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Effect of Temperature and Ionic Strength on Adsorption-Desorption Behaviour of Penoxsulam on Six Soils

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In the present study adsorption-desorption behaviour of penoxsulam on six different Indian soils at different temperatures (15, 25 and 35^{0}C) and varied ionic strengths (0.003 and 0.03M) was investigated to evaluate the effect of penoxsulam adsorption and desorption in varied soils. An increase in temperature decreased the adsorption but increased desorption of the herbicide in soils whereas on increasing the ionic strength adsorption increased effectively and desorption decreased from soils. Alkaline and neutral soils (JK-1, BD-2 and HLD-2) showed significant difference in adsorption whereas in acidic soils (LOH, HLD-1 and BH-1) this difference was only minor. Adsorption-desorption data showed statistically significant difference ($p \leq 0.05$) at different temperatures. An increase in ionic strength showed significant difference in adsorption of the neutral and basic soils (JK-1, BD-2 and HLD-2) but in acidic soils (LOH, HLD-1 and BH-1) this difference in adsorption was minor, though desorption depicted statistically significant difference ($p \leq 0.05$) in all the six soils.

Introduction

Pesticides have contributed tremendously towards increasing food production worldwide but the excessive use of pesticides has become a major topic of concern as it has ultimately ledto several environmental issues (Capel *et al.*, 1995; Torrents *et al.*, 1997). Rice food crop contributes around 21% of the world's food supply with Asia alone producing 90% of it. This has resulted in increased utilisation of various herbicides for weed control and is therefore frequently found in surface and ground water (Subhani *et al.*, 2000). Herbicides are a major group of pesticides widely used to amplify the production of crops by deteriorating the growth of weeds and minimizing farmers toil. Weeds show extremely high persistent level with 10-15% reduction in production of rice annually in Asian countries.

At present herbicides having high efficiency are gaining interests as usage of lower dose is sufficient resulting in decreased volume of herbicides utilization (Kathiresan, 2001).

Dow Agro Science in the year 2003, introduced penoxsulam [3-(2,2-difluoroethoxy)-N-(5,8 dimethoxy [1,2,4] triazolo [1,5-c] pyrimidin-2-yl)-α,α,α-trifluorotoluene-2-sulfonamide], in Chile as a rice herbicide.

Penoxsulam activity as a post emergence herbicide against annual and perennial board-leaved weeds in rice crop was excellent (Roberts *et al.,* 2003). *Echinochloa crusgalli*, *E. colona*, *Ammania baccifera* and *Cyperus sp.* were some of the most prominent weeds which were efficiently treated by applying appropriate dose of penoxsulam. Recommended dose as a pre-emergence and post-emergence herbicide was 25g/ha (3 DAT) and 20.0-22.5 g/ha (10-12 DAT) respectively (Yadav *et al.,* 2008). Penoxsulam as compared to other herbicides is comparatively mobile in aqueous medium and therefore shows lower persistence level.

The nature of the pesticides in soil is chiefly governed by adsorption-desorption phenomenon (Gao *et al.,* 1998; de Jonge and de Jonge, 1999) and their behaviour in the environment is influenced by the state variables of the region.

The present study was therefore undertaken to investigate the adsorption-desorption behaviour of penoxsulam on different soils with temperature and ionic strength as two different variables.

Materials and Methods

Experimental Methods

Analytical grade penoxsulam (white crystalline solid, purity 99%) was obtained from Dow Agro Science India Pvt. Ltd. Company, Mumbai, India. All the chemicals used in the study were of analytical or HPLC grade. Six surface (0.25 cm depth) soils, namely soil (HLD-1 and HLD-2) from Haldwani, (JK-1) from Joelikot and (LOH-5) from Lohaghat in Uttarakhand and Budaun (BD-2) and Baheri (BH-1) in Uttar Pradesh were collected from different regions of India. Soil samples were dried crushed and passed through a 2mm sieves and analysed using standard methods.

