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Studying the Hinosan toxin leak into underground water resources using GC-ECD and its elimination by active carbon

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Abstract: Contamination of water resources by pesticide toxins is considered as one of environmental issues which is because of plant pest diversity and subsequently use of various toxicants. In previous decades all over the world, the usage of organophosphorus toxins in order to preservation of agriculture products expanded. In Gilan province (Iran) there are numerous agriculture lands and gardens which are sprayed intermittently and since drinking water of the region residents is rather supplied by underground waters, then penetration of toxicants into the wells is possible. For this reason pesticide toxicants use could be a treat for drinking water supplying resources of this state. In the paper, samples of water from ten wells were collected and for measuring the quantities of toxicants, experiments were carried out during 4 seasons of year. Toxicant residues in samples were analyzed according to Gas Chromatography–Electron Capture Detector (GC-ECD) method. Due to phosphorous toxicant analyze results; it is revealed that in some cases precipitation amount has a great effect on toxicant concentration inside well water because of leaching higher layers. Also it is indicated that clay presence in soil due to toxicant holding and rain or flood occurrence cause to decrease and increase toxicant leak into the underground water respectively. Finally in order to Hinosan toxicant removal from water resources, active carbon has been utilized. The results indicated that adsorption by active carbon was of Langmuir type and this adsorbent effective cause to eliminate Hinosan toxin from water resources.

Keywords: Hinosan toxin, GC-ECD, Active carbon, Langmuir isotherm.

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1. Introduction:

The highest amount of water consumption is dedicating to agriculture industries. In respect to wide areas of Iran, inappropriate use of water resources and agriculture inputs (fertilizer and toxicant) could quantitatively and qualitatively threaten the country's water resources seriously (Ongle 1996; Tilman et al. 2002; Wauchope 1978). One of major sources of agriculture water contamination is excessive and growing use of chemical fertilizers and pesticides which in few recent years has found in great applications (Ridgway et al. 1978; Pimentel and Lehman 1993). Toxicants and pesticides use in farms cause to direct them into underground water and as result cause to enter into food chains of organisms such as human which they use these water for drinking.

Most pesticides are stable organic compounds that considering to factors such as temperature, precipitation, soil attributes and chemicals properties have passed from various layers of earth with different speeds and will approach to underground waters. Therefore use of underground water resources in agriculture sector and rural drinking water are vital in environmental and sanitary terms which often lack sanitary plumbing. So contamination control of these waters is economically important (Brooks 1974).

Measuring toxicants in natural waters using chromatography is old as many decades. Until now various procedures such as gas chromatography (GC), liquid chromatography (LC), liquid-liquid extraction, solid phase extraction and etc. have been used for measuring toxins existed in water that in these methods, different detectors such as ECD, FID and FPD have been utilized (Fernandez-Alba and Garcia-Reyes 2008; Ballesteros and parrado 2004; Alder et al. 2006; Beltran et al. 1998; Brito et al. 2002).

Because of high volatility of some toxicants, GC has been a lot of publicity. Also nowadays due to electronegative groups in molecular structure of these herbicides, ECD detector (electron capture) is used in the process of measurement which has higher sensitivity than this groups. Phosphorous compounds refer to all insecticides which there are phosphor in their chemical structure.

In family of pesticides, organophosphorus compounds could be quantitatively identified using mass detector due to its volatility and structure destruction in high temperature of injection chamber. Hinosan is an insecticide from phosphorous toxins category with general name of Edifenphos, chemical name of O-ethyl S,S-diphenylphosphorodithioate and molecule formula $C_{14}H_{15}O_2PS_2$ (Math et al. 1998).

This Brownish-yellow liquid is very stable in neutral mediums but is hydrolyzed versus strong acids and bases. So far we doesn't have any exact report concerning to the Hinosan poison distribution but, local reports shows that this kind of poison have been used with the uniform distribution pattern in whole rice fields. The usage increase of this poison in northern cities of Iran (for example Golestan, Mazandaran and Gilan provinces) is alarming. So far, different experimental and theoretical investigations (such as density functional theory (DFT) methods) in order to elimination of Hinosan toxin has been performed which in most of them, toxin adsorption was targeted (Ishizuka et al. 1972; Farmanzadeh and Rezainejad 2016). Among these studies, nano adsorbents (such as Boron nitrid nanotubes) have more impact but, micro absorbents if they are useful have economically advantages in comparison with nano adsorbents.

