Degradation of aldrin in adsorbed system using advanced oxidation processes: comparison of the treatment methods

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Abstract

In this study, Fenton, UV/Fenton, UV/H_2O_2, UV/Fe^{2+} advanced oxidation processes have been applied for degradation of aldrin adsorbed on Na-montmorillonitte and activated carbon. Aldrin adsorbed on Na-montmorillonitte was degraded more efficiently than that of on activated carbon. For example, in UV/Fenton technique 95% of aldrin was removed from Na-montmorillonitte while 50% degradation was observed on activated carbon. Degradation of aldrin adsorbed on Na-montmorillonitte has also been achieved effectively using UV/Fe^{2+} technique despite the absence of H_2O_2. All AOPs but Fenton have been observed nearly equally effective for degradation of aldrin on Na-montmorillonitte sorbent. Fenton reaction exhibited least activity in degradation aldrin adsorbed on Na-montmorillonitte. The experiments with activated carbon sorbent indicated that phenyl groups in activated carbon structure and aldrin molecules exhibited competitive behavior on reaction with OH$^\bullet$ radicals. The results of infrared spectroscopy support this assumption. The degradation efficiency of aldrin using activated carbon sorbent was determined in the following order: UV/Fenton > UV/H_2O_2 > Fenton > UV/Fe^{2+}.
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Keywords: Aldrin; Advanced oxidation techniques; Clay; Activated carbon

1. Introduction

Organochlorine pesticides (OCPs) are an important group of environmental contaminants. They have been of great concern due to their persistent nature and chronic adverse effect on wildlife and humans [1,2]. These pesticides include DDT, aldrin, dieldrin, heptachlor, chlordane, lindane, endrin, mirex, hexachloride, and toxaphene. Despite the ban and restriction on the usage of these pesticides in developed countries during the 1970s and 1980s, some developing countries are still using them for agricultural and public purposes because of the low cost and versatility in controlling various insects [3]. Aldrin is organochlorine insecticide that is extremely persistent in the environment and can accumulate in living organisms [4]. It has been used as a soil insecticide to control rootworms, beetles, and termites.

Activated carbon sorbent has been successfully used to clean up contaminated waste water [5,6]. The high porosity, extensive surface area and high surface reactivity of activated carbon make it an effective sorbent for many organic contaminants [7]. Clay sorbents also have been used for removing hydrophobic compounds in waste water [8]. Because clay is present in the composition of soil remediation using this sorbent seems reliable. Desorption rates of hydrophobic contaminants present in the sorbed phase are often much slower than their transformation rates, and therefore limit their rates of treatment. Consequently, it is important to clarify the role of the clay sorbent on the degradation process. Our objective is to determine effect of activated carbon and Na-montmorillonitte (as clay) sorbents on the oxidative treatments of aldrin.

In recent years, an alternative to conventional methods is "advanced oxidation processes" (AOPs), based on the generation of very reactive species such as hydroxyl radicals that quickly and nonselectively, oxidizes a broad range of organic pollutants [9,10]. A few researchers studied to remove chlorinated organic compounds from adsorbents by AOPs [11,12]. In this study, aldrin adsorbed to activated carbon and Na-montmorillonitte was degraded by using UV/Fe^{2+}, UV/Fenton, Fenton, UV/H_2O_2 advanced oxidation processes.

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2. Experimental

2.1. Materials

Aldrin used in this study was obtained from EPA with 99.5% purity. All chemicals were purchased from Merck and used without any further purification. Pen-ray 254 nm 15 W UV lamp was used as UV irradiation source. Radiation intensity of this lamp was determined as 0.40 μeinstein/l by uranyloxalate actinometer method [13]. Adsorption experiments were carried out with montmorillonitte purchased from Aldrich and powdered activated carbon from Chemwiron. The chemical compositions of the montmorillonite were reported by Wang et al. [14].

Montmorillonitte was treated for 24 h with 1 M NaCl solution, then centrifuged for 15 min at 6000 rpm and washed with distilled water to remove chloride ions before using as adsorbent. The presence of chloride ions in washing water produced from montmorillonitte was checked by using $AgNO_3$ method [15]. By this way montmorillonitte was changed to homoionic Na-montmorillonitte. It was dried at 105 °C for 24 h. Activated carbon was washed by 0.2 M H_2SO_4 solution to leach out undesirable inorganics such as calcium, magnesium, iron and aluminum. This was followed by water washing until the pH of washing water reached up to pH of 6 [16]. The total surface areas of Na-montmorillonite and activated carbon were determined by methylene blue method and were found 576 m^2/g for Na-montmorillonite and 632 m^2/g for activated carbon [17].

2.2. Aldrin sorption on activated carbon and clay

Cyclohexane was chosen as a solvent in adsorption experiments. Dried Na-montmorillonite (10 g) was added into the 100 ml of cyclohexane containing 10 mg of aldrin. The mixture was stirred magnetically until solvent volume decreased to 30 ml. The mixture was filtered through a cellulose nitrate membrane (0. μm pore size, 25 mm diameter; Advantec MFS, Pleasanton, USA). The aldrin concentration in the filtrate was determined by Shimadzu GC-14A gas chromatograph with electron capture detector (ECD). The column was 50%-phenyl-methylpolysiloxane capillary column from GL Science Inc. (TC-17, 30 m × 0.32 mm i.d., 0.5 μm stationary phase thickness). Adsorbed aldrin on adsorbent was calculated by subtraction of aldrin concentration in 30 ml after adsorption (which was corrected by 100/30 ratio) from initial aldrin concentration in 100 ml. After evaporation of cyclohexane, adsorption/desorption balance was changed continuously to enhance aldrin adsorption on clay and activated carbon as 1.17 and 2.00 mg/g, respectively. The aldrin adsorbed clay and activated carbon was filtered and dried in vacuum desiccator at room temperature. Recovery of aldrin with CH_2Cl_2 from Na-montmorillonitte and activated carbon have been found as $100 \pm 8\%$ and $96 \pm 12\%$, respectively.

