Study of Pesticide (Dichlorvos) Removal from Aqueous Medium By Arachis Hypogaea (Groundnut) Shell Using GC/MS

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Abstract: KOH, H_3PO_4 and $ZnCl_2$ catalyzed Groundnut shells, subjected to a one and two steps activation methods were employed to study pesticide (Dichlorvos) uptake. The study examined activation method, nature of activating agents and concentration of the pesticide, as factors affecting removal of the pesticide. Quantitation, using GC/MS gave a percentage removal of over 98% by all the sorbent in the series. The percentage removal for the one step method follows the trend 1S/KOH/10 (100%) > 1S/H_3PO_4/10 (99.780%) > 1S/$ZnCl_2$/10 (99.240%). Physicochemical data and close proximity of equilibrium results (q_e) to those of similar biowaste as reviewed in literatures are indication that Groundnut Shell based sorbent in this study could compete favorably well for pesticide(dichlorvos) uptake.
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1. INTRODUCTION

The rise in mortality is caused by the recent evolution of drug – resistant malaria, inaccessibility to effective health care facilities and the introduction of industrial by products to the environment. One of such industrial byproducts threatening the environment worldwide today is pesticides residues. Reports have shown that presence of pesticide in the environment and the threat they pose to wild life and mankind have generated great concern in the past 20 years. Pengman (1996) defined pesticide as any chemical agent used to kill or control undesired insects, weeds, rodents, fungi, bacteria, or other organisms. The impact of agricultural chemicals on surface water and groundwater quality has become an issue of global importance. Surveys carried out in Europe as well as in U.S. by researchers and cited by Gerard and Barthelemy (2003) pointed out that using agricultural and non – agricultural pesticides lead to residues in surface and ground waters (Schwartz, 1996). Many of the pesticides used are resistant to degradation by chemical and biological agents. It is not surprising, therefore, that small amounts of these chemicals have been isolated from many phases of the environment, including water supplies (Schwartz, 1996).

1.1 Health Implications of Pesticides

Pesticides are toxic and are potentially hazardous to human, animals, other organisms and the environment. The toxicity of a pesticide is a measure of its capacity or ability to cause injury or illness (Lorenz, 2007). Pesticide pollution was reported to have killed fishes and resulted in reproductive failure in birds. However, human become exposed to pesticides through oral (mouth), inhalation (lungs), ocular (eye), and or dermal (skin) contact (Lorenz, 2007). Chronic effects from exposure to certain pesticide include birth defects, toxicology to a fetus, production benign or malignant tumors, nerve disorders, blood disorders, genetic changes, endocrine disruption and reproductive effect (Lorenz, 2007). The symptoms of pesticides poisoning can range from a wild skin irritation, permanent blindness, to coma or even death. The signs and symptoms of acute exposure for several pesticides vary according to the chemical nature of the pesticide. Individuals also vary in their sensitivity to different levels of these chemicals. Some may show no reaction to an exposure that may cause severe illness in others (Lorenz, 2007).

1.2 Adsorption Using Activated Carbon

Remediation of contaminated ground water has been practiced using activated carbon adsorption. According to (Stouffer, 2001), the removal of organics in water that are weakly adsorbed and present in trace concentration require an activated carbon with a predominance of high – energy pores. Activated carbons are processed carbon materials that are capable of adsorbing various substances from gas and liquid streams, because of their highly developed pore

structure and large internal specific surface areas (Abdul and Aberuagba, 2005).

1.3 Removal of Pesticides from the Environment

Several attempts had been made in the past to minimize the level of pesticides present in the environment. Some of the pesticides are biodegradable and are naturally broken down by microorganisms (Fushiwaki and Urano, 2001). It has been observed that organic pesticides are found in nearly all living matter that has been analyzed. Micro-organisms can only metabolize pesticides if they are bioavailable and if they have chemical structure compatible with the organisms' enzymes that catalyze the biodegradation. Mechanisms of degradation include mineralization, partial degradation to secondary compounds, adsorption, humiliation and volatilization .According to Clausen *et al.,* (2001), sorption desorption is one of the key processes affecting the fate of agrochemicals in the sediment – water environment. Adsorption on soil is another important physicochemical characteristic governing the fate of pesticides in the environment (Fushiwaki and Urano, 2001).

1.4 Use of Activated Carbon to Remove Pesticides

A great deal of research has been performed on the adsorption of pesticide onto activated carbon. As a result of its tremendously large surface area, activated carbon is used widely to adsorb large quantities of materials from solution. The small tiny pores in the activated carbon structure makes removal of very small organic matter possible. Removal of pesticides from contaminated water by activated carbon adsorption is considered as one of the best available technologies (Mishra & Bhattacharya, 2007).

