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Sorption of Oxyfluorfen Herbicide in different type of soils

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Abstract: Agriculture is basically source of food and playsan important role in Indian Economy. India is the largest global producer of many crops like rice, wheat, cotton, pulses, peanuts, fruits and vegetables. The demand for food grain is increasing with the growing population. Many people including farmers or labors based on the agriculture for their employment. But Weeds are the major obstruction in agriculture which inhibit the growth of crops plant and also decrease the yield of crop. The use of herbicides is innovative approach for weed management and for improves the crop yield. Herbicides contribute about 8% of pesticides used in India. The herbicides contribute 45.2 % of the total pesticides consumption in Haryana representing the extensive adoption of herbicides in the state. Sorption (Kd 0.2 to 11.1 L/kg) of oxyfluorfen herbicide in soils following the order: Inceptisol> Alfisol> Entisol> Aridisol.Kd show direct relation with %OC present in soils ($p < 0.05$). Soils (In and Al) with high OC offered higher sorption than low OC soils (Ar and En).Kd had no relation with pH of different soils ($p > 0.05$). Although Kd of oxyfluorfen was correlated with EC of the different soils.

Keywords: Sorption, Oxyfluorfen Herbicide, soils

1. Introduction

AC is basically source of food and plays an important role in Indian Economy. India is the biggest global manufacturer of many crops like rice, wheat, cotton, pulses, peanuts, fruits and vegetables. The demand for food grain is increasing with the growing population. Many people including farmers or labours based on the AC for their employment. But Weeds are the

major obstruction in AC which inhibit the growing of crops plant and likewise decrease the yield of crop. The use of HBC is innovative approach for weed management and for improves the crop yield. HBC contribute about 8% of PTCs used in India. The HBC contribute 44.2 % of the whole PTCs consumption in Haryana representing the extensive implementation of HBC in the state. However, HBC have their own benefits and loss that we can't overlook. In intensive AC, the extreme use of HBC for weed management affected TS EVM by RD accumulation. These toxins contaminate the food matrix, drinking WR for humans and animals and also influencing the yield of the succeeding crop.

OFF (2-chloro-1-(3-EX-4-NP)-4-(TFM) benzene) stays a DPY ether HBC.

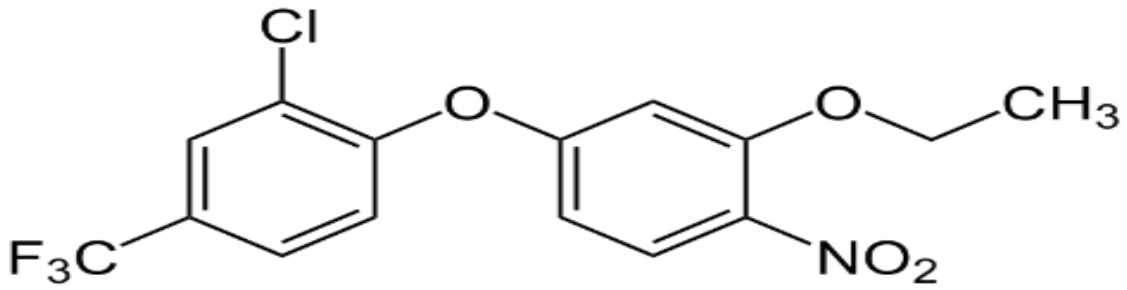

Fig. 1: Oxyfluorfen Herbicide

OFF is a pre- and post-emergence HBC which regulator the weeds in field crops. It is dark brown-yellowish semisolid at 25^0 C. It has very low aquatic solubility i.e. 0.1 mg/l at 25^0 C. OFF is broadly used to regulator broad-leaved weeds and grasslands in vegetables crops, onion, maize, soybeans, rice, carrot, fruit and other intensive yields. The research was done to see whether OFF would sorb or desorb on activated charcoal made from olive stones in the presence or absence of a surface-active agent. It was determined how the use of cationic, ionic, and non-ionic surfactants as well as contact time in an aqueous EVM affected the change in the elimination rate of OFF. In this study, SL was taken after the from DFF regions of Haryana (India) to evaluate HBC SP-DSP in SL. In Haryana, SLs are characterized in 4 major instructions viz. Entice, Inception, Arid sol and Alison.