Effect of temperature on adsorption-desorption of penosxulam

To see the effect of temperature on adsorption-desorption of penoxsulam in soils studies were conducted at three different temperatures (15, 25 and 35°C). 2gm soil was taken in thirty-six centrifuge tubes. Then, 0.1M of 1ml $CaCl_2$ and 1ml of 40 ppm penosxulam were added to the centrifuge tubes. The volume was made up to 20ml by adding double distilled water . The resultant solutions were shaken at three temperatures (15, 25 and 35°C) for 24 hours in duplicate. The quasi-steady equilibration time of penoxsulam in soils was determined earlier and was found to be 24 hours at 120 rpm. Hence the same equilibration time was observed in the present study. The contents were further centrifuged at 6000 rpm for 10 min. From clear supernatant, penoxsulam was extracted by modified QuEChER'S method (Monika *et al.,* 2017). The clear supernatants were analysed by High Performance Liquid Chromatography (HPLC). For desorption study, 0.1M of 1ml $CaCl_2$ was added to the pellet retained after the removal of supernatant and the volume was made up to 20ml by addition of double distilled water. The suspensions were equilibrated for 24 h at 120 rpm and centrifuged at 6000 rpm for 10 min. The clear supernatants were obtained and analysed as mentioned for adsorption study.

Effect of ionic strength on adsorption-desorption of penoxsulam

The effect of ionic strength on adsorption-desorption of penoxsulam was also examined by taking 2gm soil in twenty-four centrifuge tubes. One ml of stock solution of penoxsulam (40 mg/l) and different volumes of 0.1M $CaCl_2$were added to get the ionic strength of 0.003 and 0.03 respectively. Final volume was made up to 20ml by adding requisite amount of double distilled water. The resultant solutions were shaken for 24 hours at 120 rpm in duplicate. The contents were centrifuged for 6000 rpm for 10 min. From clear supernatant, penoxsulam was extracted by QuEChER'S method. The clear supernatants were analysed by HPLC. Desorption experiment was done at different ionic strength as stated above for temperature.

HPLC estimation of penoxsulam analysis

The quantitative analysis of penoxsulam solutions was done by using DionexUtimate 3000 HPLC containing C18 column, (250 x 4.6 mm i.d., 5µm) under isocratic mode with acetonitrile (100%) as mobile phase at a flow rate of 1 ml min^{-1} and UV detection at 310 nm. The retention time of penoxsulam was 4 min under the above conditions.

Results and Discussion

In general among the various physicochemical properties of soil shown in table 1, correlation with pH depicted that out of the six soils, three soils (LOH-5,HLD-1 and BH-1) were acidic, one soil (HLD-2) was almost neutral and two soils (BD-2 and JK-1) were basic in nature. In general the extent of adsorption both in case of temperature and ionic strength was higher in case of acidic soils as compared to neutral soil followed by the two basic soils.

Effect of temperature

Temperature variation affected the sorption-desorption of penoxsulam to a great extent. Increase in temperature significantly decreased the adsorption on each of the six soils. The extent of adsorption of penoxsulam in six soils followed the order LOH-5>HLD-1> BH-1>HLD-2>JK-1>BD-2 at all the three temperatures. The maximum adsorption was at 15°C followed by 25 and 35°C but desorption increased with increase in temperature and the difference was significant at $p \leq 0.05$ (Figure 1). Out of the six soils adsorption on the three acidic soils (BH-1, HLD-1 and LOH-5) was higher as compared to basic soils (HLD-2, BD-2 and JK-1) as is evident from Figure 1. Among the various soil properties the adsorption of penoxsulam showed strong correlation with soil pH (Table 1). At near-neutral pH, penoxsulam exists as an anionic species, presumably due to the deprotonation of sulfonylamido group. At lower pH the ratio of neutral species is more than the anionic species resulting in lower solubility and lower mobility in soil (Jabusch, 2005; Alister *et al.*, 2010). Soil LOH-5, with pH value of 5.36, showed maximum adsorption and minimum desorption whereas soil BD-2 having a pH value of 8.71 showed minimum adsorption and maximum desorption of penoxsulam at all the three temperatures (Figure 1). In addition to pH, lower organic content (5.94 g/kg) of BD-2 soil also attributed towards lower adsorption. The increase in temperature resulted in decrease in adsorption and increase in desorption which can be attributed to the decrease in the force of attraction between the sorbate and the sorbed phase.