1.5 Activated Carbon from Groundnut Shell

Groundnut shell, apart from its availability in abundance, has proved to be an excellent raw material for the production of activated carbon. Abdul and Aberuagba (2005) prepared an activated carbon from groundnut shell using steam activation method. It was used excellently to adsorb phosphate from aqueous solution and they recommended the adsorbent for use in waste water treatment. Removal of up to 94.5% of Malachite green on adsorbent from groundnut shell with $ZnCl_2$ activating agent was also recorded. The activated carbon was found to have higher adsorption efficiency compared to commercially available carbon (Malik *et al.,* 2006).

2. METHODOLOGY

2.1 Sampling and Sample Treatment

The precursor (A*rachis hypogaea* – shell) was sampled locally in November, 2008 in an oil mill in Zaria city, Kaduna State, Nigeria.

Method of Gimba *et al.,* (2004) was used. The sample (*Arachis hypogaea* shell) was washed with plenty of water several times and finally with distilled water to remove surface impurities and then sun dried. The dried sample was ground followed by sieving with a 2mm mesh size sieve. The sample was stored in an air tight container for further use. Analytical grades Phosphoric acid (H_3PO_4), Potassium hydroxide (KOH), Chloroform ($CHCl_3$) were supplied by May and Baker, England**.** Zinc chloride ($ZnCl_2$) and Hydrochloric acid (HCl) from British Drug House, UK, were used while the sorbate, Dichlorvos ($C_4H_7Cl_2O_4P$) was procured from Hubei Sanonda Co. Ltd, China. All chemical reagents used were of high grade (>90% purity) and were purchased from Steve Moore Chemical Company, Zaria, Nigeria.

Table 1 Chemical composition of groundnut shells

S/No	Constituent	%
1.	Cellulose	65.7
2.	Carbohydrates	21.2
3.	Proteins	7.3
4.	Minerals	4.5
5.	Lipids	1.2

Source: INPhO, (2007).

2.2 Activation (One Step Process)

Approximately 3.0g of the raw sample was mixed with $3cm^3$ of 1M H_3PO_4, $ZnCl_2$ and KOH separately. The sample mixture was kept for 24 hrs after which they were put into a furnace at 800^OC for 5mins. The sample was removed and cooled in ice water bath; excess water was drained and allowed to stand at room temperature (Gimba *et al.,* 2004). The activated carbon generated was washed using 0.1M HCl to remove surface ash followed by rinsing with distilled water to remove residual acid. The sample was then dried in an oven at 110^0C for 1 hour. Washing was completed when a pH of 6 – 8 was ascertained (Ahmedna *et al.,* 2000).

2.3 Characterization of Derived Activated Carbon

Bulk Density Determination was estimated using the method of Ahmedna *et al.,* (1997). For Ash Content, method of Bansode *et al.*, (2003) was used. Others include Moisture content (Allen *et al*.,1974, Itodo *et al*.,2009), Electrical conductivity was measured using conductivity meter model – 3392 (WINDAUS), Germany with values given in microSiemens (μS) by method proposed by Ahmedna *et al.,* (1997). pH measurement was as done as described elsewhere (Yoshiyuki and Yutaka, 2003).

2.4 The Adsorbent

Pesticide, Dichlorvos was used as the adsorbate. The pesticide was obtained from an agrochemical shop in Samaru market, Zaria, Nigeria.

Dichlorvos is the common name for 2, 2 – dichloroviny l dimethy l phosphate, also known as DDVP. It is a colorless to amber liquid with an aromatic odour of boiling point 35^0C at 0.05mmHg, vapor pressure 1.2×10^{-2} mmHg at 20^0C. Its solubility in water at room temperature is about 1%. Dichlorvos is a contact and stomach insecticide with fumigant and penetrates action, especially against dipteral and mosquitoes (Hubert, 1968).

2.5 Preparation of Working Standard of Dichlorvos

The dichlorvos used is in conce nitration of $1000g/dm^3$ and was used as such (as the stock solution). The working concentrations were prepared from the stock with lower dilutions of 10 & $20gdm^{-3}$.

