



DEGRADATION OF IMAZAPYR AND IMAZAPIC IN AQUEOUS SOLUTIONS AND SOIL UNDER DIRECT SUNLIGHT

(Degradasi Imazapyr dan Imazapic dalam Larutan Aqueus dan Tanah di bawah Cahaya Matahari)

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Abstract

Photolytic degradation of imazapyr and imazapic in aqueous solutions (pH 3, 7 and 9) and soil under direct sunlight were studied. A total of 0.1 mL of aqueous solutions containing herbicides were collected at 0, 1, 2 and 3 days and were directly analyzed using high performance liquid chromatography equipped with ultraviolet detector (HPLC-UV) without further clean-up process. Soils that were treated with herbicides were sampled at seven different days (0, 1, 5, 10, 16, 23 and 30). The photolytic results showed that imazapyr and imazapic degraded faster in solutions compared to soils (> 90%). Photolysis of imidazolinone herbicides became more effective as the pH value increased. The half-lives for imazapyr and imazapic degradation on soil surface under sunlight were calculated at 126 days and 85.56 days, respectively. Low degradation of imazapyr and imazapic in soil becomes a concern since it may contribute to the persistency of imidazolinone herbicides in this media. The use of these herbicides should be planned well to reduce the risk of herbicides leaching into groundwater and posing risk to non-target crops and organism.

Keywords: photolysis, imazapyr, imazapic, aqueous solutions, soil

Abstrak

Kajian degradasi fotolitik bagi imazapyr dan imazapic dalam larutan akueus (pH 3, 7 dan 9) dan tanah di bawah cahaya matahari telah dijalankan. Sebanyak 0.1 mL cecair larutan yang mengandungi racun rumpai telah diambil pada hari 0, 1, 2 dan 3 dan terus dianalisis menggunakan kromatografi cecair berprestasi tinggi dengan pengesan ultra-ungu (HPLC-UV) tanpa melalui sebarang proses pembersihan. Tanah yang telah dicampurkan dengan racun rumpai telah disampelkan pada tujuh hari yang berbeza (0, 1, 5, 10, 16, 23 dan 30). Keputusan fotolitik menunjukkan imazapyr dan imazapic lebih cepat terurai di dalam cecair berbanding dengan tanah (>90%). Fotolisis racun rumpai imidazolinon adalah lebih berkesan apabila pH meningkat. Jangka masa separuh hayat untuk imazapyr dan imazapic terurai di permukaan tanah di bawah cahaya matahari masing-masing adalah 126 dan 85.56 hari. Degradasi rendah bagi imazapyr dan imazapic dalam tanah telah menjadi suatu kebimbangan kerana ia boleh menyumbang kepada pengekalan racun rumpai imidazolinon di dalam media ini. Penggunaan racun rumpai ini perlu dirancang dengan sebaiknya bagi mengurangkan risiko untuk racun larut terlesap ke dalam air bawah tanah dan menimbulkan risiko kepada tanaman dan organisma yang bukan sasarannya.

Kata kunci: fotolisis, imazapyr, imazapic, larutan akueus, tanah

Introduction

As one of the main contributors to Malaysian economy, the agriculture sector takes up a major part of the land used in this country [1]. Additionally, Malaysian government has invested millions of ringgit to ensure this sector is well developed and this includes introducing modern agricultural input such as herbicides [2]. This contributes to the increase of herbicide application in Malaysian agricultural areas [1]. Herbicide is the most common method used to prevent or control the unwanted weeds in agricultural areas. Not only that, it is also used to maintain the quality of crops and reduce the percentage of yield losses [2]. Some common examples of herbicides are 2,4-D dimethylamine, paraquat, glyphosate and propanil [1]. However, the use of herbicide is harmful in certain quantities as some herbicides may leach into the root zone once they are introduced into the environment. Consequently, this can either result in better weed control or cause damage to surrounding environment as not all of the applied chemicals are able to reach the target site [3]. Therefore, it is very important to understand the fate of the chemicals in the environment.

Currently, commercial herbicides containing two active ingredients (imazapyr and imazapic) are widely used in rice field area to control the growth of weedy rice [4, 5]. The growth of weedy rice in rice field affects the annual rice yield in Malaysia [2, 6] and this contributes to economic loss among farmers [3]. Thus, the combination of imidazolinone-tolerant rice (IMI-TR) seeds developed by MARDI and BASF (Malaysia) with a single application of imazapyr/ imazapic in rice field area [4, 5] are found to be able to reduce weed management cost and yield higher quality of rice [6]. Imazapyr and imazapic belong to imidazolinone group that can eliminate subjected weeds by inhibiting the action of plant enzyme acetohydroxyacid synthase (AHAS) and interfering with their growth [7, 8].