Table 1
Desorption percentage of aldrin on Na-montmorillonite with reaction time

Reaction time (min)	Aldrin (%)
0	0.3
5	0.7
10	1.0
15	1.2
20	1.3
30	1.3
40	1.3

In order to determine desorption percentage of aldrin adsorbed on Na-montmorillonite and activated carbon the experiments carried out at the same reaction condition and sampling time in absence of UV light and H_2O_2. Desorption of aldrin on activated carbon was not able to determined because of very low desorption limit. Desorption percentages obtained using Na-montmorillonite sorbent are given in Table 1. Desorption percentage of aldrin was determined as 1.3% at the end of the reaction. Therefore, it can be concluded that oxidation of aldrin was carried out in adsorbed phase on Na-montmorillonitte rather than in solution via desorption during the oxidation processes.

2.3. Determination of optimum H_2O_2/Fe^{2+} values at various Fe^{2+}/aldrin ratios

In this part of the study, 0.1 mg adsorbent on which aldrin adsorbed and 50 ml distilled water were placed in a 75 ml glass cylindrical reactor. The pH of the mixture was adjusted to 3 using 0.1 M H_2SO_4. Fe^{2+} solution was added into this mixture and stirred magnetically for 5 min. Five milliliters of samples was taken from the suspension before addition of H_2O_2 and at the end of 2 h after addition of H_2O_2. The suspension samples were filtered and solid residue on filter paper was kept in a vacuum desiccator for drying. Then, it was extracted with CH_2Cl_2 together with filter paper and concentrated to 5 ml for analysis of aldrin by GC.

2.4. AOPs experiments

In this study, four types of AOPs, Fenton, UV/Fe^{2+}, UV/H_2O_2, UV/Fenton were applied to treat aldrin adsorbed on clay and activated carbon. 0.4 g of adsorbent on which aldrin adsorbed was placed in a 250 ml glass reactor. Two hundred milliliters distilled water was added and pH was adjusted to 3 with 0.1 M H_2SO_4. Fe^{2+} solution was added into this mixture (Fe^{2+}/aldrin = 10). Before adding H_2O_2, 5 ml of sample was taken while suspension was mixing ($t = 0$ min). In UV combined experiments UV lamp was immersed in the center of the reactor. After adding H_2O_2 with H_2O_2/Fe^{2+} = 5.76 (mol/mol) ratio samples were drawn from the reactor at $t = 4, 8, 12, 20, 25, 30,$ and 40 min. The samples were filtered through 0.1 μm filter paper following dried in vacuum desiccator and extracted with CH_2Cl_2. The extracts was concentrated in rotary evaporator and analyzed

by GC. Weight of the adsorbent was determined by subtraction of weight of filter from total weight that consists of filter paper and adsorbent.

For characterization of intermediate products, which were formed during the degradation of aldrin on Na-montmorillonite sorbent in UV/Fenton application, 200 ml of reaction mixture after 10 min reaction time was extracted with CH_2Cl_2 and concentrated until 2.5 ml using rotary evaporator. The extract derivatized with N,O-bis(trimethylsilyl) acetamide (Sigma) before analyzed by GC/MS. The degradation products of aldrin were determined by ThermoFinnigan Trace GC/MS using Zebron capillary column (100% polydimethylsiloxane, 30 m × 0.25 mm × 0.25 μm). The oven temperature program was 40 °C (5 min), then 4 °C/min to 280 °C (10 min); injector temperature, 250 °C; and detector temperature, 280 °C.

2.5. Determination of Fe^{2+} concentration

The concentration of Fe^{2+} was determined by titration with standard solution of potassium dichromate using o-fenantroline indicator before and after addition of H_2O_2. The reagents used in this stage were more concentration than those of in the experimentation to make possible the detection in the titration. Five milliliters of sample was taken from the mixture in various reaction time and filtered through 0.1 μm filter paper. Iron ions in the filtrate solution were determined by Hitachi Polarized Zeeman atomic adsorption spectrophotometer. Subtraction of total iron ions in the filtrate solution from Fe^{2+} concentration of the solution gives the iron ions adsorbed on Na-montmorillonitte.

3. Results and discussions

3.1. Determination of optimum H_2O_2/Fe^{2+} ratio for degradation of aldrin adsorbed on Na-montmorillonitte

Three different ratios of Fe^{2+}/aldrin (10, 20, and 30 mol/mol) were studied for degradation of aldrin adsorbed on Na-montmorillonitte. H_2O_2/Fe^{2+} ratios were varied at each constant Fe^{2+}/aldrin ratio. These ratios are given in Fig. 1. Tang and Huang [18] reported that degradation of trichloroethylene (TCE) increased by increasing H_2O_2/Fe^{2+} ratios until 5 at constant Fe^{2+}/TCE ratio in aqueous systems. Their results were not observed in adsorbed systems, which we studied (Fig. 1). At the Fe^{2+}/aldrin ratio of 10 and 30, although H_2O_2/Fe^{2+} ratios were varied from 1.92 to 11.52 degradation of aldrin has been determined almost constant and degradation levels observed to be 60–65 and 70–75%, respectively.