Therefore, the contemporary research was commenced through following intentions:

- SP and DSP of HBC OFF HBC in Enisles, Inceptions, Arid sols and Alf sols SLs of Haryana.

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2. MATERIALS AND METHODS

The present search was aimed for estimating SP-DSP conduct of OFF HBC in four main SL orders viz. Enisles, Arid sols, Inceptions and Alf sols of Haryana.

➢ SL Samples

Four DFF type of SLs i.e. Aridisol (Ar), Entisol (En), Incept sol (In) and Alison (Al), representing variation in their physic-chemical characteristics such as OGN carbon, pH, EC texture etc. were collected at 0-15 cm depth from the following sites:

- Ar- Hisar, Haryana
- En- Rewari, Haryana
- In-Fatehabad ,Haryana
- Al- Karnal, Haryana

Fig. 2: Distribution of SL texture in Haryana

Preparation of SL sample

In laboratory, SLs stood air dried pulverized to fine precipitate, homogenized and processed by passing finished a 2mm size filter before characterization to remove the plant debris and other extraneous particle. These processed SLs were properly labelled and stored in polythene bags for further experiments.

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Table 1: Soil Analysis

Sr. No.	SL type/order	Proportion (%)			pH	EC	OGN carbon OC %
		Sand 0.04-2 mm	Silt 0.001-0.06 mm	Clay <0.004 mm			
1.	Aridisol	88.6	6.8	0.15	8.7	0.15	0.06
2	Entisol	82.55	8.5	8.6	7.4	0.19	0.25
3.	Inceptisol	63.2	29	7.8	9.2	0.47	0.45
4.	Aflisol	48.45	31.75	19.8	7.8	0.35	0.64
	Method Used	International Pipette method (Piper 1966).			pH method (Richard, 1954)	Conductivity Bridge method (Richard, 1954)	Wet Digestion Technique (Walkley 1939)

- **SL pH and EC** was measured with glass calomel electrode (Richard, 1954) (conductivity bridge method) in 1:2 (w/v) SL: aquatic. The EC of SL was expressed as Decisiemens per meter (dS/m).
- **1 N Potassium dichromate**

Soften 48.04 g of AR rating K_2C_r2O7 in approximately 500 ml of distilled aquatic and kind the size to 1 litre.

- **Concentrated H_2SO_4.**
- **0.5 N ferrous AMN sulphate:**

Soften 186.1 g of AR ranking $FeSO_4$ $(NH_4)_2SO_4.6H_2O$ in near 400 ml of condensed aquatic. Add 20 ml of focussed H_2SO_4 and type the size to 1 litre by distilled aquatic.

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- **Sodium fluoride**

➢ Phosphoric caustic (85%).

- **DPY amine needle:**

Liquefy 0.5 g of DP Yamine gage in an assortment of 20 ml of concentrated aquatic and 100 ml of concentrated H_2SO_4.

❖ **Procedure**

- Transfer 1 gm SL in a 500 ml conical carafe.
- Enhance 10 ml of 1N $K_2C_r3O_7$ and 21 ml of concerted H_2SO_4.
- Spin the contents of the flask 2 otherwise 3 periods and agree the carafe to opinion for 30 minutes on asbestos sheet aimed at the answer to wide-ranging.
- Increase 200 ml of distilled aquatic to the decanter to insipid the interruption.
- Complement 10 ml of Orthophosphoric biting or 0.5 g of NaF and 1 ml of DPY amine pointer. A bottomless violet colour resolve look as if.
- Titrate it through 0.5N ferrous AMN sulphate box the colour variations from purplish-blue to blue and in conclusion bright khaki.
- Memo the VLM of the ferrous AMN sulphate second-hand in titration.
- Carry obtainable a complete titration (without SL), the similar way.