For carrying out this paper, initially it is decided that a sampling will be carried out from ten wells used to supply drinking water in Gilan state and during four seasons of year. Then in order to analyze the amount of Hinosan toxin in water, GC and GC-MS methods were utilized and finally this toxin were eliminated using active carbon adsorption method.

2- Materials and Methods

All utilized chemical materials such as hydrochloric acid, sodium chloride and n-Hexane solution were purchased from Merck ltd. Also distilled water has specific conductance less than 10 µs/cm. All GC measurements were carried out using gas chromatograph thermo-1 (trace GC Ultra model) along with systemic conditions listed in Table 1. Thermal programming was from 180 to 250 ℃ at 5 ℃/min and was maintained in 180 and 250 ℃ for 5 minutes. So each assay takes 25 minutes.

Table 1: Parameters related to GC and GC-MS device used for Hinosan analysis.

Parameter	GC	GC-MS
Carrier gas	N_2 (99.99%)	He
Column	Jenway- OV 17 Length. 30 m Internal diameter. 0.25 m	HP5MS Length. 30 m Internal diameter. 0.25 m
Detector	ECD Radiation source. 63Ni beta ray	ECD
Oven temp.	200 °C-280 °C (prog.)	100 °C-240 °C (prog.)
Injection	Injection Temp. 180 °C Injection volume. 0.5µLit	Injection Temp. 200 °C Injection volume: 1µLit
Carrier gas flow	5 ml/min (splitting)	15 ml/min (splitting 1:50)

GC-MS device used was from HP Agilent 6890N (G1530N) and corresponding to system condition listed in Table 1. Speed of Helium gas was equal to 4 mm/min and thermal programming was the same as method suggested in GC section. Quality detection was performed based on spectrums interpretation and for more reliability was compared with standard spectrum. Before any daily measurement, GC-MS device was calibrated with $(C_4F_9)_3N$.

In order to perform the test, initially water samples were acidified by chloridric acid in pH=1 and were held in refrigerator. For extraction, one liter of acidified water samples were filtered through passing filter paper and after adding 20 g NaCl (for improving extraction performance) during 4 stages, each stage with 10 ml n-Hexane (total volume 40 ml) the process of extraction was performed .Then the extracted solution was dehydrated with sodium sulphate and final volume decreased to 2 ml and was transferred into the sample tube. in order to feed to GC firstly one calibration curve was plotted from extrinsic Hinosan standard through method of calculating the area under peak in terms on concentration and it has been utilized for quantitative measuring the samples. The prepared samples were injected into the gas chromatograph and were analyzed under temperature conditions of column. Then determining samples concentration was carried out through comparing samples spectrum with standard spectrums and comparing the area under curve. For each sample, feeding was repeated three times which the obtained responses has been reported. The significant note is that standard sample for feeding into the GC-MS was diluted as much as 50 times with methanol. For studies related to GC-MS, firstly the standard solutions of Hinosan toxin were prepared and its pick were observed at 50 ppm concentration (t= 24.3 min).

In order to obtain isotherm curve for adsorption of Hinosan toxin on the active carbon, the Batch procedure was also utilized. in this regard, inside one beaker, 30 gr various types of active granular carbon was weighted and 100 ml toxicant-impregnated water was added to it at 10, 20, 30 and 40 ppb concentrations. Then in order to perform the absorption process, the toxicant was placed on the column for 48 hours along with agitating. Finally the examined sample was extracted with liquid-liquid procedure and it feed into the gas chromatograph in order to determine concentration of residue toxicant (unabsorbed).

3- Results and Discussion

3-1- Wells Water Analysis

10 wells in the region were analyzed during four seasons so that in addition to amount of Hinosan toxin, some general features of well such as salinity or acidity was measured too. Because concentration range of Hinosan in analyzed water was inside ppb limit and very much below this, so GC method with ECD detector has been recognized suitable for analyzing natural samples because its sensitivity is more suitable. In the Table 2 the specifications of ten wells (ten samples of water) have been listed. Also the obtained data of studied wells in the various seasons is observed in the Table 3 through 6 which obtained concentrations in these tables have reached in terms of ppb and after 3 times of

experiments.