At the Fe^{2+}/aldrin ratio of 20, maximum degradation of aldrin was about 77%. In this ratio, degradation of aldrin increased slightly with increasing H_2O_2/Fe^{2+} ratios up to 5.76; after this value, decreases in degradation level were observed with increasing H_2O_2/Fe^{2+} ratios. The results
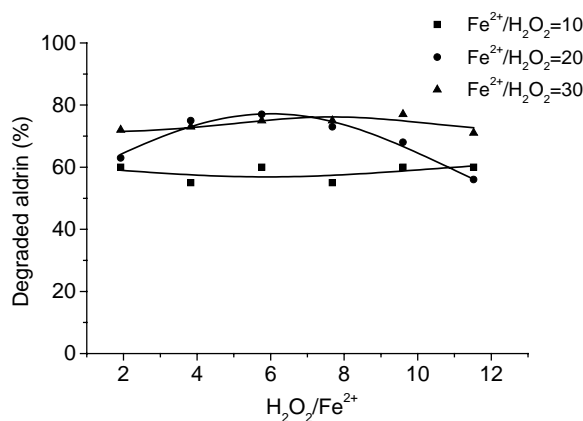

Fig. 1. Degradation of aldrin on Na-montmorillonite by different H_2O_2/Fe^{2+} ratios at various Fe^{2+}/aldrin = 10, 20, and 30 (mol/mol) ratios.

of Fe^{2+}/aldrin ratio of 20 consistent with the reported study in which degradation was observed optimum in the range of 5–11 ratios for some dissolved organics in water [18].

During the study with adsorbed systems and hydrophobic organics, three extra factors affect the oxidation rate. First, $OH^{\bullet}$ radicals generated by Fenton reaction in aqueous system cannot react easily with adsorbed aldrin because of the hydrophobic character of this compound. Consequently, degradation in this system was very low. The other factor, aldrin that is non-polar molecule is selectively adsorbed on neutral sides on clay mineral and these sides are dispersed randomly on clay [8,19]. The surface of the clay mineral covered with aldrin was not same as the other parts of the clay surface. Thus, $OH^{\bullet}$ radicals/aldrin ratios are not the same all over the clay mineral. $OH^{\bullet}$ radicals that cannot reach to react with aldrin are inhibited by Fe^{2+}, Fe^{3+} and other $OH^{\bullet}$ radicals. The last factor is the hydrolysis of clay mineral in acidic (pH = 3) medium [15]. After hydrolysis,
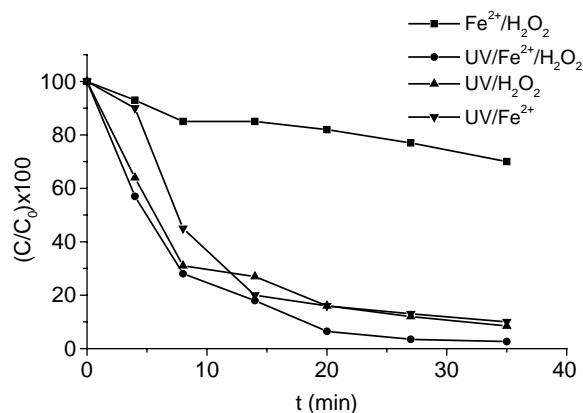

Fig. 2. Degradation of aldrin on Na-montmorillonite by different treatment. Evolution of the normalized remaining percentage of aldrin with time (Fe^{2+}/aldrin = 10, H_2O_2/Fe^{2+} = 5.76).
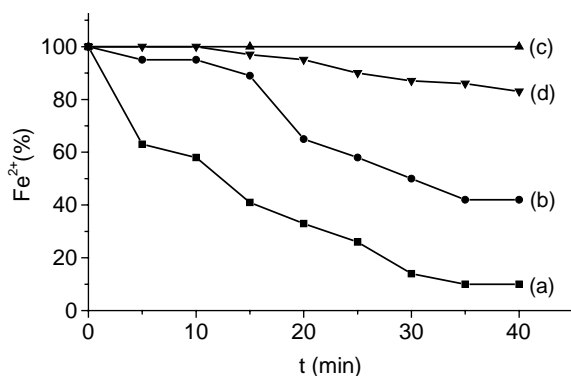
Fig. 3. Decreasing of Fe^{2+} with time: (a) in presence of H_2O_2, (b) in presence of UV, (c) in absence of UV and H_2O_2, and (d) total decrease of iron (Fe^{3+} adsorbed on Na-montmorillonite with time).
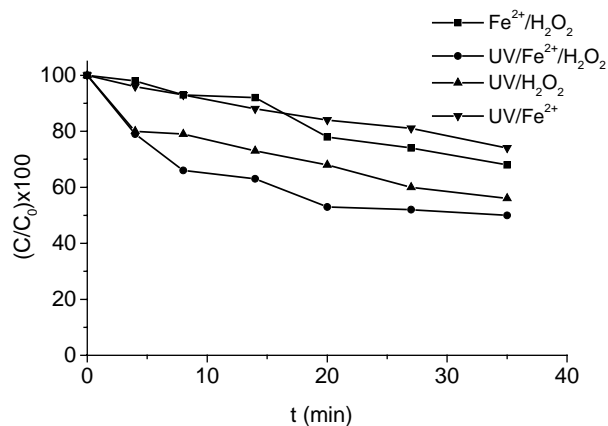

Fig. 4. Degradation of aldrin on activated carbon by different treatment. Evolution of the normalized remaining percentage of aldrin with time (Fe^{2+}/aldrin = 10, H_2O_2/Fe^{2+} = 5.76).

crystal structure of the clay mineral decomposes and as a result of that, adsorption surfaces change. Therefore, the surface on which aldrin adsorbed may be enhanced in the some part of the clay and $OH^{\bullet}$ radicals/aldrin ratios in reaction medium changed continuously. Thus, the curves of degraded aldrin versus H_2O_2/Fe^{2+} for adsorbed systems have been resulted different from those of observed in aqueous systems (Fig. 1).