2.6 Adsorption Studies of Dichlorvos

Batch (discontinuous) adsorption was carried out using the method of Rozada *et al.*, (2003) with little modification. 0.1g of activated carbon was interacted with 10ml of dichlorvos solution in 50ml – Erlenmeyer flasks. The flasks were closed to avoid evaporation and were kept standing for 24 hrs. After the selected contact time had elapsed, the contents were filtered through Whatman No. 40 filter paper. The filtrate was analyzed by gas chromatography (GCMS-QP2010 Plus, Shimadzu, Japan) and the difference in pesticide concentration was noted. A blank with same amount of liquid without adsorbent was subjected to the same procedure to serve as control.

2.7 GC/MS Conditioning

A gas chromatography equipped with a mass spectrophotometer detector (with a model GCMS QP2010 plus Shimadzu, Japan) was used in this analysis. The column was held at 60^oC in injection volume of 1μL and then programmed to 250^oC. it was set at a start m/z of 40 and end m/z of 420. The detector (mass spectrophotometer) was held at 250^oC above the maximum column temperature. The sample size was 1μL, which was split 100^{-1} onto the column and so the total charge on the column was about 1. Helium was used as the carrier gas at a linear velocity of 46.3cm/sec and pressure of 100.2kPa. Ionization mode is electron ionization (EI) at a voltage of 70eV. In this analysis, Amplification and resolution for test herbicide was achieved by adjusting the threshold to 6000. Thus, worse interference and solvent peaks were screened out leaving majorly the deflection of target compound (Dichlovors) as it was made pronounced on the chromatogram. Baseline disturbance was linked to either hydrocarbon impurities. Impure carrier gas can also cause baseline instability (Robert and Eugene, 2004). It can be corrected by changing the purifier when pressure drops reaches 10 – 15 pSi routinely monitoring the pressure. Sorption efficiency of an adsorption process was defined based on the fractions of extracted and unextracted sorbates (Itodo et al., 2010a and b).

Table 2 Physiochemical parameters of adsorbents from groundnut shells

Adsorbents	Bulk ρ (g/cm^3)	Moisture (%)	Conductivity (μS/cm)	pH	%Ash	%Yield
CGS	0.218	6.0	830	7.42	6.9	53.75
1S/K-1M	0.362	4.1	572	7.85	3.9	72.52
1S/K-0.1M	0.313	4.8	725	8.11	4.1	68.43
1S/K-0.075M	0.307	5.3	713	8.08	4.9	57.68
1S/K-0.01M	0.293	5.4	649	7.90	5.0	64.07
1S/P	0.337	6.0	679	3.19	5.3	69.11
1S/Z	0.217	11.0	848	9.62	9.1	58.94

CGS= Carbonized groundnut shell

3. RESULTS AND DISCUSSION

3.1 Physicochemical Parameters

The density of a generated activated carbon plays great role on adsorbate uptake. Generally, higher density carbons hold more adsorbate per unit volume (Jibril, *et al.*, 2007). From table 2 the type of activation method has effect on the density of the AC. Adsorbent 1S/K-1M poses the highest value of bulk density ($0.362 g/cm^3$) and the same adsorbate was shown in table 4.2(a) to have the highest dichlorvos removal of (RE = 100%). It thus indicates that bulk density of a carbon is an important property to be considered in preparation of adsorbent for pesticide removal.

Nature of activating agent also plays a role on the density of adsorbent. Table 2 also revealed that the trend of bulk density with respect to the activants follows the order: KOH> H_3PO_4>$ZinCl_2$ carbons. Their respective values (in g/cm^3) include 0.362>0.337>0.217. CGS appeared to have lower density ($0.212 g/cm^3$) than the rest of activated carbons from the same source. This could be due to the fact that activation with KOH yield AC with a highly microporous structure and narrow pore-size distribution, while activation with and H_3PO_4 leads to a broader pore-size distribution and a larger production of micropores (Kezami *et al.*, 2007). According to Itodo *et al.,* (2008) bulk density has impact on sorbate-retention level by any adsorbent. It also affects adsorption and possibilities for regenerating spent carbon for re-use (Itodo *et al.,* 2008).