Table 2: Specifications of ten wells (ten samples of water).

Samples (wells)	Soil kind	Well depth (m)	Distance from the farm (m)
1	Clay and gravel	66	20
2	Clay and gravel	75	20
3	Clay and sandy	92	200
4	Gravel and sandy	48	15
5	Gravel and sandy	56	7
6	Clay	60	20
7	Clay and gravel	54	150
8	sandy	70	500
9	Clay	56	5
10	Clay	20	15

Table 3: The sample results by Hinosan concentration (µg/L) in the spring.

Samples	Concentration (ppb)	Salinity	Conductivity	pH	Samples	Concentration (ppb)	Salinity	Conductivity	pH
1	0.431 0.429 0.416	0.3	695	7.4	**6**	0.395 0.394 0.381	0.3	680	7.69
2	- - -	1.1	1348	7.6	**7**	- - -	0.2	380	7.32
3	- - -	0.2	623	7.6	**8**	0.347 0.344 0.341	0.5	1050	7.49
4	0.377 0.372 0.368	0.4	958	8	**9**	0.294 0.293 0.291	0.4	874	7.45
5	- - -	0.5	1049	8.1	**10**	- - -	0.1	416	7.34

Table 4: The sample results by Hinosan concentration (µg/L) in the summer.

Samples	Concentration (ppb)	Salinity	Conductivity	pH	Samples	Concentration (ppb)	Salinity	Conductivity	pH
1	0.347 0.346 0.344	0.3	695	7.4	**6**	- - -	0.3	680	7.69
2	- - -	0.5	961	7.8	**7**	0.379 0.376 0.365	0.1	279	7.46
3	- - -	0.2	623	7.6	**8**	0.405 0.402 0.395	0.5	1050	7.49
4	0.280 0.270 0.268	0.4	958	8	**9**	0.267 0.264 0.260	0.4	874	7.45
5	0.306 0.296 0.287	0.5	1049	8.1	**10**	- - -	0.1	416	7.34

Table 5: The sample results by Hinosan concentration (µg/L) in the autumn.

Samples	**Concentration (ppb)**	**Salinity**	**Conductivity**	**pH**	**Samples**	**Concentration (ppb)**	**Salinity**	**Conductivity**	**pH**
1	0.466 0.450 0.393	0.2	652	7.2	**6**	- - -	0.2	622	7.69
2	0.413 0.408 0.406	1.1	2473	7.5	**7**	0.418 0.360 0.334	0.2	365	7.40
3	- - -	0.2	621	7.9	**8**	0.323 0.283 0.248	0.5	1068	7.58
4	1.200 1.127 1.089	0.5	1144	7.9	**9**	0.475 0.462 0.402	0.1	375	8.04
5	0.618 0.580 0.553	0.5	1046	7.9	**10**	- - -	0.5	972	7.19

Table 6: The sample results by Hinosan concentration (µg/L) in the winter.

Samples	**Concentration (ppb)**	**Salinity**	**Conductivity**	**pH**	**Samples**	**Concentration (ppb)**	**Salinity**	**Conductivity**	**pH**
1	0.615 0.568 0.543	0.3	698.7	6.9	**6**	- - -	0.3	707	7.31
2	- - -	1	1437	7.6	**7**	- - -	0.3	380	7.35
3	0.598 0.589 0.521	0.2	625	7.8	**8**	- - -	-	724	7.6
4	- - -	0.4	945	7.2	**9**	0.722 0.695 0.679	0.2	322	7.39
5	- - -	0.5	1070	7.6	**10**	0.776 0.752 0.741	0.5	938	7.18

3-2- Statistical Analysis

The obtained results of Hinosan toxin analysis were statistically studied from two views which first aspect was to study the relation among the concentration of residue toxicants in water samples and various seasons (aim: studying the effect of environmental conditions and amount of precipitation on the contamination of underground water resources) and second aspect was to study the relation among the concentration of residue toxicants and distance from sampling place to farms. In this regard, Levene test statistical method in the SPSS environment and comparing significant level were utilized in order to study the type of data variance for each well.