The applications of imidazolinone herbicides are assumed to be environmentally safe because of their low toxicity effects on mammals as well as being highly effective with a very low application rate [4, 9, 10]. This in turn reduces the amount of herbicides released into the environment and ecosystem [6]. However, the application of herbicides in rice field for a long period of time may give rise to several environmental issues. One of the environmental concerns is the persistency of imidazolinone herbicide in soil [11 – 14] and groundwater [15]. Since these herbicides are able to remain for a long period of time in the environment, it may pose risks to non-target organisms such as fish [16, 17].

There are many factors affecting the persistency of herbicides molecule in the environment and these may include sorption, volatilisation, leaching and degradation (abiotic and biotic) [3, 14]. Photodegradation may play an important role for the breakdown of herbicides in environment because all pesticides are susceptible to this process to a certain degree [3]. Since imazapyr and imazapic are applied to foliage or soil surface, they are more prone to break down by sunlight [3]. Therefore, the aims of this study were to determine the capability of imazapyr and imazapic herbicides to break down under direct sunlight as well as to calculate their half-life in aqueous solutions and soil surface.

Materials and Methods

Chemicals

Imazapyr and imazapic with 99.5% and 99.9% purity respectively were purchased from Active Advance Technology Company. Acetonitrile (ACN) grade for liquid chromatography (LC), acetic acid, monopotassium phosphate and sodium hydroxide (NaOH) were obtained from Merck (Malaysia). Potassium biphthalate, borax and hydrochloric acid (HCl) were purchased from Juara Saintifik (Malaysia). Imazapyr and imazapic solutions were prepared by dissolving the weighed herbicide in ACN.

Preparation of buffer solutions

Three different buffer solutions (pH 3, 7 and 9) were prepared based on United States Environmental Protection Agency's (USEPA) Fate, Transport and Transformation Test Guidelines [18]. The buffer solutions were prepared by mixing 0.1N HCl with 0.1M potassium biphthalate (pH 3); 0.1N NaOH with monopotassium phosphate (pH 7); and 0.025 M borax with 0.1N HCl for pH 9. All buffers solutions and glassware used in this experiment were sterilised by using autoclave [9].

Photolysis of imazapyr and imazapic in aqueous solutions

Outdoor photodegradation experiments for imazapyr and imazapic in aqueous solutions and soil were conducted in greenhouse at Universiti Teknologi MARA Puncak Alam Campus. The photolysis activity was tested for individual and mixture of the herbicides using USEPA protocol [19]. All three prepared buffer solutions were then treated with herbicide solution in order to obtain $10 \mu\text{g mL}^{-1}$ of imazapyr and imazapic concentration respectively as well as a mixture of imazapyr and imazapic in the ratio of 1:3. 10 mL buffered solutions of herbicide (pH 3, 7 and 9) were placed in three different sterilized glass test tubes before being exposed under sunlight. All these solutions were prepared in triplicate along with two control samples. The average temperatures during experimental days were varied between 26°C to 36°C . The sunlight intensity was also measured during the exposure. An amount of 0.1 mL of aliquots was pipetted aseptically from each test tube on day 0, 1, 2 and 3 into 2 mL amber vials for further analysis with High Performance Liquid Chromatography (HPLC) [20].

Photodegradation of imazapyr and imazapic on soil

For this research, the study of photodegradation on soil surface was carried out in reference to USEPA Guideline [21]. A soil sample was collected from the surface layer (0 to 10 cm) from the field. The sample was air-dried at room temperature, passed through 2 mm sieve and was later autoclaved at 121°C twice [9]. An amount 5 grams of sterilized soil was weighed into sterile petri dish and herbicide solution was applied on the top of spread soil to obtain the initial concentration of $5 \mu\text{g g}^{-1}$. For control samples, the petri dishes containing soil-herbicide were wrapped with aluminum foil to keep out light and maintain darkness. The samples were exposed to the sunlight and then were collected at 0, 1, 5, 10, 16, 23 and 30 days. Three exposed and control samples were sampled for each sampling day and transferred into sterile centrifuge tube for herbicides extraction. Herbicides were extracted from the soil samples by shaking 20 mL of 0.5 M NaOH and centrifuging at 2000 rpm for 10 minutes. These steps were repeated twice. The decanted supernatants were filtered through $0.45 \mu\text{m}$ filter and were analyzed directly using HPLC [20].

HPLC analysis

An Agilent 1200 High Performance Liquid Chromatography equipped with UV detector was used for quantification of imazapyr and imazapic residues [20]. The wavelength for the detector was set up at 251 nm. ACN: acidified water (pH 2.88) (35:65, v/v) was used as mobile phase with flow rate of 1.0 mL min^{-1} while for chromatography, An Agilent Zorbax SB-C18 column (4.6 mm i.d. x 250 mm, $5 \mu\text{m}$) was used.

Data analysis

The percentages of imazapyr and imazapic degradation were calculated using equation 1 [22]:

$$\text{Photodegradation (\%)} = (C_0 - C_t)/C_0 \times 100\% \quad (1)$$

Calculations for imidazolinone herbicides half-life were performed using kinetic equation 2 and 3, respectively [9, 19, 23]:

$$\ln(C_0/C_t) = kt \quad (2)$$

$$t_{1/2} = 0.693/k \quad (3)$$

where, C_0 refers to the initial concentration of herbicide, C_t represents the herbicide concentration at time t , k is photolytic rate constant, and $t_{1/2}$ exemplifies the half-life.