For carbon used in water purification, moisture content is of little significance but it should be taken into account when assessing the relative capacities of different materials. Table 2 revealed that the type of activation method has little effect on the retained moisture. Moisture contents, according to Aziza *et al.,* 2008 has a relationship with porosity (α) of a given carbon. Sorbent with high moisture content is expected to swell less, thus retarding pore size expansion for sorbate uptake. The low moisture content of 1S/K-1M adsorbent (4.1%) and its subsequent high dichlorvos removal (100%) is in agreement with this report. The possibility of adsorption by ion exchange could not be ruled out in any physisorption process. On the same fashion, the role played by electrical conductivity has a direct link to the nature of activating agent (Itodo, 2008). Generally, high conductivity of carbon adsorbents is undesirable in the adsorption process of nonionic pollutants (Bansode *et al.*, 2003). This is because it interferes with the leachable minerals associated with the carbon surface. This study showed that $ZnCl_2$ treated sorbents posses the highest conductivity than the rest of the adsorbents. The KOH and H_3PO_4 treated adsorbents appeared to have lower conductivity values than the $ZnCl_2$ adsorbents. That could be responsible, among other factors for higher dichlorvos removal by these adsorbents. The overall trend follows $ZnCl_2$ (848) > H_3PO_4 (697) > KOH sorbent (572) with units in μS/cm. Because conductivity showed little or no effect in the overall adsorption process, it could therefore be inferred that the adsorption process was a physical one. Similarly, because $ZnCl_2$ sorbents posses higher conductivity (848 μS/cm).

Ash is a measure of inorganic impurities in the carbons (Bansode *et al.*, 2003). It also reduces the overall activities of the activated carbon, thereby reducing the efficiency of re-activation while metal oxide like Fe_2O_3 can leach out of activated carbon, resulting to coloration (Itodo, 2008). According to

Ahmedna *et al.,* (2000), ash content of activated carbon is dependent on the ash content of the starting material. In this study, ash content is also found to be a function of the activating agent. $ZnCl_2$-modified sorbent presents the high % of ash (9.10%) with one step method.This could possibly be the reason for its lower adsorption performance compared to KOH and H_3PO_4 treated carbons with much lower % ash.

The pH of activated carbons prepared from agricultural by products is said to be of the same order of magnitude. Generally, adsorbents with pH of 6-8 are acceptable in most applications (Okeimen *et al.,* 2004). The experimental pH recorded for the carbonized and some activated carbons from groundnut shell falls within the stated limit, pH as high as 9.62 for $ZnCl_2$ - treated carbons . The pH of the untreated carbon (CGS) was found to be within the neutral limit. It could therefore be concluded that the variation in pH by the adsorbents could be as a result of chemical activation which resulted in higher pH for KOH and $ZnCl_2$ – treated carbons (basic), while lower pH for H_3PO_4 – treated carbons (acidic).

3.2 Yield of Activated Carbon (%)

Inorganic impregnation with chemicals such as KOH, H_3PO_4, $ZnCl_2$, e.t.c., followed by activation dehydrates the cellulose material resulting in weakening of the precursor structure and in creation of pores. This is responsible for decomposition of the organic materials to release volatiles and development of microporous structures (Malik *et al.,* 2006).

Report has shown that low volatile matter content implies the high porosity of the adsorbent since volatile matter remain clogging in the carbon pores (Wahi *et al.*, 2009). In this research KOH-modified sorbent present higher carbon yield (72.52% and 70.03%) compared to other carbons. This could probably be as a result of charring power of KOH. Followed by KOH carbons is H_3PO_4 adsorbents. The CGS gave even better carbon yield than 2S/Z and 2S/P carbons. This could be attributed to the direct carbonization of the raw GS at 800^0C. The overall trend observed for percentage yield for the one step include: 72.52> 69.11> 58.94 with KOH, H_3PO_4 and $ZnCl_2$ activants respectively.

3.3 Batch Adsorption Study (GCMS Quantitation)

The analysis was carried out with a fixed variable sorbate doses. Quantitative measurement was done using GCMS (model QP2010 plus) Shimadzu Japan at NARICT, Basawa, Zaria.

Tables 3, 4 and 5 presented the experimental data of dichlorvos uptake by the generated sorbents with varied molar concentration of KOH and that of untreated carbon (CGS).

Table 3 revealed a complete (100%) removal by sorbent 1S/KOH. This total uptake could be traced to either the effectiveness of the carbon and or method of preparation of the activated carbon. Hence, a total amount of 1 $x10^{-3}$mg dichlorvos was adsorbed by a unit mass of the activated carbon.

