

## Synthesis and Characterizations of two Herbicides with Zn/Al Layered double hydroxide nano hybrides.

Abbas M. Bashi, Salih M. Haddawi and Ashoor H.dawood  
Chemistry department –Faculty of Science-Karbela University.

### الخلاصة:

تهجين نانوي تم الحصول عليه من تخليق مزيج من 2,4-ثنائي كلوروفينوكسي و 4-كلورو فينوكسي خلات وهما من عائلة المبيدات العشبية ويستخدمان في تنظيم النمو للنبات، الأنيونين قد ادخلا بين طبقات الزنك/المنيوم بواسطة الترسيب المشترك للانيونين والثنائي الطبقة وبنسب 2,3,4 شخص التركيب بواسطة حيود الشععة السينية ظهر المتويات البلورية العائدة الى (003),(006),(009),(012) لمزيج من طورين الاول يعود الى 2,4-ثنائي كلورو – والآخر الى 4-كلورو فينوكسي خلات .

### Abstract:

Afunctional hybrid nanocomposit based on the intercalation of mixed cohydrolysed anions 2,4Dichlorophenoxy acetate (24D) and 4-chlorophenoxy acetate (4CPA), they are from the family of herbicides , which are used as plant growth regulators, this two anions intercalated by in direct method in layer double hydroxid (LDH) type of Zn, Al synthesized by co precipitation with LDH,  $Zn / Al = R = 4$

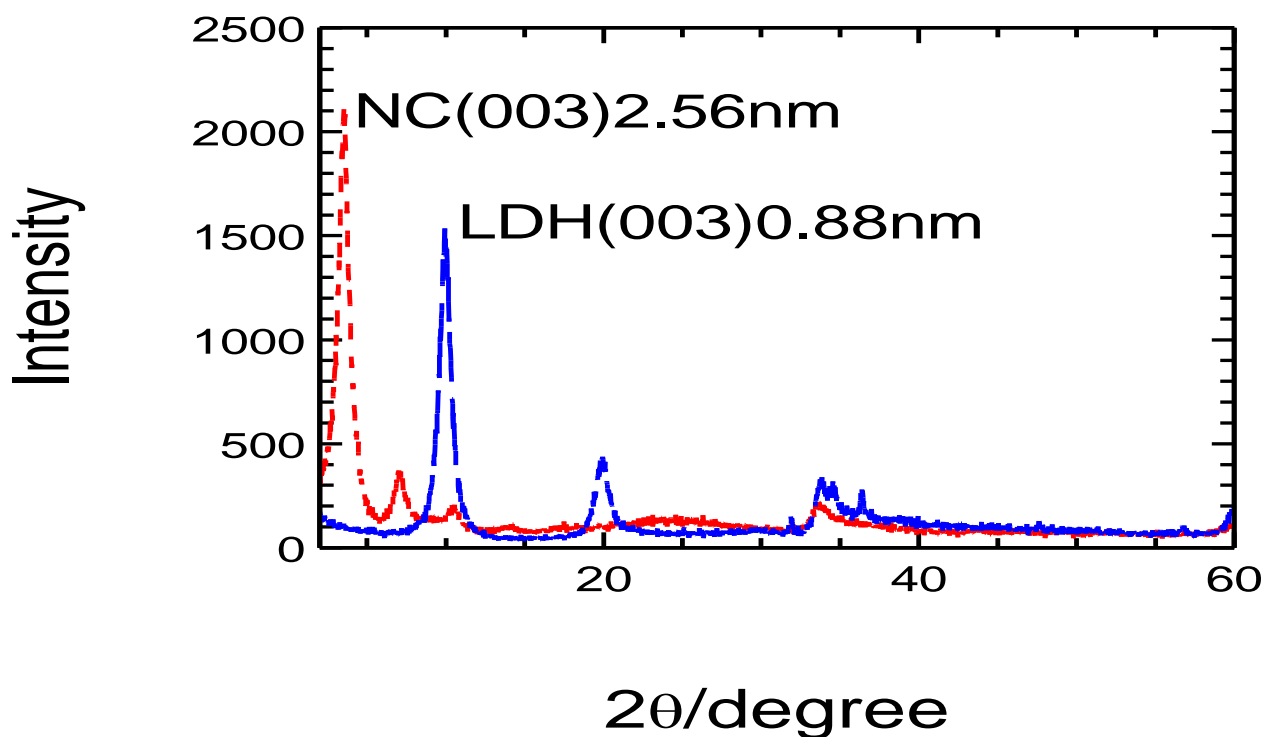
The characterized by gas chromatography coupled with mass spectroscopy (GC-MS) , showed the existence fragments of two different phase belong to 24D and 4CPA, X-Ray Diffractions ( XRD) confirm the intercalations of two anions by the existence of two phases through a series of diffracted harmonies d(003), d(006), d(009) and d(0012), Fourier Transformation Infra Red ( Ftir), thermal analysis. (TG- DTG). All those techniques succeed to detecting the existence of a mixture of two phases belongs to the intercalations of the two anions in between interllmilar distance of the LDH, which act as a host matrixes for the intercalation of guest anions to synthesis hybrid organic-inorganic nanocomposit .

