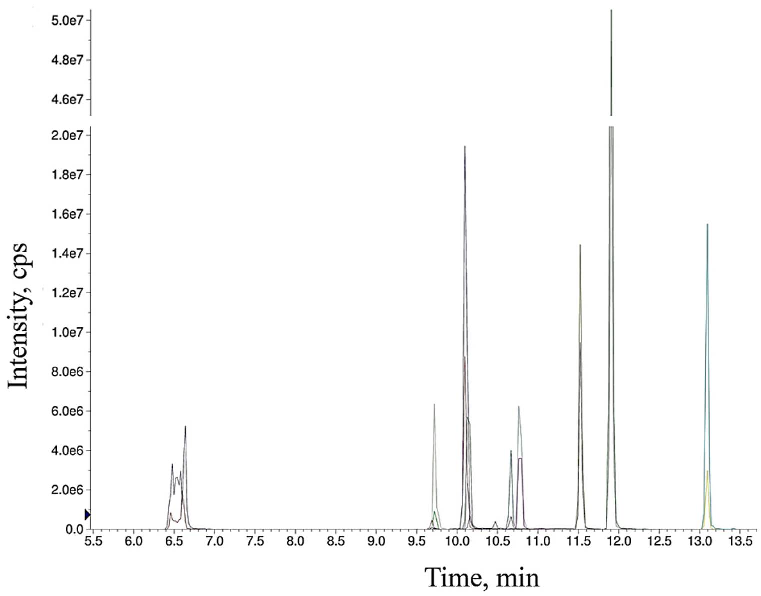


Figure 2. Dynamics curve of prosulfocarb disappearance without addition of PRO and fed with biopreparation (PRO/MIK) in hydrophytic bed at 14 days

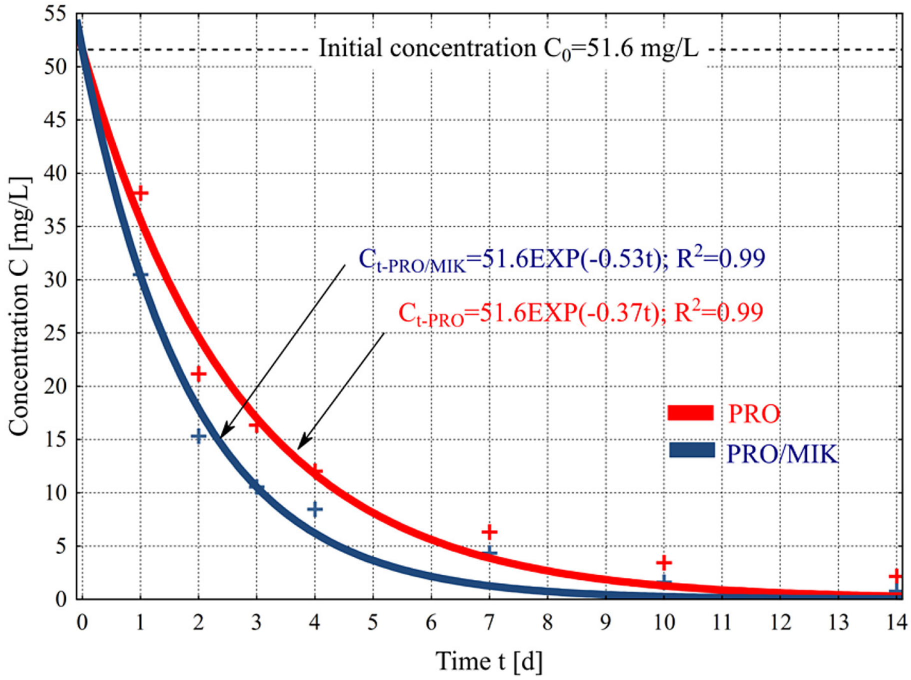


Figure 3. Degradation efficiency η_r [%] (A) and mass deposit m_{rp} [%] (B) of prosulfocarb without PRO and fed with biopreparation (PRO/MIK) in a hydrophytic bed at 40 days