According to analysis of 4, 5, 7 and 9 wells similar to well-1 Levene test results did not show the homogeneity variance of data and significance values of 0.115 , 0.155 , 0.155 and 0.330 respectively show being not significant of seasons difference on the contamination of these wells.

According to Tables 7 and 8, Leven test for well-6 and well-8 respectively shows the homogeneity variance in the data. Although significance value of 0.055 indicates the above variance similarity to nonparametric form but with regard to test result, Anova table was used for being significant of differences. Significance value of 0.000 indicates no significant of difference among seasons of the year in well-6 and well-8 contamination.

Table 7: Anova test statistical results of contamination variance and homogeneity test of well-6's contamination variance.

ANOVA						**Test of Homogeneity of Variances**			
Pollution 6						Pollution 6			
	Sum of Squares	df	Mean Square	F	Sig.	Levene Statistic	df1	df2	Sig.
Between Groups	0.566	3	0.189	749.064	0.000	3.892	3	8	0.055
Within Groups	0.002	8	0.000						
Total	0.568	11							

Table 8: Anova test statistical results of contamination variance and homogeneity test of well-8's contamination variance.

ANOVA						**Test of Homogeneity of Variances**			
Pollution 8						Pollution 8			
	Sum of Squares	df	Mean Square	F	Sig.	Levene Statistic	df1	df2	Sig.
Between Groups	0.285	3	0.095	263.283	0.000	3.902	3	8	0.055
Within Groups	0.003	8	0.000						
Total	0.288	11							

It is necessary to note that wells of 2, 3 and 10 were not statistically studied because of special use in the winter. In Table 9, in order to study the effect of factor of distance from farm in the wells contamination, wells distance and contamination of each well had been considered in SPSS software as two columns of independent and dependent data. Levene test and significant value obtained from it indicate that the data are nonparametric. For the same reason in order to study correlation among data, Spearman test was used. Test results indicate that the correlation among farm distance and wells contamination was not significant.

Table 9: Statistical results of correlation test of contamination variance.

Correlations				
		Parameter	Pollution	Distance from the farm (m)
Spearman's rho	Pollution	Correlation Coefficient	1.000	0.012
		Sig. (2-tailed)	-	0.927
		N	60	60
	Distance from the farm (m)	Correlation Coefficient	0.012	1.000
		Sig. (2-tailed)	0.927	-
		N	60	60

According to the results, wells of 1 and 9 four seasons had variable amount of Hinosan toxin which comparing these values among various seasons, did not show significant correlation between toxin concentration and various seasons. reason of this could be found in soil texture and precipitation intensity of the region because it seems that soil texture is such that the Hinosan toxin is very slowly transferred to lower soil layers which it should be accurately studied in a distinct research. Increasing the toxin quantity in water samples of autumn and winter rather than spring and summer is due to more precipitation and toxins leaching from higher soil layers into the lower layers and due to decreasing vegetation and soil humus amount in these seasons. In well 4 and 8 in three seasons of autumn, spring and summer and in well 5 and 7 in two seasons of autumn and summer, residue toxin has been detected and measured. Statistical tests did not record any significant difference among various seasons, reasons of which could be found in various gradation and permeability properties of the soil.

Moreover, not detecting the toxin in above wells in winter could be considered due to less toxin solubility in water at less temperature (cold air). In the wells of 2, 3 and 10 only in the special season, some toxin were detected which indicates the relation among toxin concentration and the special season. That is why performing statistical analysis was not possible on the samples. occasional toxin use in the special area and cross and sudden changes at environmental and ecological soil conditions such as temporary precipitation and flood streams could be as two reason for the obtained results . Also the soil kind and its gradation could be effective in water transfer amount to various soil layers and in passing and leaching ability of toxin toward water basins such that gravel and sandy soils has also passed through less toxin quantities because of high infiltration capacity while clay soils because having of high water holding and absorbing capacity have maintained higher toxin concentrations and gradually passed them through.