Table 3 Batch equilibrium experimental data for dichlorvos uptake by sorbent prepared using one-step scheme and interaction of 0.1g sorbent with 10g/dm^3 initial dichlorvos concentration

Adsorbent	Co (g/dm^3)	Ce (g/dm^3)	Ca (g/dm^3)	% RE	M ($x10^{-3}$g)	q_e($x10^{-3}$ mg/g)
1S/KOH	10	0.000	10.000	100.00	0.1000	1.000
1S/H_3PO_4	10	0.022	9.978	99.780	0.0998	0.998
1S/$ZnCl_2$	10	0.076	9.924	99.240	0.09924	0.992

Table 4 Batch equilibrium experimental data for dichlorvos uptake by sorbent prepared using one-step scheme and interaction of 0.1g sorbent with 20g/dm^3 initial dichlorvos concentration

	Co (g/dm^3)	Ce (g/dm^3)	Ca (g/dm^3)	% RE	M($x10^{-3}$g)	q_e(10^{-3} mg/g)
1S/KOH	20	0.187	19.813	99.065	0.3960	3.960
1S/H_3PO_4	20	0.038	19.962	99.810	0.3992	3.992
1S/$ZnCl_2$	20	0.119	19.881	99.405	0.3976	3.976

Table 5 Batch equilibrium data for dichlorvos uptake by 1S/KOH with varied molar concentrations (M)

Molar conc. Of KOH (M)	Co (g/dm^3)	Ce (g/dm^3)	Ca (g/dm^3)	RE (%)	M ($x10^{-3}g$)	q_e (10^{-3} mg/g)
1.0	10	0.000	10.00	100.0	0.1000	1.000
0.1	10	1.892	8.108	81.08	0.0811	0.8110
0.075	10	2.013	7.987	79.87	0.0799	0.7990
0.01	10	2.405	7.595	75.95	0.0759	0.7590

Table 6 Batch equilibrium data for dichlorvos uptake by untreated GS (CGS)

Co (g/dm^3)	Ce (g/dm^3)	Ca (g/dm^3)	RE (%)	M ($x10^{-3}g$)	q_e(10^{-3} mg/g)
10	3.276	6.724	67.24	0.06724	0.6724
20	6.784	13.216	66.08	0.1322	1.322

3.4 Effect of Activating Agents

The nature of activating agent plays a significant role on the sorbate uptake. This is pronounced with the $10g/dm^3$ initial dichlorvos concentration. The % sorbate removal follows the order 1S/KOH/10 (RE=100%) > $1S/H_3PO_4/10$ (RE=99.780) > $1S/ZnCl_2/10$ (RE=99.240%). It has been shown that KOH – activated carbons are essentially microporous with high surface area. Hence activation with KOH proves better dichlorvos removal (RE=100%) at lower concentration compared to H_3PO_4 and $ZnCl_2$.

At a higher sorbate dose ($20g/dm^3$ dichlorvos), sorbents prepared with H_3PO_4 gave better adsorption for both one step and two steps generated carbon. $1S/H_3PO_4/20$ (RE = 99.810). The untreated carbon (CGS) showed some significant dichlorvos uptake. Table 4 and 5 indicate removal of up to 67.24 and 66.08% for 10 and $20g/dm^3$ respectively. This is an indication of significant influence by activating agent in dichlorvos removal. All the sorbents prepared compared to CGS performed excellently in dichlorvos and thus revealed that activating agents play a very significant role in dichlorvos removal.

3.5 Effect of initial sorbate concentration

Comparative study of Tables 4 and 5 explained the effect of sorbate concentration. Apart from the 1S/KOH adsorbents, higher % dichlorvos uptake (99.405% and 99.810%) of $1S/H_3PO_4/20$ and $1S/ZnCl_2/20$ was reported. The values are higher than those of their corresponding $10g/dm^3$ uptake on Table 5 (with values of 99.240% and 99.780% by $1S/H_3PO_4/10$ and $1S/ZnCl_2/10$ respectively). The same study carried out on the CGS and revealed similar characteristics to KOH. Table 4 indicates higher percentage of sorbate removal with $10g/dm^3$ (67.24 & 66.08%) for 10 and $20g/dm^3$ respectively. It thus follows that (i) the adsorbents prepared, especially H_3PO_4 can adsorb better at certain high sorbate dose and (ii) there could be possibilities of desorption due to high pore size development when the sorbate dose is less (Itodo *et al.*, 2008).