**1.Introduction:** The positive charges in the LDH results from the substitution of  $M^{+3}/M^{+2}$  ratios in LDH representing the layer charge density ranging from (0.25-0.33)[1] , LDH also called anionic clays , are received considerable attention in recent years due to their potential technical applications intercalation of 4-Chloropenoxy acetate molecule has been reported [ 2 ]by anion exchange and co precipitation, such work had been carried out for plant growth regulator, herbicides[3] pharmaceutical[4]synthesis of hydrotalcites [5] adsorption of industrial dye [6] and promising developments are expected for environmental domain [7 ] anion exchange for the applications of removal of contamination from water or for scavenging hazardous molecule [ 8-10].The type of solvents , experimental conditions as PH and the ratio of LDH are highly affecting factors for LDH with a certain affinities for anion following the order of the homeister series [ 11] that is the affinity for anion increase with increasing charge and decreasing ionic radius that the  $NO_3^-$  ion is exchanged more readily than other inorganic anions such as  $Cl^-$  and  $CO_3^{2-}$ , that was focusing on LDH- $NO_3^-$  an important precursor for intercalation [12], and it may be useful for DNA and ATP storage due to higher stability of the biological material in LDH type of Zn/Al, interlamellae This work aimed at the synthesis and characterizing the intercalation of mixed cohydrolysed anions of 2,4D and 4CPA as guests anions and the LDH ,as host molecule .

**2.Materials and Method:** All chemicals used in the synthesis were obtained from various chemical suppliers and were used without further purifications, all solutions were prepared using deionized distilled water. The formation of nano composite by intercalation of the two anions 2,4-dichloro- and 4-chlorophenoxy acetate with Zn/Al LDH, was done by self-assembly method from mixed cohydrolysed anions dropping on aqueous solution of  $Zn(NO_3)_2 \cdot 6H_2O$ , and  $Al(NO_3)_3 \cdot 9H_2O$  with initial molar ratio Zn/Al (R)=2,3,4,5 and adjusting PH=7.5 by slow addition of 2M NaOH under  $N_2$  atmosphere with continuous vigorous stirring. The slurry obtained was aged for 18h in an oil bath shaker at  $70C^{\circ}$  the resulting precipitate was centrifuge washed four times with deionized distilled water, then dried in an oven at  $70C^{\circ}$  overnight and kept in sampling tube for further use and characterization. The products were denoted-N24D and N4CPA. The mixed 24D+4CPA- intercalated LDHs were synthesized by the route of intercalated N24D and N4CPA with R= 4 were prepared by indirect method of ion exchange.