Table.1 General properties of soil samples

Soil Properties							
Soil sample	**Mechanical analysis**			**Soil textural class**	**pH**	**EC (dSm^{-1})**	**OC ($g\ kg^{-1}$)**
	Sand (%)	**Silt (%)**	**Clay (%)**				
JK-1	13.6	42	44.2	silty clay	7.88	0.377	20.65
BD-2	38.0	36	25.9	loam	8.71	0.228	5.94
HLD-2	30.4	37	32.6	clay loam	6.83	0.239	10.87
BH-1	20.8	40	39.2	clay loam	6.48	0.135	39.92
HLD-1	48.4	25	26.6	sandy clay loam	6.19	0.118	8.96
LOH-5	15.6	38	46.4	clay	5.36	0.927	13.91

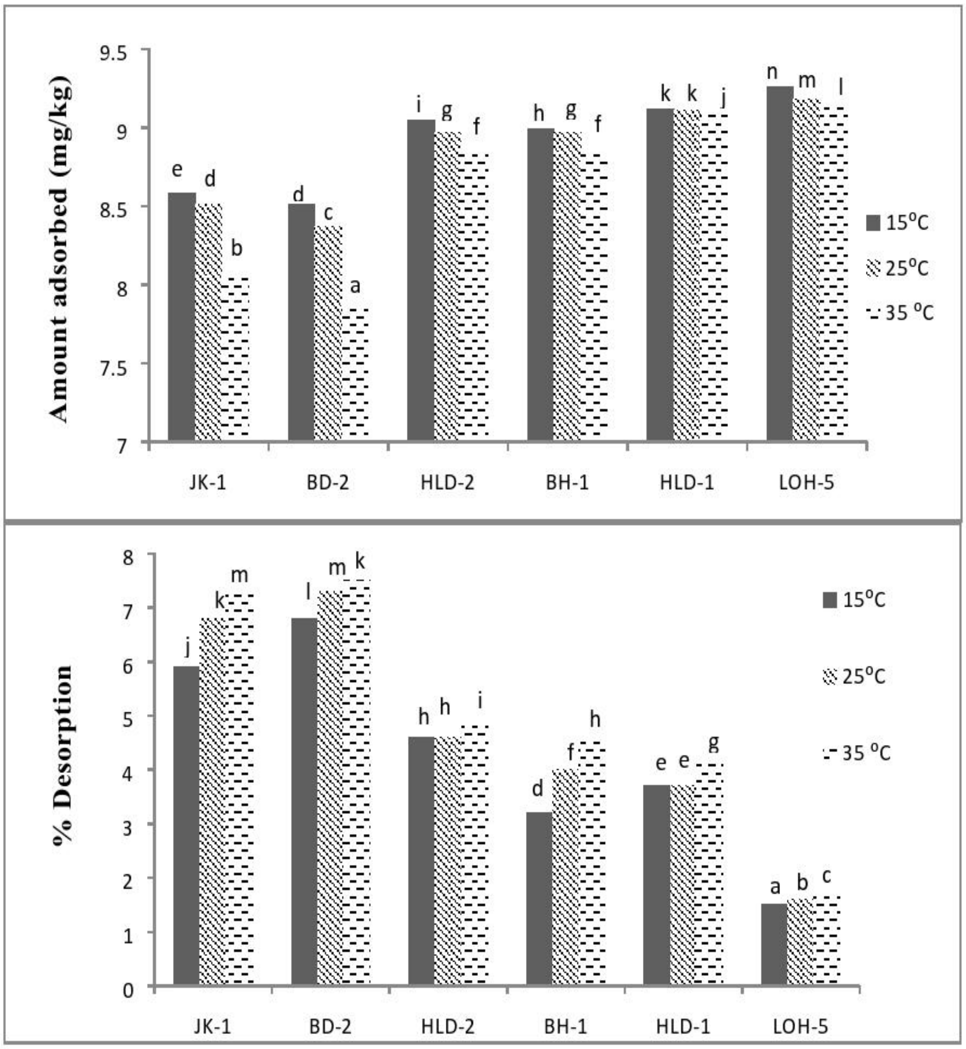

Fig.1 Penoxsulam adsorbed onto six soils and % desorption over a range of temperatures. Dissimilar letters over the histograms indicate statistically significant differences at $p \leq 0.05$.