3.2. Degradation of aldrin adsorbed on Na-montmorillonite by AOPs

UV, UV/Fenton, Fenton and UV/H_2O_2 techniques were used at Fe^{2+}/aldrin = 10 and H_2O_2/Fe^{2+} = 5.76 ratios using Na-montmorillonite sorbent (Fig. 2). Among

these techniques, UV/Fenton was observed to be most effective method in degradation of aldrin adsorbed on Na-montmorillonite. By this method, 95% of adsorbed aldrin was degraded. UV/Fe^{2+} and UV/H_2O_2 methods exhibited similar activity for the degradation of aldrin ($\approx 90\%$) (Fig. 2). The Fenton reaction (absence of UV light) exhibited less activity than the other applied methods. 30% of degradation was observed in this method due to aliphatic structure of aldrin. Fenton reaction is more effective method in aromatic structure than aliphatics [20]. In UV/Fe^{2+} system, despite the absence of H_2O_2 degradation of aldrin was observed to be efficient. In this system, the clay mineral behaved as photocatalyst in the presence of
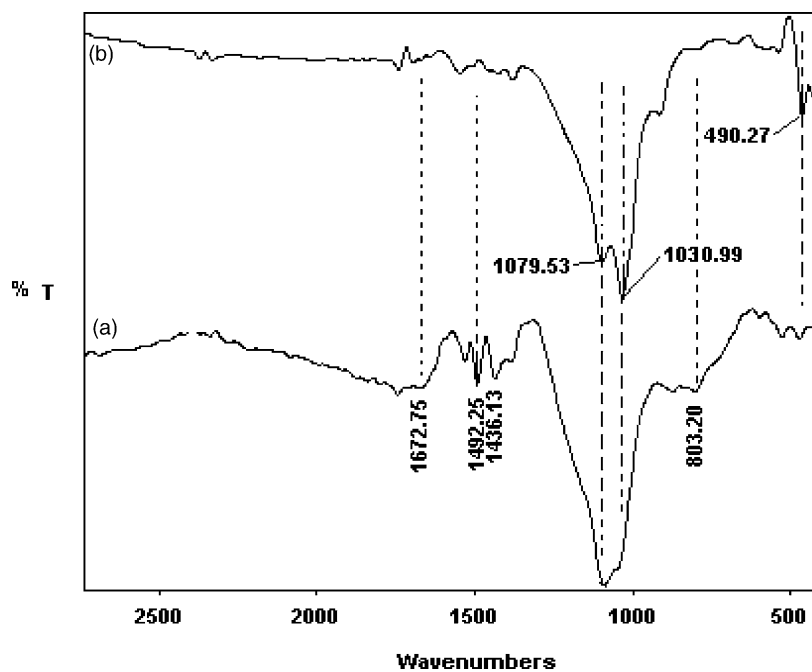

Fig. 5. IR spectra of activated carbon: (a) before reaction with $OH^{\bullet}$ radicals and (b) after reaction with $OH^{\bullet}$ radicals.

UV light. The primary reason for the high degradation rate in this system is attributed to composition of clay mineral, which composed with silica (tetrahedron) and aluminium oxide (octahedron). When clay mineral is illuminated with UV light semiconductor silica structures absorb UV light and electrons are promoted from valence band to the conduction band to give electron–hole pairs. The valence band (h_{VB}^+) potential is positive enough to generate hydroxyl radicals at the surface as in TiO_2 or ZnO semiconductor. The resulting positive holes oxidize water to hydroxyl radicals, which oxidize aldrin molecules. Some researchers have also observed that constitutes of soil behaved as cat-alyst for degradation of some organics by UV irradiation [12,21–23].
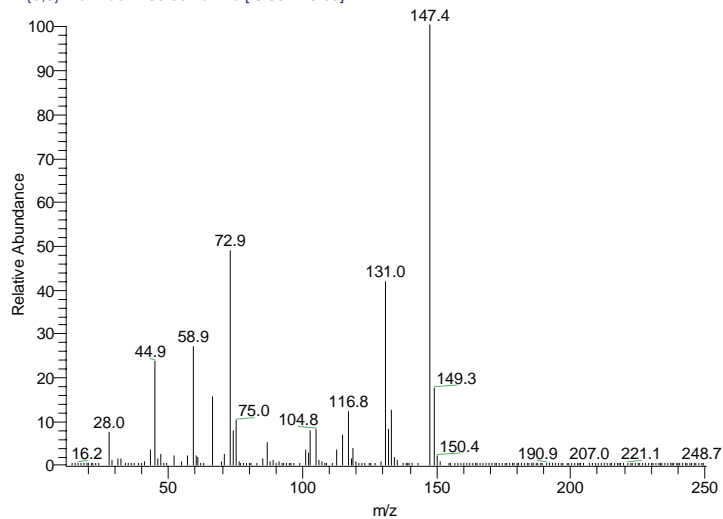
3.2.1. Behavior of iron(II) in reaction mixture during applied AOPs

The Fenton reagent is a mixture of H_2O_2 and ferrous ion, which produces hydroxyl radicals ($Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^\bullet + OH^-$). Fenton reaction is propagated from Fe^{2+} regeneration, which takes place by the reduction of Fe^{3+} with H_2O_2, with hydroperoxyl radical ($Fe^{3+} + HO_2^\bullet \rightarrow Fe^{2+} + H^+ + O_2$), with organic radical
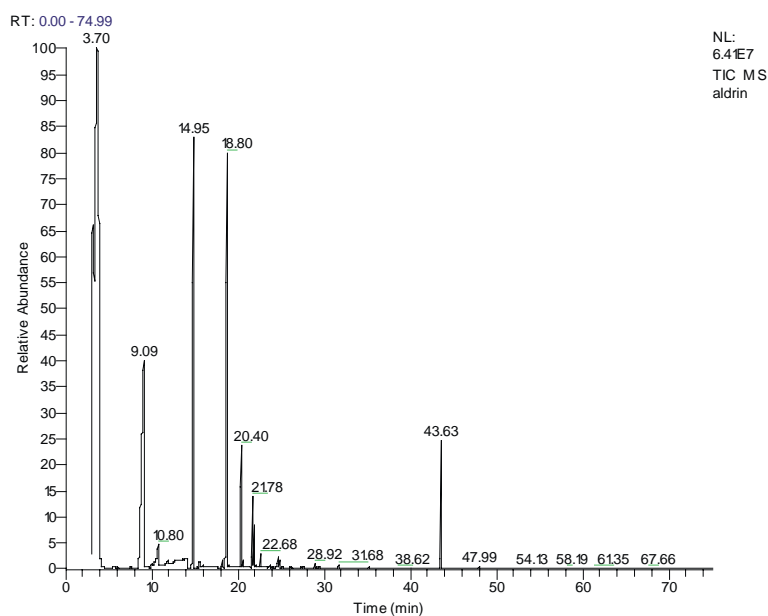

Fig. 6. Total ion chromatogram of degradation products of aldrin. (a–k) Mass spectra of the chromatographic peaks.