OGN Carbon % = (Blank-Reading) X 0.003 X 100/ 2 X Weight of SL taken = Z

OGN Carbon % = Z X 1.3

OGN matter % = OGN Carbon % X 1.724

Mechanical AS of SLs stayed determined by international pipette technique (Piper, 1966). The relative percentage of shingle, silt and stone of SLs were resolute to decide their textural class.

❖ **Apparatus:**

AnalyticalBalance, Graduated cylinder,1litre,with1000mlmark36±2cmfrombottom, Stopwatch, Thermometer, Robinsonpipette, Dryingoven.

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❖ Reagents

- 10%Hydrogenperoxide
- 2NHCL

❖ Procedure

- Weight 10 g SL sample in a 500 ml mug. Add 10% H_2O_2 30 ml boil overnight inWR bath to remove the OGN matter then add 2N 25 ml HCL oxidation with H_2O_2requiresacid medium.
- Filter through Buchner funnel by what man strainer paper No. 1.residue washed per warmaquaticto removethechlorideions.
- Transferthewashedresiduein500mlbeakerwithminimumamountofWR.
- Residual SL particles passed through 0.2 mm sieve to get the coarse sand particle dry itintohot oven. Notedown theweight as 'X'in gram.
- Residual part except coarse sand transfer in a Winchester bottle or tight cap bottle (1 litre)with500mldistilledWR.
- Inwhichadd2beadsofNaOH.Shakefor3hoursonmechanicalshaker.
- Transfer whole amountin1litre calculating cylindersize prepared upto1litre withaquatic.
- Check theroom temperaturestirwell TS suspension.
- Take a weight of three beakers label as W1, W3 and W5. Start stop clock, every 60seconds record the temperature and time.
- Remove 25 ml suspension from 10 ml layer in aW1markedbeakeratthestimulatedtimeforclayandsilt.
- Record weight as W^6. Fine sand is $W^6 - W^5$ and total sand is $\{x + (W^6 - W^5)\}$.

Calculation

- % ofcoarsesand=$\frac{X}{10} \times 100$
- % of fine sand=$\frac{(W6-W5)}{10} \times 100$
- % ofsilt+clay=$\frac{(W2-W1)}{10} \times 100 \times \frac{100}{10}$
- % of clay=$\frac{(W4-W3)}{25} \times 100 \times \frac{100}{10}$

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- %ofsilt=Equation 3–4
- Calculated%ofSLparticlesfittedintothetexturaltriangleanddeterminedthetextureofstudiedSL. Textural trianglepresented belowinFigure 3.