**2.Characterization and Results:** X-ray powder diffraction patterns (XRD) were obtained with Shimadzu XRD-6000 powder diffractometer using ( $\lambda=1.540562\text{\AA}$ ) at 40kV and 30mA, scan rate =  $0.5\text{min}^{-1}$ .

Fourier transform infrared (FTIR) spectra were recorded by using a Parkin-Elmer 1750X spectrophotometer in the range of  $4000-400\text{cm}^{-1}$ . GC-MS-QP5050Z, with temperature program from  $40-340^{\circ}C$ , column inlet pressure = 21KPa, flow rate =  $0.6\text{ml/min}$ , velocity =  $28.8\text{cm/sec}$  and split ratio = 14.

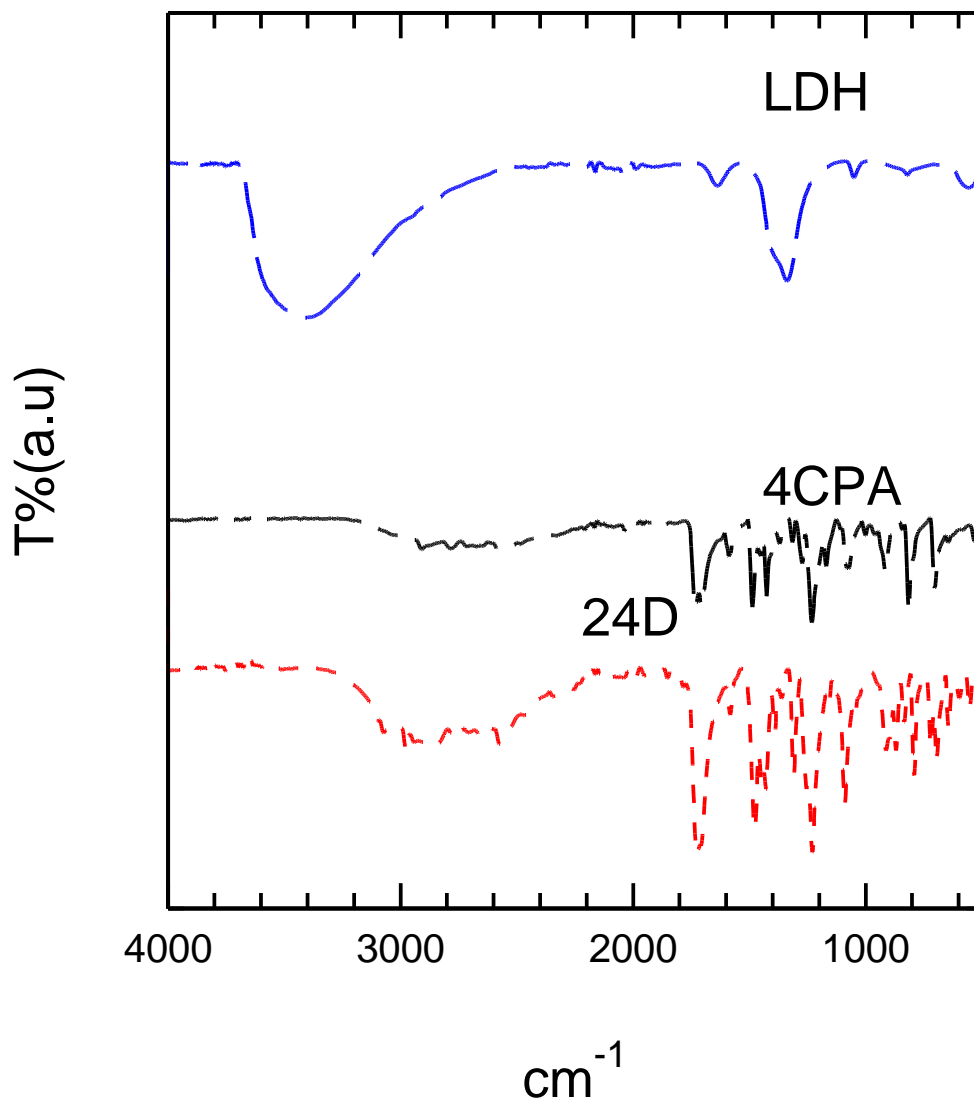


**Fig.1** XRD pattern of LDH and (24D+4CPA) shows the intercalation of mixture of two phases resulted.

Fig. 1 shows obviously sharp (001).