the activity of microorganisms in the degradation of prosulfocarb. The authors [12-14] studied the degradation of chlorpyrifos in a hydrophytic bed with subsurface flow with common reed (*Phragmites australis*) and found that the average degradation effectiveness was 96.2%. The authors [7] confirmed the high degradation effectiveness of selected herbicides from fruit and vegetable industry wastewater in a bed populated with common reed (*Phragmites australis*) with subsurface horizontal flow. The pesticides azoxystrobin, boscalid, epoxiconazole, fenarimol, fenazaquin, nicosulfuron, procymidone, pyraclostrobin, thiachloprid and trifloxystrobin at an increasing CWS bed load of 0.01, 0.02 and 0.03 $m^2/m^2/d$ degraded at an average rate of 99.8%.

The selection of the SFO model for determining the half-life of prosulfocarb was based on available literature sources, including Gajbhiye et al. [25], which describe herbicides as biodegradable chemical substances that can be modeled using a first-order mathematical equation. The use of models of greater complexity most often results in the introduction of significant limitations and large uncertainties. Based on laboratory results, the values of the k-factor (Equation 1) were calculated. The correctness of the first-order kinetic reaction equations model is confirmed by the high value of the determination coefficients $R^2 = 0.99$. Based on the literature data, a comparable reaction order value in their studies has likewise been documented by other researchers, including Fenoll et al. [20]. Based on the change in prosulfocarb concentration values, their DT_{50} half-lives were determined for the various conditions considered.

Figure 4 illustrates the degradation dynamics of prosulfocarb in sewage samples that have been subjected to a hydrophytic bed, with and without the presence of PRO. The samples are categorized as either "without added biopreparat" (PRO) or "enriched with biopreparat" (PRO/MIK). The value of the process rate constant k [1/d] in the pesticide degradation dynamics Equation 1 was calculated in Statistica software using Gauss-Newton nonlinear estimation.

The equation $C_{t\text{-PRO}} = 51.6 \cdot \exp(-0.37 \cdot t)$ describes the dynamics of prosulfocarb degradation without microorganisms, while the relationship $C_{t\text{-PRO/MIK}} = 51.6 \cdot \exp(-0{,}53 \cdot t)$ represents the dynamics of degradation in prosulfocarb enriched with microorganisms. According to the values of the determination coefficients, R2 is equivalent to 0.99, it can be concluded that there is a strong functional relationship between the analyzed independent and outcome variable parameters. Based on Formula 2, the calculated half-lives of prosulfocarb DT_{50} are 1.87 days without the

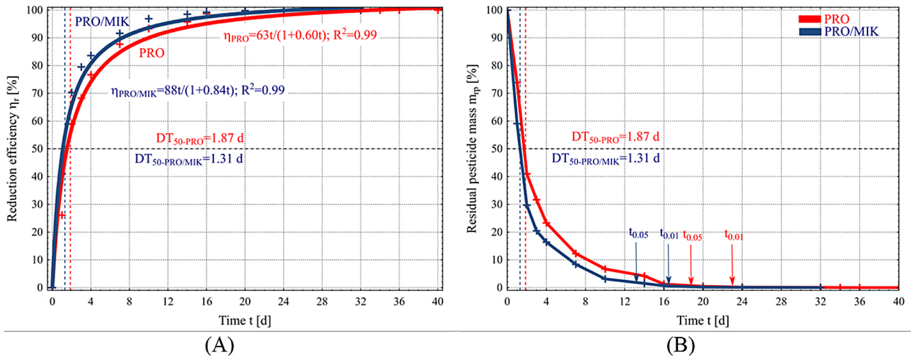


Figure 4. Chromatogram of a herbicide with a c = 0.50 mg/dm³

addition of microorganisms and 1.31 days after the addition of microorganisms. In wastewater fed with biopreparation, prosulfocarb will reach a concentration value of 0.05 mg/dm³ in a theoretical time of 13 days, which is about 6 days faster compared to the sample without the addition of biopreparation. In contrast, prosulfocarb will attain a concentration value of 0.01 mg/dm³ without the addition of the biopreparation after 23 days and with the addition of the biopreparation after 16 days, respectively (Table 5).