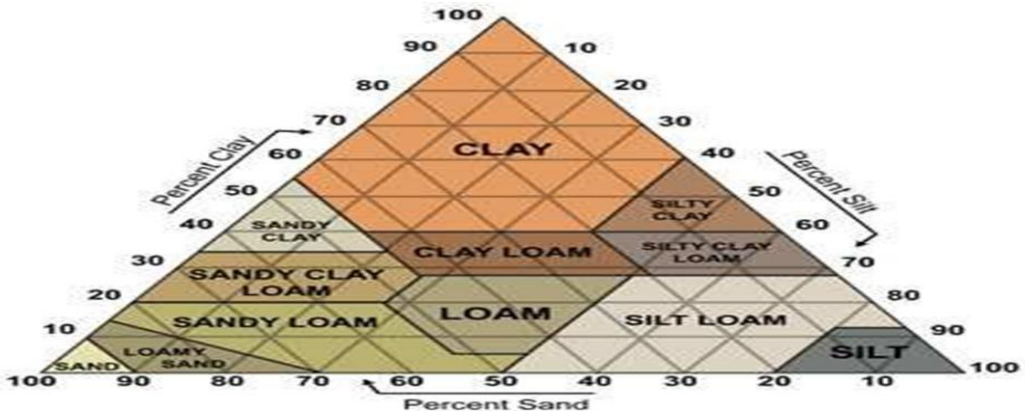

Fig. 3:SLtexturaltrianglebyUSDAusedfordeterminesSLtexture

❖ **HBC:** In the present investigation OFF HBC was selected to see the SP behavior in four DFF type of SL with low OC (Aridisl and Entisol) and high OC (Inceptisol and Aflisol). Reference grade of OFF (99.70%), elements and solvents were used in the experiment stood purchased from Merck India Ltd. OFF is chosen for the present study due to usually utilization in variety of crops in all around Haryana.

Table 2: Oxyfluorfen Herbicide

Mutual name	OFF
Organic name	2-chloro-1-(3-ehtoxy-nitrophenoxy)-4 --- benzene
Biochemical family	Biphenyl ether
Source of analytical grade	Sigma Aldrich, Germany
Mode of action	Irreversible cell damage via inhibiting Protoporphyrinogen oxidase

❖ **Preparation of analytical standard ST**

➢ **Stock STs of HBC**

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In this SP-DSP experiment, standard ST of OFF HBC were used for the grounding of stock explanation by taking MN (A.R.) as solvent and kept beneath refrigeration at 4° C.

- **1000 µg/ml stock ST of OFF**

0.1g of OFF were taken in a 100 ml VM decanter and VLM stood made to 100 ml with MN forming 1000 µg/ml stock explanation.

- **Preparation of standard working ST**

Working ST of OFF HBC at lower absorptions was organized from the typical ST using consecutive dilutions with MN. 0.5 ml of the key stock explanation (1000 µg/ml) was engaged in a 50 ml VM flask and dimensions was completed with MN to elasticity a standard rest of 10 µg/ml attentiveness.

- **Planning of GC-MS standardisation STs**

Aimed at the planning of 1 µg/ml standard explanation of OFF HBC, 1 ml of 100 µg/ml stayed transferred since stock ST per pipette to 100 ml VM flagon and made size by MN, Since the operational ST, serial explanations in MN stood prepared to realize absorptions ranging since 0.01 to 1 µg/ml of mix of HBC and set aside in refrigerator.

- **Preparation of standard curve**

The standard ST essential for preparation of standardisation curve (0.01, 0.05, 0.1, 0.5 and 1µg/ml) for OFF HBC was prepared since stock explanation by serial weakening using MN and stood stored at 4ºC. Regular curves stood plotted (aimed at 0.01 to 1 µg/ml concentrations over GC-MS) by taking DFF concentrations injected alongside x-axis and area of conforming amount in contradiction of y-axis.

- **Instrumentation**

Samples of OFF HBC were detected by Agilent Technologies GC-MS arrangement having model 7890 auto united to the 7000 triple-quadruple MS with HP-5 column having 31 m length, 0.31 mm i.e. along 0.25 µm film breadths of 6% biphenyl and 94% dimethyl Polysiloxane. Injection port heat 280°C , Oven heat maintained at 70°C by 3 min hold trailed by surge in heat at 15°C min^{-1} up to 270°C and clutch aimed at 3 min. The operating strictures for frame detector were foundation temperature 230°C; production current 35 µA; production liveliness, –69; reveller power 10 V; ion figure 12 V; extractor –7.4V; ion effort –7.3V; quadruple single temperature 150°C; quadruple dual heat (MS^2) 150°C.

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Helium and NTG were worked as the hauler gas with current rate of 2.35 and 1.25 mL/min in collision cell. The Vacuum at high-pressure 2.33×10^{-5} tort and rough space was 1.41×10^{2} tort, Inoculation capacity remained 2 μl pulsed in split-less method. MS bands stood acquired done an m/z range 100-500. Device uncovering bound stayed 1 μg/L. Retention time (min.) of OFF 14.26.