(a) Oxalic acid di-TMS

intermediate ($Fe^{3+} + R^{\bullet} \rightarrow Fe^{2+} + R^{+}$) and/or with photoreduction of Fe^{3+} species via photo-Fenton reaction in the presence of UV light ($Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + OH^{\bullet}$) [24]. Therefore, determination of Fe^{2+} concentration in reaction solution is important. Oxidation of Fe^{2+} to Fe^{3+} in reaction mixture in the presence and the absence of H_2O_2 and UV light are shown in Fig. 3. When H_2O_2 existed in reaction mixture of adsorbed system, Fe^{2+} was oxidized to Fe^{3+} slowly and 10% Fe^{2+} was observed without oxidation at the end of the experiment (40 min). Fenton reaction carried out in this adsorbed system did not take place fast

when compared with aqueous system. This indicates that clay mineral reduced the reaction between Fe^{2+} and H_2O_2 (Fig. 3a). When UV light existed in the adsorbed system (UV/Fe^{2+}) photo-oxidation was performed (Fig. 3b). At the end of the reaction, 40% of Fe^{2+} was remained without oxidation in this system. 20% of iron in the reaction mixture was observed to be adsorbed on clay mineral at pH = 3 at the end of the 40 min (Fig. 3d). In the absence of UV and H_2O_2, iron(II) in the reaction mixture did not change, that means no iron(II) was observed on clay mineral (Fig. 3c).
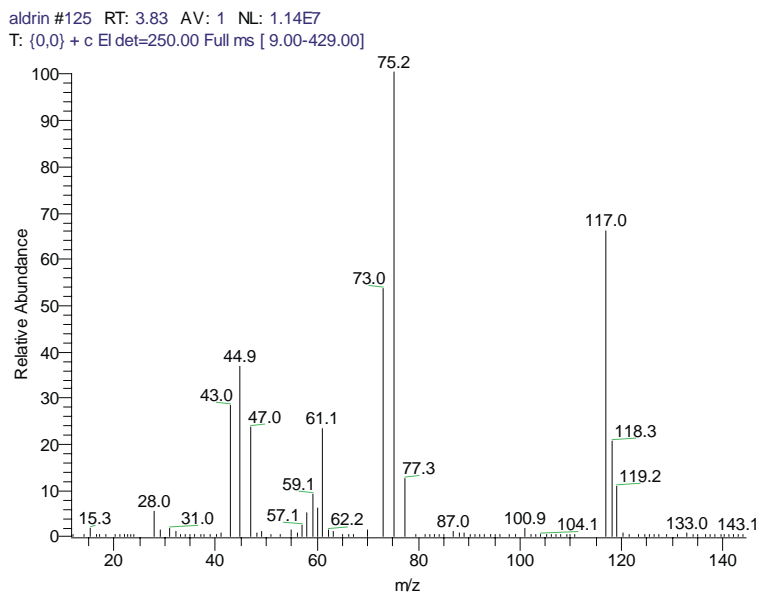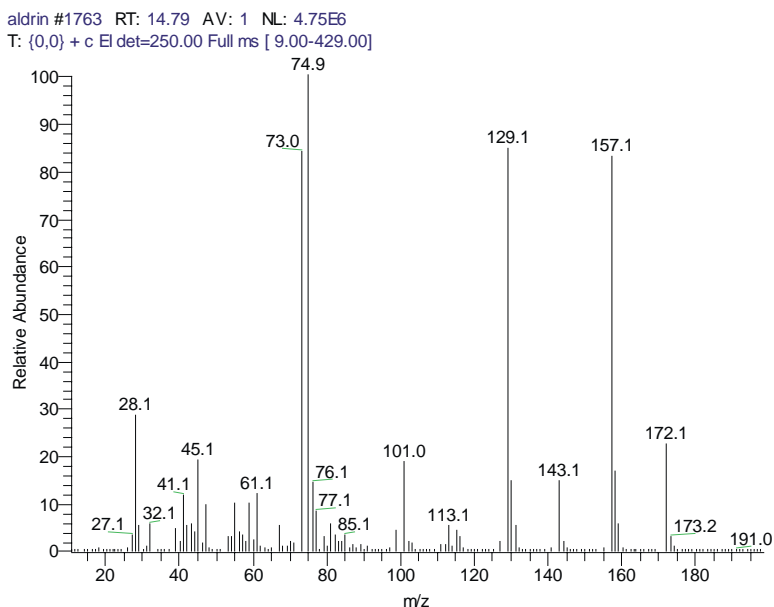