Results and Discussion

Photolysis of imidazolinone herbicides in aqueous solutions

The results for degradation of imidazolinone herbicides in aqueous solutions were shown in Table 1. These findings suggested that both imazapyr and imazapic herbicides were able to completely degrade ($> 90\%$) within 72 hours under direct sunlight (light intensity ranged 162 to 1059 watt/m^2). The half-life values of imazapyr under direct sunlight were 16.54 hours (pH 3), 12.42 hours (pH 7) and 12.18 hours (pH 9). Imazapic was found to have half-lives of 32.35 hours, 10.06 hours and 10.76 hours in pH 3, 7 and 9, respectively. Trials on combination of both

herbicides under acidic pH level showed that imazapyr was completely degraded within 24 hours while imazapic residue was calculated at 20.94 percent within 72 hours.

Table 1. Photolysis of imidazolinone herbicides under direct sunlight in buffer solutions

Sampling Days		Percentage of Residues (%)								
Herbicide		Imazapyr			Imazapic			Imazapyr: Imazapic (1:3)		
pH solution		3	7	9	3	7	9	3	7	9
0		100	100	100	100	100	100	100:100	100:100	100:100
1		65.87	23.73	23.69	55.89	17.42	17.09	0:51.76	25.29:16.80	26.03:17.39
2		15.98	5.01	4.09	28.83	5.91	2.10	0:30.29	4.04:2.16	4.74:2.74
3		4.89	1.80	1.67	21.38	0.72	0.97	0:20.94	1.39:0.88	1.68:1.08

Results presented in Table 1 suggested that pH values of buffer solutions affected the photolysis rate for imazapyr and imazapic. Degradation rate of imidazolinone herbicides tested increased as pH increased, which was in agreement with previous studies [23, 24, 25]. This might be due to the effect of higher molar absorption coefficients at higher pH value [24]. Imazapyr and imazapic herbicides were more rapidly degraded in solution compared to on soil surface (Table 1 and Table 2). However, the photolysis rate of imidazolinone herbicides in actual water samples might be slower due to the presence of light screening compounds such as humic acid and natural organic matter (NOM) [3, 26].

Photodegradation of imidazolinone herbicides on soil

The percentages of photodegradation of two imidazolinone herbicides were tabulated in Table 2. Imazapic had a higher degradation rate ($t_{1/2}$ = 85.56 days) compared to imazapyr ($t_{1/2}$ = 126 days). The ability of these herbicides to remain longer might be due to the properties of the soil itself which absorbed the photons, therefore reducing the availability of photons to degrade the herbicides compounds [9, 27]. Previous study showed that imazapyr and imazapic had an enhanced adsorption and a lower desorption in rice field soil due to the presence of high clay content and organic matter [28], especially at low pH value. The soil sample used consisted of 57.50% clay, 37.50% silt, 0.90% sand, 4.26% total organic carbon and a pH of 5.29. Since the soil sample used in this study had the properties of high clay content and organic matter which were similar to a previous study [28], it suggested that these two imidazolinone herbicides were tightly bound to soil particles. This indicated that very little of these compounds were available for degradation via photolytic activity. Moreover, air-drying step of soil sample preparation in this study might cause an increase in soil-herbicide binding as the soil water content decreased [27]. Once the herbicides penetrated underneath the soil surface, the photodegradation activity became low [27] and this might contribute to their persistency in the environment. Since imazapyr and imazapic were able to remain longer in the soil, these herbicides also had a higher probability to leach into groundwater as reported previously [14, 29].

Table 2. Photodegradation of imidazolinone herbicides on soil exposed with direct sunlight

Sampling Days		Percentage of Residues (%)		
Herbicide		Imazapyr	Imazapic	Imazapyr: Imazapic (1:3)
0		100	100	100: 100
1		98.24	92.77	98.69: 97.07
5		96.99	90.88	95.25: 94.20
10		94.52	87.66	93.58: 93.25
16		93.18	83.03	91.30: 92.01
23		92.04	81.03	87.73: 83.53
30		84.75	78.40	78.12: 81.16

Conclusion

Photodegradation of imidazolinone herbicides could be an important factor for their breakdown in the environment as demonstrated in the tabulated results. Degradation of imazapyr and imazapic in aqueous solutions were faster compared to on soil surface under direct sunlight. Low photolytic degradation in soil became a concern since it might pose risk to non-target crops and organisms. Further study on biotic degradation might expand new angle in this field since microbe could be used as a degrading organism to break down imidazolinone herbicides, especially under anaerobic condition. The approach in this paper could be taken as a general applied method to analyses other degraded pollutants, especially those that had similar functional group.

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