present well-defined (001), (003) reflection demonstrating substituting small  $NO_3$  ions with large organic (24D and 4CPA) ions, the (001) the formation of LDHs-like structure. Generally, upon peaks of the intercalates shift to lower  $\theta$  values, indicating that the hydroxide layers are further expanded upon intercalation of bulky anionic molecules [13]. and (003) peak, demonstrating The reflections can be

indexed to a hexagonal lattice with-3m rhombohedral symmetry [14] the high crystallinity of products. Interestingly, The parameter  $a$  ( $=3d_{003}$ ) is a function of the average radii of the metal cations, i.e., the distance between two adjacent metal cations in the same brucite-like layer. The interlayer spacing of 24D+4CP products are greatly increased to ca. 2.500 nm, implying the possible different interlayer anionic arrangements. The 24D+4CPA-LDH present similar diffraction features to 24D+ 4CPA-LDH, while the 24D+ 4CPA-LDH shows the rough base line and overlapped weak (0 0 3) peak, which might be caused by the formation of a secondary phase due to co intercalation of counter ion ( $\text{NO}^{-2}$ ) from salts. It can be deduced that the intercalate prepared by ion exchange route with high loaded possess better layer and interlayer organizing order than those with lower loaded, consistent to the Exchanged samples, probably due to strong interaction between the hydroxide layer and the interlayer anions.



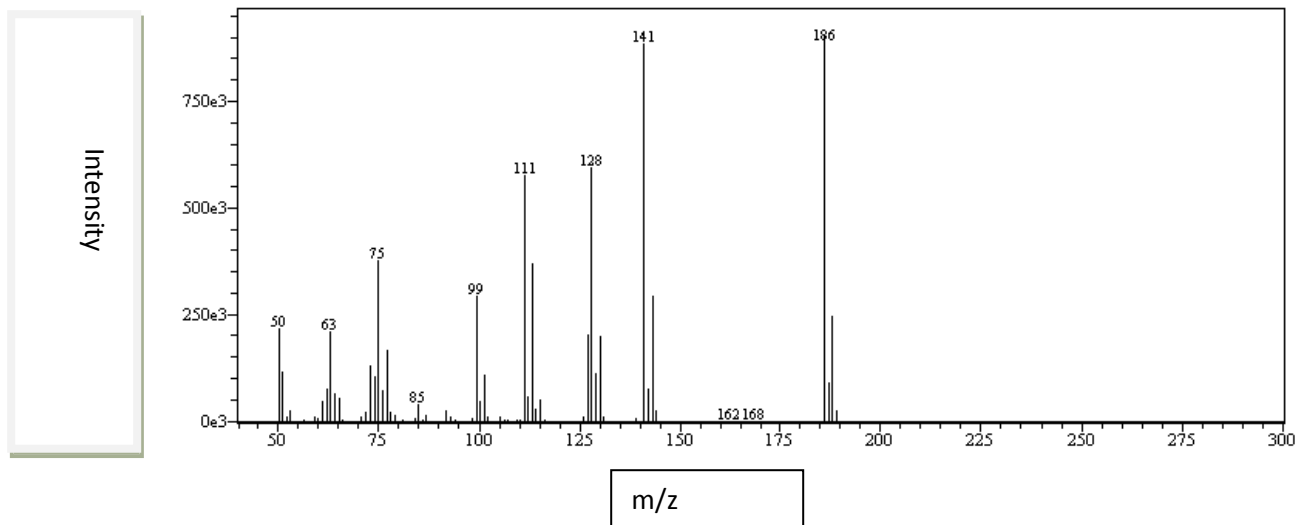
**Fig.2** FTIR spectrum pattern of LDH,4CPA, 24D and 4CPA+24D-LDH.