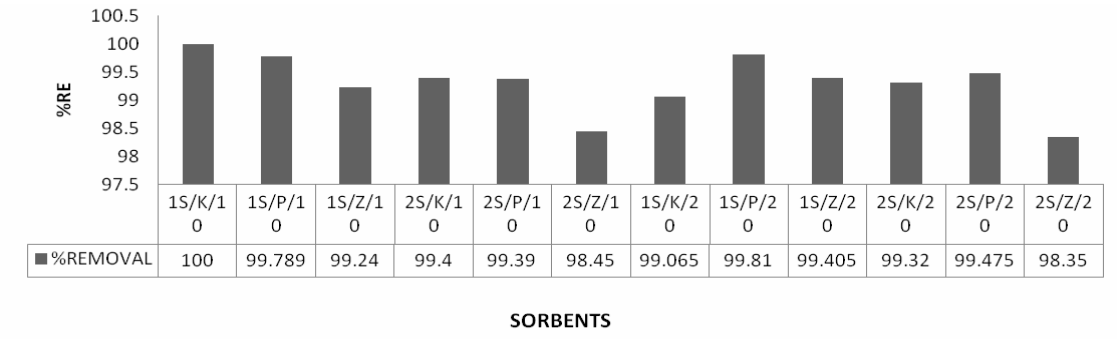

Figure 1 Sorption efficiency of dichlorvos uptake (%RE) by groundnut shell adsorbents

3.6 Effect of varying molar concentrations of Activating Agents (AA)

Molar concentrations of activants have some effect on sorbate removal. This effect was investigated by varying the molar concentration (M) of KOH. Three different adsorbents were obtained (1S/K-0.1M, 1S/K-0.075M and 1S/K-0.01M). Table 2 revealed a direct relationship between molar concentration of AA and dichlorvos uptake. The trend follows 1M>0.1M>0.075M>0.01M. This is in line with what was reported by Jibril *et al.*, (2007). They reported a significant increase in sorbates densities as molar concentration of AA-KOH was increased. Conversely, higher density carbon provides greater volume activity and normally indicated better quality activated carbon (Carbochem, 2005).

4.CONCLUSION

Removal of pesticide from solution using activated carbon prepared from groundnut shell has been achieved. Apart from GS all the adsorbents prepared performed above 98% removal. This is an indication that GS could be an excellent precursor for preparation of AC for dichlorvos uptake. However, out of the AAs used (KOH, H_3PO_4 and $ZnCl_2$), KOH proved to be more effective especially at lower concentration of adsorbent.

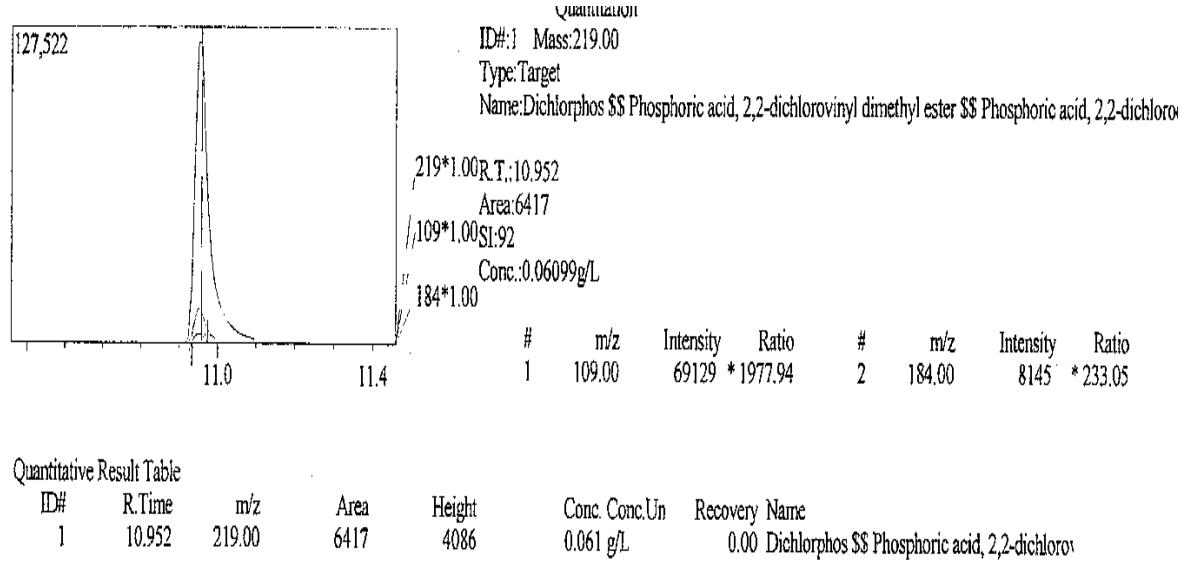

Figure2 GC/MS chromatogram, quantitative measurement and spectral information of equilibrium phase Dichlorvos after adsorption onto 2S/H_3PO_4/10 sorbent

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