❖ **SP studies**

SP behaviour of OFF

Method for estimation of OFF in SLs will be validated by execution recovery tries at DFF spiking levels equal to LOQ using GC-MS. Batch SP studies will be performed following OECD 106 guideline (OECD/OCDE, 2000). The expanse of HBC sorbet C_s (mg/kg) will be estimated expending the mass steadiness equation and the SP coefficient K_d (L/kg) will be worked out for SP studies. The tests stood achieved in the subsequent set: blank; spiked sample in $CaCl_2$ ST.

All the samples were taken in triplicate

- SL samples (air dried) were weighed (5 g) into a 50 ml polypropylene separator tube plus equilibrated with 0.01 M $CaCl_2$ (sorbent ST ratio-1:5 (w/v)) on an end over and end shaker.
- After 24 h, samples remained spiked with 0.5 mg/L with OFF in each tube.
- Again, samples were taken to the shaker i.e. rot spin for further 24h at the *ambient* test site temperatures (24 ± 3°C).
- The postponement stood centrifuged at 3500 rpm aimed at 15 min.
- For SP study of OFF the supernatant was decanted off to 250 ml separator pipe and stood partitioned thru n- hexane prior to AS per details given below. Blanks of 0.01 M $CaCl_2$ solitary and thwarting ST of 0.5 mg/L of OFF HBC and stood also run in triplicate by the examples.

❖ **DSP studies**

- DSP studies in SL were carried out after complete decanting of supernatant obtained from ASP process by totalling 25 ml of 0.01 M $CaCl_2$ST.

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- The samples stood re-suspended using vortex and equilibrated for 24 hrs.
- After equilibration, the samples stood centrifuged and supernatant stood collected to analyse the HBC concentration in the ST.
- The tubes were weighed at each step to account for the tiny VLM of residual ST entrained from earlier procedures.
- The computation for the actual amount desorbed was rectified using the known concentration in ST before to beginning the following DSP stage.
- The DSP process was repeated thrice using 0.01 M $CaCl_2$ ST.
- The amount of HBC outstanding sorbet on TS was designed as the variance B/W early sorbet and the desorbed sum.

❖ **StatisticalAS**

All data stand articulated as the means ± SD in this education. The means and SD stood calculated by Excel 2019 software One-way AS of modification was achieved to AL the noteworthy difference amid DFF behaviors and CR AS was showed to disclose the inter-relation B/W the SP performance of OFF HBC and SL physic-chemical goods by Excel 2019 software.

➢ **Results**

The experimental results obtained from the present investigations in four DFFSL order of Haryana have been presented and discussed in this chapter under following headings.

- Physic-chemicalpropertiesofSL
- SPofOFF HBCin Ar, En, In and Al SLs of Haryana.
- DSPof OFF HBCin Ar, En, In and Al SLs of Haryana.

➢ **Physic-chemicalpropertiesofSL**

SLswere moderatelyalkaline(*p*H = 7.1-8.0)and non - saline (0.07-0.51 dS/m)in nature. OGNcarboncontentmixedsincelow (0.06%)to moderate(0.64%).In those four SLs, Al abstains the higher OGN matter (0.64%) and clay contented whereas Ar has lowest OGNmatter(0.06%)andclaygratified. ThesurfaceofSLdiverseaftersandytoclayloam. Of the four SLs, ECrangedB/W0.15-0.47dS/m.