Carbamate herbicides, which include prosulfocarb, can affect the hormonal system of living organisms. There are no reports in the literature on the effectiveness of degradation of carbamates from wastewater by hydrophytic methods. The goal of this study [27] was to assess the impact of leaching prosulfocarb through packed soil columns under various conditions: applying green compost as an organic amendment (20% w/w), subjecting the pesticide to a 28-day incubation period in soil (with vs. without incubation), and implementing two distinct irrigation regimes (saturated and saturated-unsaturated flows). The results indicated that pesticide incubation in the columns led to reduced peak concentrations in both amended and unamended soils across both flow regimes. Additionally, leached quantities decreased after a 28-day pesticide incubation, with reductions of 2.1 and 1.9 times in S soil, and 2.9 and 1.6 times in S + GC soil, under saturated and saturated-unsaturated flow conditions, respectively.

In their seminal study, Kahle et al. [28] investigated the presence and transformation of certain azole fungicides, utilized as biocides and pharmaceuticals, in wastewater treatment facilities and surface waters in Switzerland. They detected these pesticides in influent wastewater at concentrations ranging from 10 to 110 ng/dm³. Subsequent analysis of both untreated and treated wastewater revealed that fluconazole, propiconazole, and tebuconazole demonstrated minimal sensitivity to the treatment processes, while clotrimazole exhibited a substantial reduction of 80%. In our own research, we observed the degradation and significant sorption of prosulfocarb, with a calculated half-life for its degradation of 1.87 and 1.31 days. The estimated time for the herbicide to reach a concentration of 0.01 mg/L was approximately 23 and 16 days, respectively. Notably, more than 50% of the initial prosulfocarb mass was removed within a single day, and over a 10-day period, degradation exceeded 90%.

Table 5. Parameters of degradation curves and prosulfocarb degradation efficiency in wastewater treated on bed without PRO and fed with biopreparation (PRO/MIK)

No.	Parameter	Symbol	Unit	Prosulfokarb	Prosulfokarb/MIK
1	Initial concentration	C_0	mg/dm³	51.6	51.6
2	Process rate constant	k	1/d	0.37	0.53
3	Half-life	DT_{50}	day	1.87	1.31
4	Time of reaching concentration 0.05 mg/L	$t_{0.05}$	day	19	13
5	Time of reaching concentration 0.01 mg/L	$t_{0.01}$	day	23	16
6	Reduction efficiency equation	η_r	%	η_r = 63t/(1+0.6t)	η_r = 88t/(1+0.84t)

CONCLUSIONS

A comprehensive review of the extant research in this field suggests the following conclusions:

1. Hydrophytic beds can be used with great success to decompose prosulfocarb applied for spraying agricultural crops. Full reduction of the discussed herbicide was obtained after 34 days for MIK and 42 days without MIK.
2. The employment of a three-layered filtration system, comprising granulometrically differentiated and chemically inert materials, ensured an appropriate permeability coefficient, thereby facilitating high treatment efficiency. Over the course of the experimental period, the wastewater entering the bed underwent effective treatment.
3. The herbicide group under study attained a reduction rate that exceeded 90%.
4. The determined half-lives of prosulfocarb in DT_{50} wastewater were 1.31 for MIK and 1.87 without MIK.
5. The theoretical times for reaching a level of 0.05 mg/dm³ ($t_{0.05}$) determined from the obtained equations were 13 days for MIK and 19 days without MIK, while the concentration of 0.01 mg/dm³ ($t_{0.01}$) was 16.

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