(b) Acetic acid-TMS
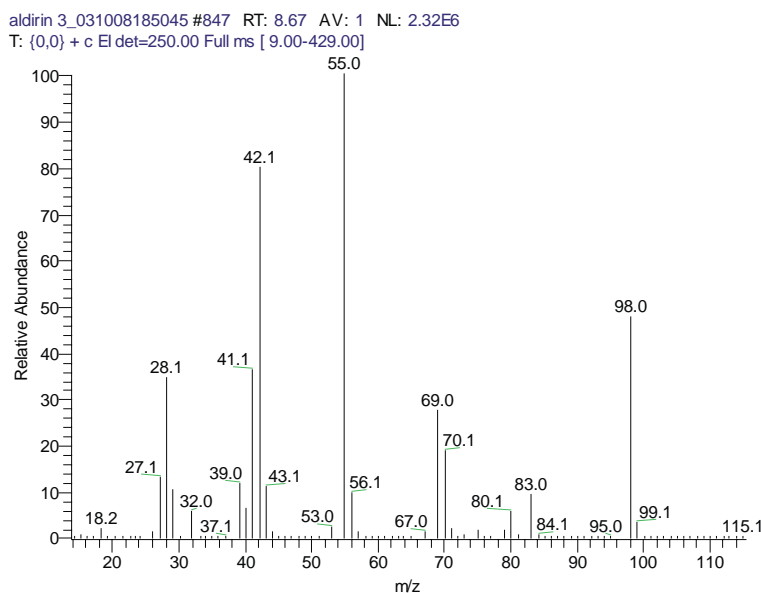
(c) Cyclohexanone

Fig. 6. (*Continued*)

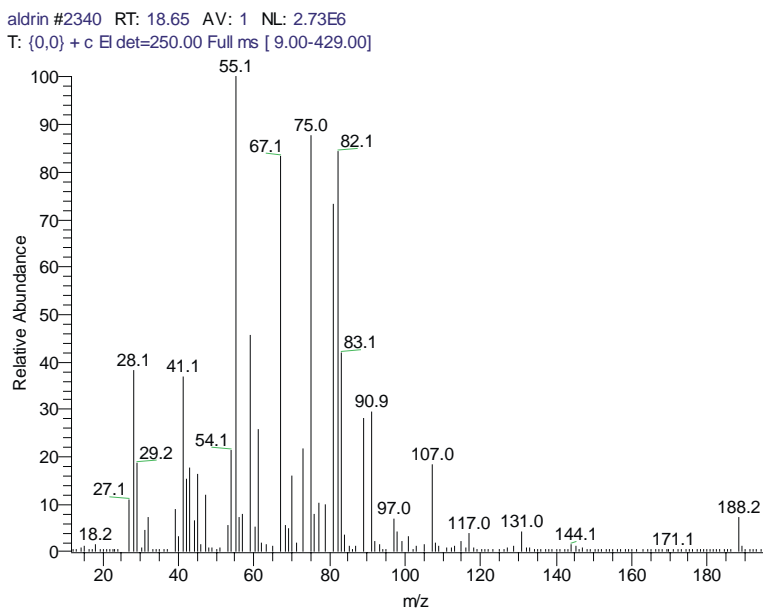### 3.3. Degradation of aldrin adsorbed on activated carbon

In this stage of study, degradation of aldrin performed on activated carbon that is different sorbent from Na-montmorillonitte. The same methods (UV, UV/Fenton, UV/H$_2$O$_2$, and Fenton) were used as applied on clay sorbent under similar experimental conditions. UV/Fenton technique was observed to be most effective technique for this system (Fig. 5). At the end of 40 min, 50% of aldrin was degraded on activated carbon by UV/Fenton. UV/H$_2$O$_2$ technique showed less activity than UV/Fenton, 56% of aldrin was detected without degradation in this technique. Degradation of aldrin adsorbed on activated carbon by UV/Fe^{2+} and Fenton performed the same activity until 20 min, then Fenton began to exhibit more activity. Finally, at the end of the experiment 68% aldrin determined in Fenton while 74% aldrin was present in UV/Fe^{2+} reaction system (Fig. 4).

When only UV light was used for degradation of aldrin adsorbed on activated carbon 26% of aldrin decomposed. Nearly the same result was obtained when Fenton system was used. However, decomposition of aldrin adsorbed on

aldrin #1763 RT: 14.79 AV: 1 NL: 4.75E6
T: {0,0} + c EI det=250.00 Full ms [9.00-429.00]

(d) Cyclohexanol-TMS

aldrin #2340 RT: 18.65 AV: 1 NL: 2.73E6
T: {0,0} + c EI det=250.00 Full ms [9.00-429.00]
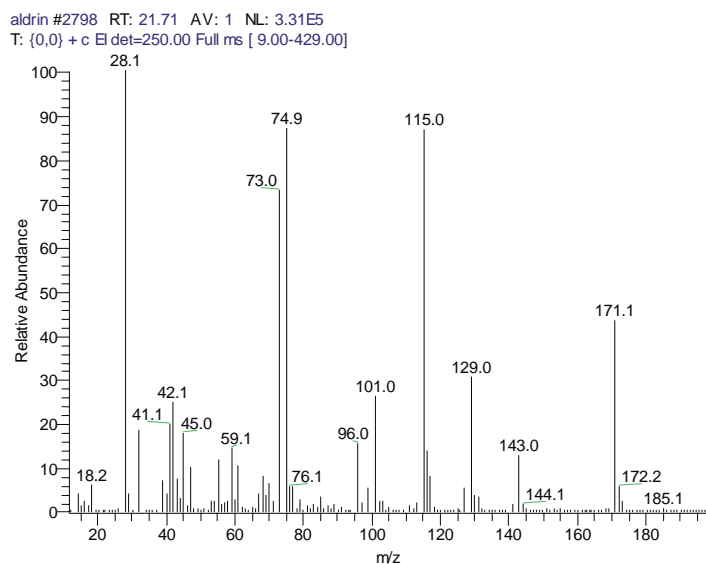
(e) Cis-2-(TMSoxy)-cyclohexanol

Fig. 6. (*Continued*)