Statistical analysis related to distance among sampling place until farms showed that there is not a significant relationship because of different kind of soil layers and environmental conditions.

3-3- Removal of Toxin from Water Samples

The carried out studies about removal of Hinosan toxin (to level of Europe standard) from drinking water of the wells used in this research indicated that most economical method was the active carbon column and removal throughput is varied for this toxin depending on the amount of sorbent used for every liter water. It means that increasing the toxin concentration in every liter of passed water in respect to fixed amount of sorbent cause to decrease the absorption performance which this could be due to saturating loading capacity of absorbing carbon. So for more studying and performance increase, the amount of sorbent has been increased which was the result of removal throughput increase and toxin reduction in drinking water under its permissible limit by Europe union standard (0.5 ppb). In next stage, calculations related to isotherm curves was carried out for each granular active carbons using obtained data and absorbed toxin amount was calculated using the equation 1.

$$q_e = \frac{V(C_o - C_e)}{m} \qquad (1)$$

q_e: mg Hinosan toxin / g active carbon
V: Analyzed water volume (liter)
C_o: Initial toxin concentration (before absorption) (mg/l)
C_e: Last toxin concentration (after absorption) (mg/l)
m: Active carbon mass (g)

Following the tests performed and obtained results, various adsorptions was investigated with putting the obtained data to get the best curve consistent on data. Among the dominant isotherm adsorption curves, two curves of Langmuir and Freundlich were more consistent on our data in figure 1 rather than other isotherms.

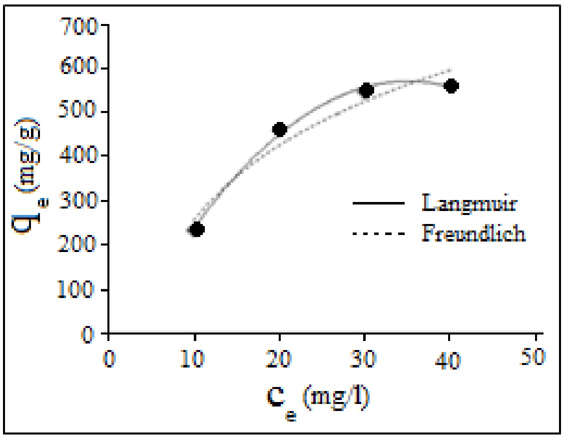

Figure 1: Adsorption graphs on active carbon and absorption mode determination.

Langmuir equation is based on the relation 2.

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \qquad (2)$$

In the above equation q_m is the toxin absorption amount/g active carbon at highest required amount (when adsorption has been made as much as one whole layer) and b is a fixed value which is related to the curve slope.

Freundlich isotherm curve equation is according to relation 3.

$$\ln q_e = \ln K + \frac{1}{n} \ln C_e \qquad (3)$$

In this equation the values of K and 1/n are fixed which depends to adsorption capacity and sorbent surface uniformity respectively.

Table 10: Studying the efficiency of carbon column at removal of Hinosan toxin from water per 10 g sorbent material.

Langmuir			**Freundlich**		
q_m(mg/g)	**B(L/mol)**	**P**	**K($mg^{1-(1/n)} l^{1/n} g^{1/n}$)**	**1/n**	**P**
710	0.62	1.56	233.6	0.42	12.71

Considering Table 10, about studying the removal methods of Hinosan toxin from drinking water, adsorption method was studied with active carbon sorbent. The active carbons were prepared and absorption curves of each were calculated and plotted using Batch method. The obtained results indicated that among adsorption isotherms, there was an appropriate consistency between Langmuir curve and Hinosan adsorption graph on granular active carbon ($p<5$).

4- Conclusione

Because of chemical stability, agriculture toxicants are infiltrated from upper soil layers into underground water resources due to leaching and for the same reason precipitation amount is a vital factor of that occurrence. The kind of toxicant-sprayed soils if it is a clay kind then will have ability to hold toxicant and prevent its further influx into the water resources. The method of adsorption is an economical and applied procedure for removing Hinosan toxin from water resources. Active carbon could well be able to remove Hinosan from contaminated sources according Langmuir isotherm.

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