➢ **CharacterizationofHBC**

Capillary GC-MS grounded on chromatographic practice for the estimate of micro numbers

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ofHBC was standardized preceding to attractiveup theAS of test examples. The peak area recorded for 0.01-1.0 µg/ml of mixture of OFFvalueshasbeenplottedincurvesdepictingtheirR^2values. Good linearity stood achieved by a CR constant of 0.991 for OFF HBC.\

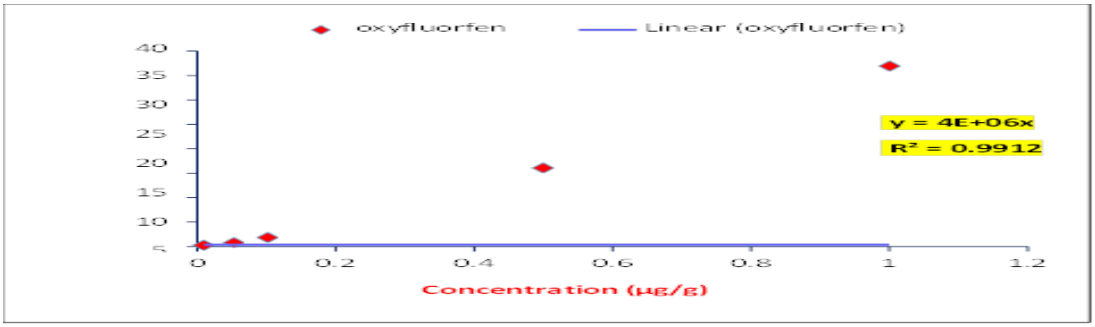

Fig. 4: Standard curve of OFF

- **SP of OFF HBC in Ar, En, In and Al SLs of Haryana**

The results revealed that SP of OFFHBC in SLs provided lowest SP coefficient (K_d = 0.15 to 14.56 L/kg) following the order: - Inceptisol>Alfisol> Entisol> Aridisol. TheSPbehaviorof OFFHBCinDFFSLordersarepresentedbelow in Table 3:

Table 3: Sorption coefficient of Oxyfluorfen herbicidein Ar, En, In and Al soil

SP	Aridisol	Entisol	Alfisol	Inceptisol
R1	0.15	1.2	6.8	3.5
R2	0.26	2.1	4.88	3.8
R3	0.18	1.33	8.26	2.8
R4	0.88	1.2	5.47	4.1
R5	0.41	1.12	7.52	3.5
R6	0.95	2.45	8.2	4.33
R7	1.12	2.85	9.11	7.5
R8	1.25	3.7	6.21	7.9
R9	2.35	1.66	8.25	13.55
R10	2.55	2.7	7.22	12.11
R11	1.65	1.76	10.17	8.88
R12	3.87	3.57	9.87	14.56

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The average SP coefficient of OFF in Arid sol SLwas RF 0.15to 3.87L/kg . Meanwhile, average K_d provided by Entisol was RF 1.12 to 3.57 L/kg fortheOFF HBC. The average SP coefficient of OFF in Alison **SL** was RF 4.88 to 10.17 L/kg. Meanwhile,average$K_d$providedbyIncept sol was RF 2.8 to 14.56 L/kg fortheOFF HBC.

Table 4: RelationshipfromregressionanalysesB/W$K_d$valuesof Oxyfluorfen herbicide and OC pH of the soils

HBC	K_d and % OC	K_d and *Ph*
OFF	0.991	0.772

Four SLs represented a wide range of DFF properties, since the SP parameters were affected by OC and pH, hence CR AS were conducted to evaluate inter-relationship among SL property and SP behaviour of OFF HBC. Thus, SP coefficients of every HBC stood plotted in contradiction of total OC%, pH of TS.

These CR data indicate that OC was positively and significantly correlated with SP coefficient of OFF HBC (R^2> 0.99; $p < 0.05$). Still, there stayed no momentous relationship B/W the K_d value of OFF HBC and pH ($p > 0.05$). K_d value of OFF showed positive relationship with EC of TSs.