The FTIR spectra of the intercalation products and pure are shown in Fig. 2. For all intercalates, indicatives of chlorophenoxy acetates intercalated in LDHs interlayer space is soundly observed. The broad absorption band at ca.  $3440\text{ cm}^{-1}$  arises from the stretching mode of OH groups in the brucite-like layer and physisorbed as well as interlayer water molecules as commonly observed for LDHs materials [15]. The band at  $1624\text{ cm}^{-1}$  can be attributed to the deformation vibration of water

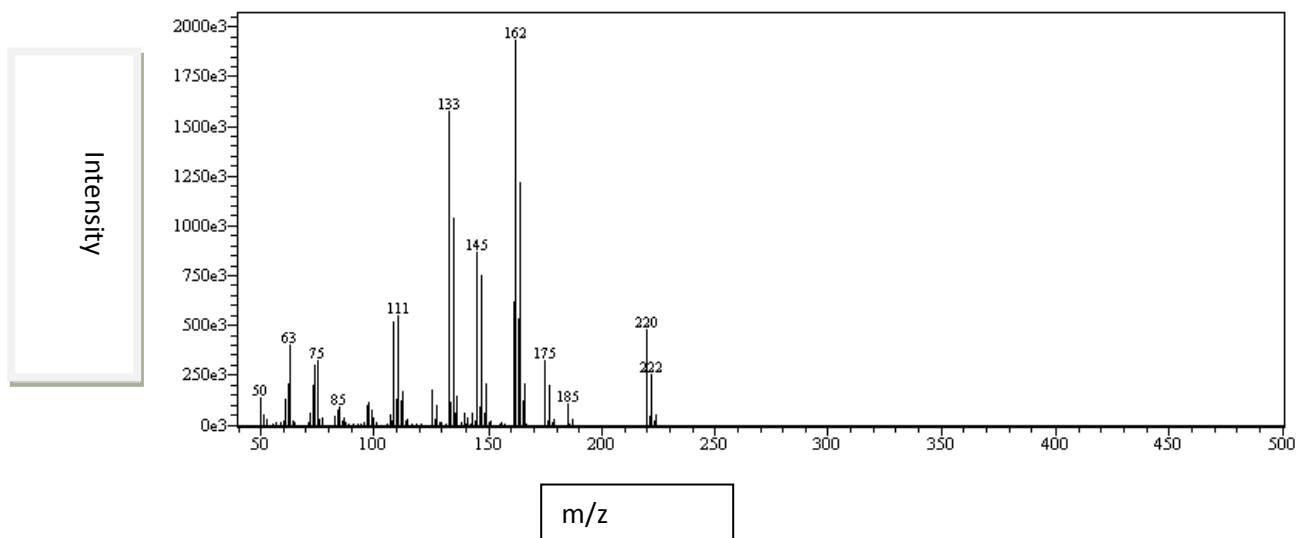
molecules in the interlayer region. The two bands at ca. 1567 and 1364  $\text{cm}^{-1}$  due to the anti-symmetric and symmetric stretching modes of  $\text{COO}^-$  group shift to lower wave numbers for intercalated samples, compared to free carboxyl functional group in chlorophenoxy acetate (1648 and 1381  $\text{cm}^{-1}$ ), indicating that the intercalation of chlorophenoxy acetate<sup>-</sup> in interlayer space involves strong hydrogen bond between  $\text{COO}^-$  groups and hydroxyl groups of the layer. However, for intercalated samples, the asymmetric stretching mode of  $\text{COO}^-$  group presents obvious downshift, while the symmetric one shift only a little, but with great broadening, implying possible different interlayer orientation of chlorophenoxy acetate<sup>-</sup> ions between the layers strongly related to the synthesis routes. The band at ca. 1243  $\text{cm}^{-1}$  due to the deformation mode of interlayer water and anti-symmetric stretching mode of  $\text{COO}^-$  [16] presents similar changes compared with that for chlorophenoxy (in Fig. 2 at 1255  $\text{cm}^{-1}$ ), implying that (coo<sup>-</sup>) group is also involved in hydrogen bond within the interlayer domain. The characteristic M-OH layer lattice vibrations at ca. 600, 558, and 427  $\text{cm}^{-1}$  are well defined in the intercalated products, indicating the quite ordered inlayer structure of the LDH upon indicating the quite ordered inlayer structure of the LDH. Besides above common features, the positions of two bands at ca. 1492 and 1452  $\text{cm}^{-1}$  due to the C-C stretching modes of aromatic ring in 24D and 4CPA [17]. In addition, the intensity ratio of these two bands increases with increasing R of intercalates. These observations apparently indicate the possible occurred of host-guest interaction via hydrogen bonding between  $\text{COO}^-$  group of phenoxy acetate<sup>-</sup> ions and OH group of the layer, and guest-guest interaction through conjugation of the phenyl groups of interlayer<sup>-</sup> ions related to the varied compositions (R) and synthesis paths [18]. In order to further illustrate the effect of the host-guest and guest-guest interactions for intercalates, the UV-Vis spectra of the products with  $R \approx 4$  and pure chlorophenoxy acetate are recorded. As shown in Fig. 3, the absorptions of products are clearly green shifted. These broad absorptions are characteristic of highly ordered solid-state arrays and are probably a consequence of intermolecular electron delocalization such as conjugation through UV absorbing anion parts [19]. The green shift in the spectrum might be due to the host-guest interaction, i.e., the low symmetry ligand distortions in the spatial restricted interlayer galleries and/or guest-guest interaction function [20]. Moreover, the higher the layer charge density of intercalates, the larger the green shift occurs, consistent with the IR analysis. On the basis of elemental analyses, the 24D+4CPA loadings are obtained. Commonly, the chlorophenoxy acetate<sup>-</sup> loadings of the intercalation products increase as density increases because of the positive charge compensation [21].