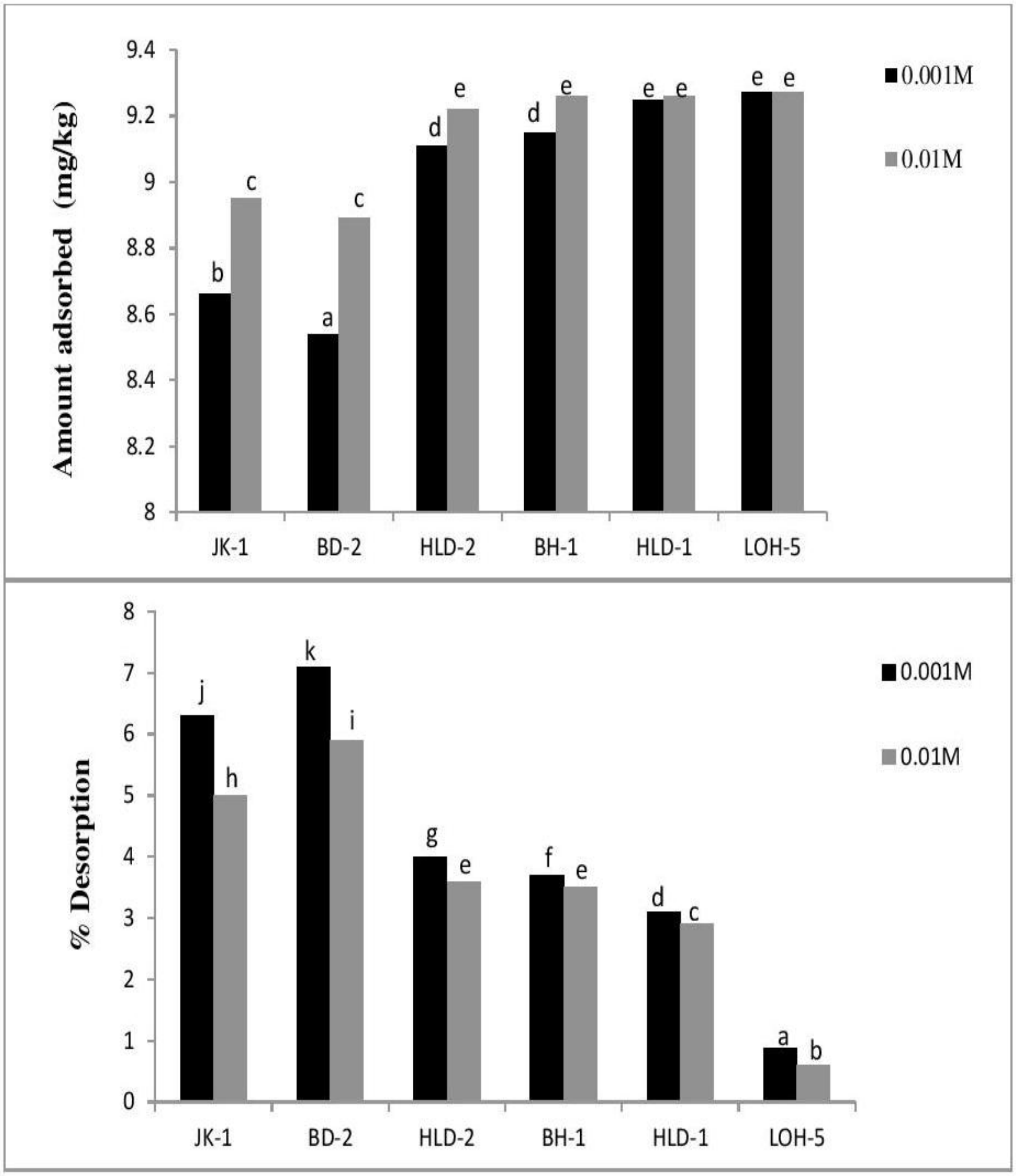

Fig.2 Penoxsulam adsorbed onto six soils and % desorption at two different ionic strength. Dissimilar letters over the histograms indicate statistically significant differences at $p \leq 0.05$.

Thus, penoxsulam can contaminate surface and ground water at high temperatures (above 35°C) due to lower adsorption and higher mobility in soils.

The trend basically predicts that the process is exothermic with involvement of physical forces in nature. Yaron and Saltzman (1972) reported the adsorption of parathion on soil at three different temperatures (10, 30 and 50°C). The adsorption was maximum at 10°C followed by 30 and 50°C. Rani and Sud (2015) also reported a similar adsorption-desorption trend of triazophos insecticide at 10, 20 and 40°C with maximum adsorption and minimum desorption at 10°C followed by

20 and 40°C.

Effect of ionic strength

An increase in ionic strength resulted in higher adsorption of penoxsulam on soils. As evident from Figure 2, increase in adsorption was significant for the alkaline soils but in case of acidic soils (LOH-5, HLD-1 and LOH-5), adsorption was only minor when the ionic strength was increased from 0.003 to 0.03. Similar letters in histograms of acidic soils (LOH-2, HLD-2 and BH-1) in case of adsorption show insignificant change at $p \leq 0.05$.However, the overall adsorption of penoxsulam in acidic soil was more which didn't increase much as ionic strength was increased. In case of alkaline soils dissimilar letters show significant change at $p \leq 0.05$. Desorption in case of all the soils decreased with increase in ionic strength with significant difference. This increase in adsorption with increase in