- **DSPofOFF HBC from in Ar, En, In and Al SLs**

The amount of OFF desorbed from Ar, En, In, and Al after 1st DSP step (24 h) varied from 14.87 ± 0.39, 9.29 ± 0.11, 5.03 ± 0.1, 3.57 ± 0.44 µg RPL and furtherdecreasedwithsuccessiveDSPsteps. AftertwoDSPsteps 5.58 ± 0.85, 3.41 ± 0.09, 2.39 ± 0.07, 1.53 ± 0.21 µg ofOFFwasdesorbedfromthe fourSLs. TotalcumulativeDSPintotalwas20.45±1.24,12.7±0.2,7.42±0.17and 5.1±0.65 fromAr,En,In,andAlwithpercentDSP20.4,12.7,7.4and5.2 %RPL.

Table 5: DSP of OFF in DFF the soils Total DSP (%) is cumulative effect of three succeeding DSP steps.

Sorbents	OFF (in µg)				
	SP	DSP 1 Mass in solvent	DSP 2 Mass in solvent	DSP 3 Mass in solvent	Total DSP %

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Aridisol	100 ± 2.89	14.87 ± 0.39	3.83 ± 0.8	1.75 ± 0.05	20.4
Entisol	100 ± 0.74	9.29 ± 0.11	2.24 ± 0.07	1.17 ± 0.02	12.7
Inceptisol	100 ± 0.33	5.03 ± 0.1	1.87 ± 0.06	0.52 ± 0.01	7.4
Alfisol	100 ± 0.64	3.57 ± 0.44	1.35 ± 0.19	0.18 ± 0.02	5.2

➢ **DSPstudies**

DSP plays an effective role to find out the statement rate and impending mobility of HBC in SL. DSP was carried out over the period of 24 h bysuccessive withdrawal and dilution of supernatant and re-establishing of equilibrium in SL containingpreviouslysorbet HBC.

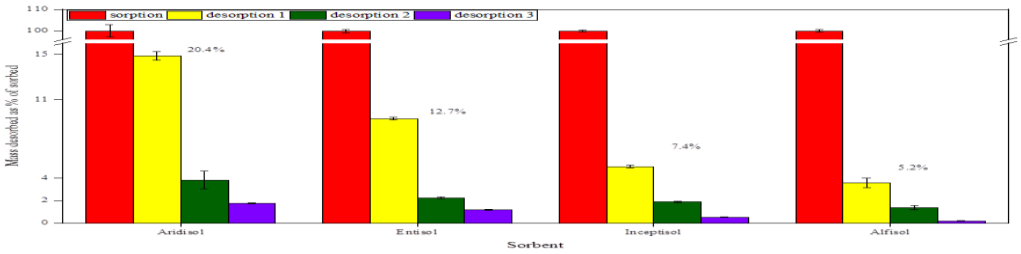

Fig. 5:DSP of OFF in DFF SLs. Total DSP (%) is cumulative effect of three succeeding DSP steps

OFF observed the 5.2% to 20.4% cumulative DSP from three DSP steps took place from unlamented SLs. The % DSP of OFF from 3 DSP cycles varied after 20.4% in Ar, 12.7% in En, 7.4% in In and 5.2% in Al. DSP of OFF in 4 SLs varied in the instruction: Arid sol> Entice> Incept sol > Alison.

The results obtained by the DSP of OFF are well satisfied by Sireesha *et al*. (2013) which reported that SL OGN matter and clay satisfied play an vital role in the ASP- DSP of OFF HBC.

3. Conclusion

- SP(K_d0.15to14.56 L/kg)of OFF HBC in SLs following theorder: Inception> Alison>

Entice> Arid sol.

- K_d show direct relation with %OC present in SLs ($p < 0.05$). SLs (In and Al) with high OC offered higher SP than low OC SLs (Ar andEn).
- K_d had no relation with pH of DFF SLs ($p > 0.05$). Although K_d of OFF was correlated with EC of the DFF SLs.
- Oxyflourfen showed least cumulative DSP (below 25%) in Ar, En, In, Al SLs.

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