direct insertion mass spectroscopy (DIMS) of the 4-Chlorophenoxy acetic acid, 2,4-Dichlorophenoxy acetic acid and nano hybrid (CDBN) was studied and the result shows that is the case. The mass spectroscopy of 4-Chlorophenoxy acetic acid Fig.3(a) displayed the parent ion at  $m/z = 186$  and characterized peaks at  $m/z = 141, 128, 111$  attributed to ions ( $\text{C}_7\text{H}_6\text{ClO}^+$ ,  $\text{C}_6\text{H}_5\text{ClO}^+$ ,  $\text{C}_6\text{H}_4\text{Cl}^+$ ), the 2,4-Dichlorophenoxy acetic acid Fig.3(b) appeared parent ion at  $m/z = 220$  and characterized peaks at  $m/z = 186, 175, 162, 144, 111$  attributed to ions ( $\text{C}_8\text{H}_7\text{ClO}_3$ ,  $\text{C}_7\text{H}_5\text{Cl}_2\text{O}^+$ ,  $\text{C}_6\text{H}_3\text{Cl}_2\text{O}^+$ ,  $\text{C}_6\text{H}_3\text{Cl}_2^+$ ,  $\text{C}_6\text{H}_4\text{Cl}^+$ ). whereas the present of the two anions simultaneously in the nano hybrid indicated that the sample contains 4-Chlorophenoxy acetic acid and 2,4-Dichlorophenoxy acetic acid Fig.3(c), in which both anions were intercalated together into the LDH interlayers as can be observed by the present of peaks with  $m/z$  values of  $=185$  and  $220$ , respectively. As well as displays the segments which that expected of fragmentation of both ions whereas the spectrum show the sharing peak at  $m/z = 111$  showed in both mass spectra of ions