ionic strength can be explained on the basis of the salting out phenomenon. The addition of salt affects the interaction, majorly electrostatic and H-bonding forces at the herbicide-soil interface. In the case of penoxsulam-soil interface the addition of divalent salt ($CaCl_2$) increased the availability of the vacant sites on the soil surface which were otherwise being occupied by the water molecules. The salt interacts with the water molecules thereby increasing the sorption rate. Hence soils of higher ionic strength can prevent leaching of penoxsulam herbicide and not lead to ground water pollution. Kyriakopoulos*et al.*, (2006) reported similar effects of ionic strength (0.01, 1 and 2M) on the adsorption of herbicides (Prometryn, Alachlor and Trifluralin) onamberlite XAD-4 polymeric resin. The adsorption increased significantly as the ionic strength increased with maximum at 2M concentration.

The adsorption-desorption of penoxsulam by soils is affected both by temperature and ionic strength. Adsorption was comparatively more on acidic soils than in basic soils. Increase in temperature decreased the adsorption whereas desorption was increased with increase in temperature. High temperature favours desorption of penoxsulam thereby making it highly mobile leading to surface and ground water contamination. On the other hand in all the six soils adsorption increased by increase in ionic strength but desorption decreased which can prevent leaching of penoxsulam to ground water. Thus, it can be recommended that penoxsulam herbicide applied in soils with higher ionic strength, at low temperature should not contaminate ground water.

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