Na-montmorillonitte by using UV light showed significant improvement in decomposition level. 90% of aldrin was degraded using Na-montmorillonite sorbent. According to these results, it can be concluded that clay mineral exhibits photocatalytic activity. On the other hand, activated carbon has exhibited competitive effect on reacting OH$^{\bullet}$ radicals. Therefore, degradation of aldrin in activated carbon decreased significantly comparing with that of in Na-montmorillonitte. This assumption was supported by taking IR spectra of activated carbon before and after reaction with OH$^{\bullet}$ radicals in large excess (Fig. 5). A peak near

1079 cm^{-1} in spectra (a) splits into two peaks (1079.53 and 1030.99 cm^{-1}) in spectra (b) due to reaction with hydroxyl radicals. These peaks correspond to aryl C–O stretching of aromatic ethers and deformation of phenols [25]. Reactions of OH$^{\bullet}$ radicals with phenolic compounds leaded to degradation and decreased in the amount of phenolic compounds. As a result of this, the intensity of 1079.53 cm^{-1} absorption peak was decreased and split into two peaks in spectra (b). The absorption band of 803.20 cm^{-1} in spectrum (a) disappears after reaction with hydroxyl radicals. This peak is owing to out-of-plane stretching vibrations of aromatic
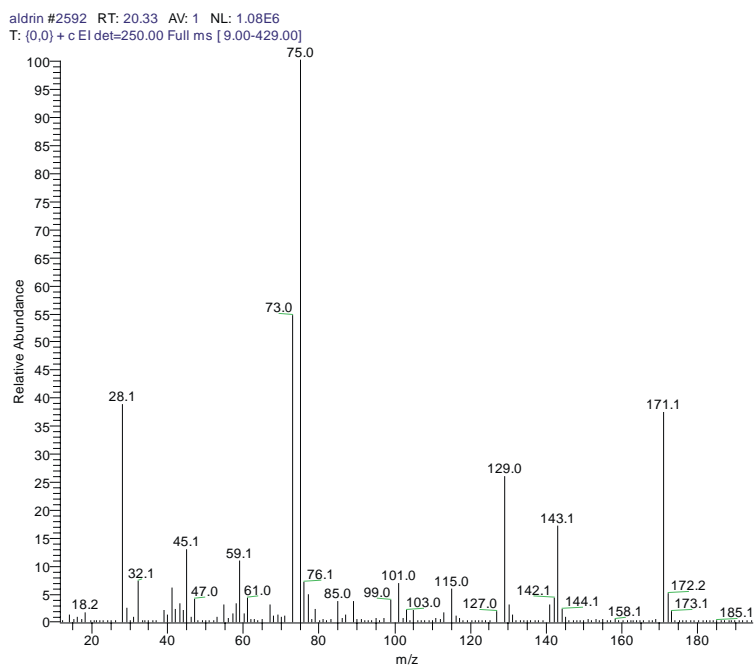
(f) Cis-2-methylcyclohexanol-TMS
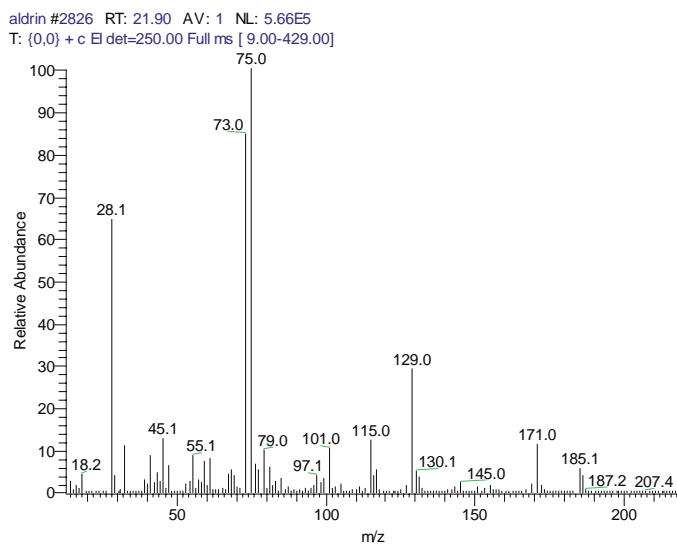

(g) 4-(TMSoxy)-cyclohexanone

Fig. 6. (*Continued*)

C–H bond. Intensity of the peaks at 1672.75, 1492.25 and 1436.13 cm^{-1} in spectrum (a) are seen with less intense in spectrum (b). These findings may be evident of reaction activated carbon with hydroxyl radicals. It must be taken in account that because of low amount of hydroxyl radicals at the reaction conditions the damage of activated carbon is negligible.
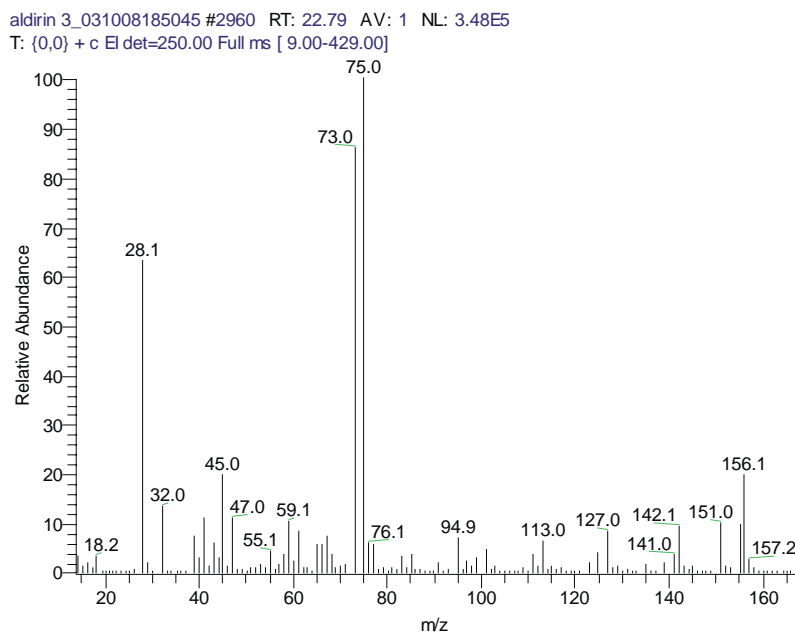
Competition between activated carbon and OH$^{\bullet}$ radicals reduced the degradation efficiency. The degradation level of aldrin in Fenton reaction was observed to be same for both sorbents. Aromatic rings in activated carbon were hydroxylated by OH$^{\bullet}$ radicals which led to the formation of cyclohexadienyl-type radicals. It is expected that these rad-