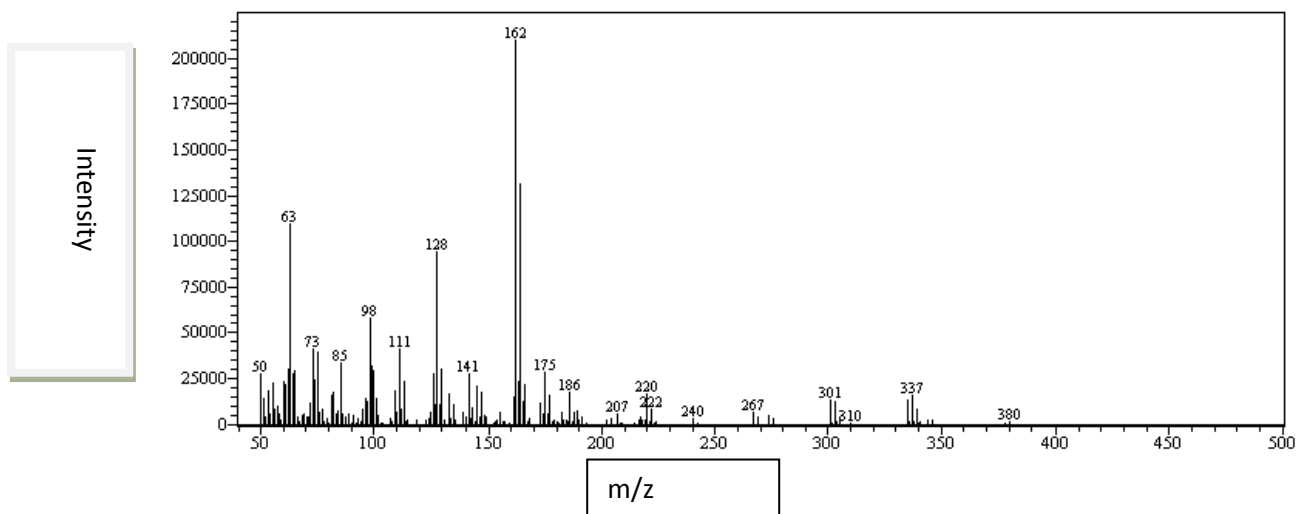
The following segmentations Fig. 4 and Fig. 5 analysis indicates the original of related segment for each phase:



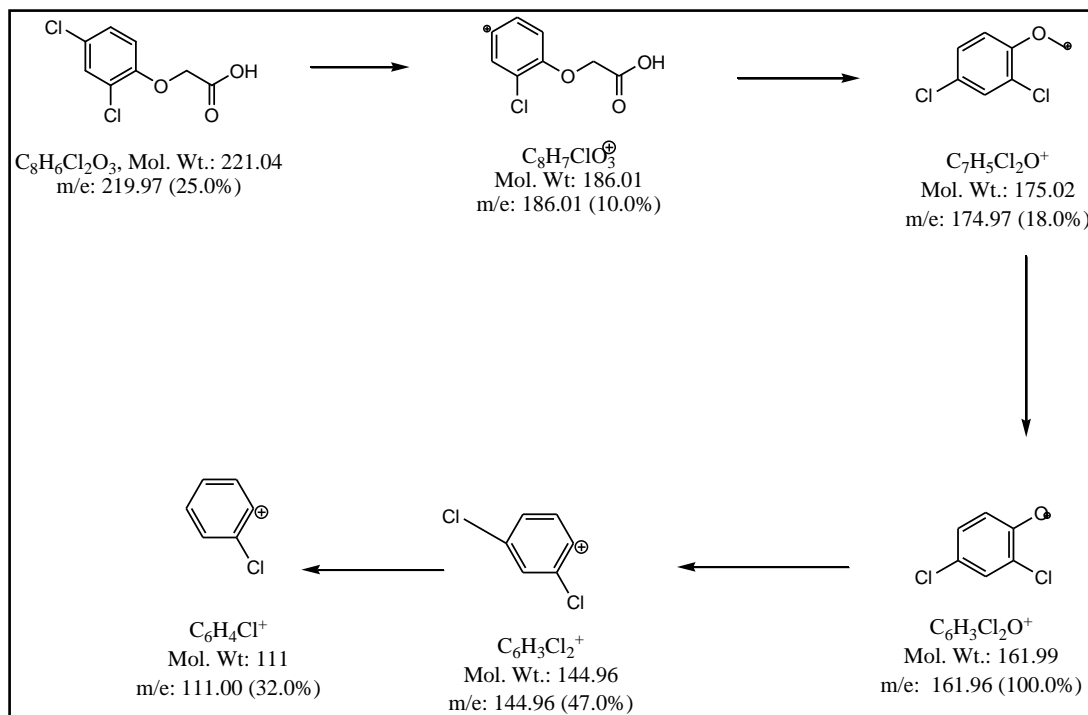
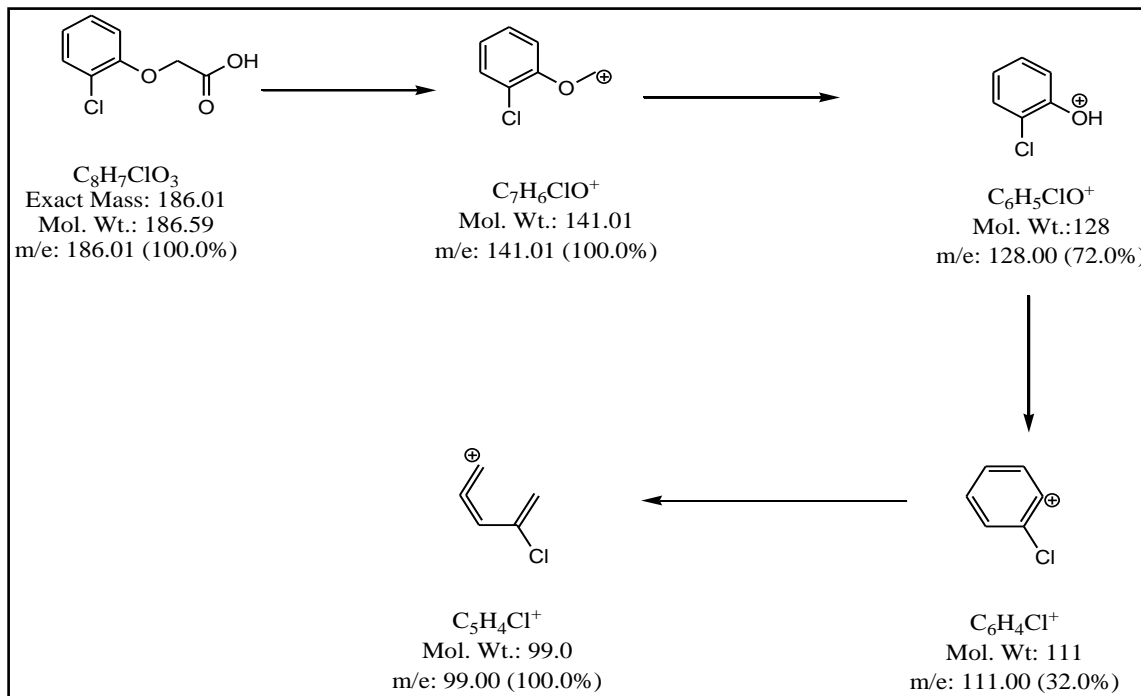
**Fig.3(a)** Mass spectrum of 4-chlorophenoxy)acetic acid



**Fig.3(b)** Mass spectrum of 2,4-dichlorophenoxy)acetic acid



**Fig.3 (c)** Mass spectrum of 2-(2-chlorophenoxy)acetic acid and 2-(2,4-dichlorophenoxy)acetic acid



**Fig. 5** Mass fragmentation of (2,4-dichlorophenoxy)acetic acid

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