icals react easily with aldrin molecules. The cyclohexadienyl radical is stabilized by resonance interactions of electron over the adjacent aromatic rings. This combined action may delay the degradation first 20 min of the reaction time for oxidation of aldrin adsorbed on activated carbon. When the reaction mixture is exposed to UV light, which excites the electrons in the conjugation system of cyclohexadienyl radicals degradation of aldrin is enhanced.

Oxalic acid, acetic acid, cyclohexanone, cyclohexanol, *cis*-2-hydroxy- cyclohexanol, *cis*-2-methylcyclohexanol, 4-hydroxy-cyclohexanone, *cis*-4-methyl-cyclohexanol, 1-cyclopropyl-1-hydroxyethylene, *trans*-dihydroxy-cyclohexane were detected as intermediates after 10 min of the reaction
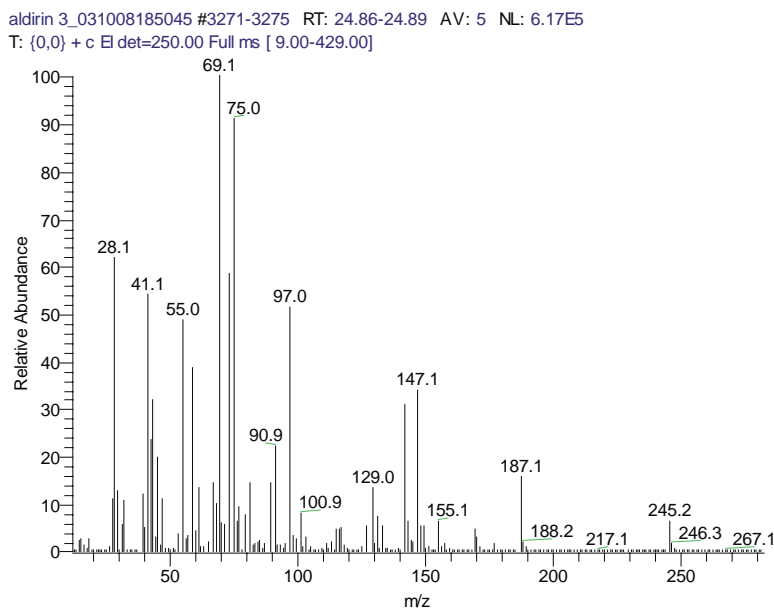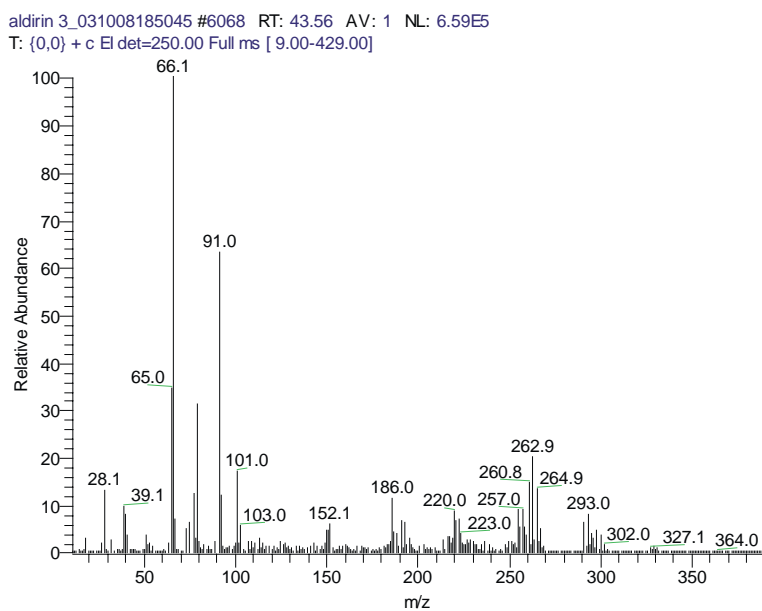

(h) Cis-4-methylcyclohexanol-TMS

(i) 1-cyclopropyl-1-(TMSoxy)ethylene

Fig. 6. (*Continued*)

aldirin 3_031008185045 #3271-3275 RT: 24.86-24.89 AV: 5 NL: 6.17E5
T: {0,0} + c EI det=250.00 Full ms [9.00-429.00]

(j) Trans-1,2-dihydroxycyclohexane di-TMS

aldirin 3_031008185045 #6068 RT: 43.56 AV: 1 NL: 6.59E5
T: {0,0} + c EI det=250.00 Full ms [9.00-429.00]

(k) aldrin

Fig. 6. (*Continued*).

time in UV/Fenton application using Na-montmorillonite as sorbent (Fig. 6). All the reactants were used 10 times higher concentrations to make detection possible in GC/MS analysis.

4. Conclusion

Degradation of aldrin has been performed on Na-montmorillonitte and activated carbon using advanced oxidation processes. UV/Fenton system was observed to be most effective technique for both sorbents. In UV/Fe^{2+} experiments, clay mineral exhibited photocatalytic activity in degradation of aldrin and 90% degradation achieved despite the absence of H$_2$O$_2$ oxidant. AOPs showed less activity towards the degradation of aldrin adsorbed on activated carbon sorbent. Phenyl groups in activated carbon structure reacted with OH$^\bullet$ radicals and caused a decrease in degradation levels of aldrin.

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