APPLICATION OF SOLAR-FENTON PROCESS IN LINDAN DEGRADATION FROM WASTEWATER

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ABSTRACT

Over the past two decades, environmental regulations have become increasingly stringent because of increased awareness of human health and ecological risks associated with environmental pollutants like pesticides, especially Lindane. Due to its high resistance to microbial degradation, this pollutant having carcinogenic and mutagenic properties has been accumulated into environment polluting ground and surface water.

Because application of classical treatment cannot allow an easy Lindane degradation, development of more powerful water treatment techniques, like Advanced Oxidation Processes (AOPs) is necessary.

Combination of H_2O_2 with Fe^{2+}under UV-VIS irradiation, the so-called solar-Fenton process is one of the AOPs successfully applied, which can significantly enhance degradation of many refractory organic compounds, based on the oxidant action of *in-situ* generated OH• radicals upon pollutants.

It was investigated the degradation of Lindane from wastewater by solar-Fenton process and the assessment of the working parameters on the degradation efficiency. The photooxidadation experiments were performed at pH=3 and tens μg/L pollutant initial concentration, in a tubular collector type solar photoreactor (26 UV-VIS permeable silica glass tubes series connected), plugged in a total recycle loops.

Based on the obtained results it was established the treatment solution for advanced degradation of Lindane from wastewater up to the limits immposed by national and european legislation for surface receivers (Lindane ≤ 0.02μg/L).

Keywords: *Lindane, solar-Fenton process, wastewater treatment*

INTRODUCTION

The application of organochlorinated insecticides in agriculture is a well-established effective practice for crop protection against pests and certain vectors of disease/1/. γ-HCH, also called Lindane, the effective component of HCH technical insecticide, had been widely used in agriculture worldwide since 1940s. It is estimated that around 10 million tones technical HCH were used between 1947 and 1997/2/. The technical HCH has been gradually banned in the developed countries since 1970s and in developing countries since 1980s due to its proven adverse effect on human and animal health and to serious environmental problems /3/. It was widely detected in soil and water, also due to its slow transformation in the environment /4,5/. As a result, there is a need to develop technological approaches for rapid degradation of Lindane in water, of which advanced oxidation processes are promising methods. Although this insecticide exhibits very slow rate of direct photolysis, it does react rapidly via •OH radicals. In aqueous solution, Lindane can be degraded by H_2O_2 assisted photolysis or photocatalysis in the presence of polyoxometalates $PW_{12}O_{40}^{3-}$ or TiO_2 /6-10/. In addition, the photochemical conversion of Lindane in the presence of humate-coated α-Fe_2O_3 has been reported/11/.
Another study indicates that a combination of H_2O_2 and solar irradiation in the presence of Fe^{2+}, the so-called solar-Fenton process, can significantly enhance decomposition of many refractory organic compounds. Until now, the solar-Fenton process has been applied for the degradation of other classes of pesticides and refractory compounds/12,13/. The acceleration of organic compounds degradation is produced by the photoreduction of iron aquacomplex, which provides a new important source of OH• radicals.
In the present study, we investigated the Lindane degradation from groundwater by solar-Fenton process. The influence of working conditions: Fenton's reagents dose, pollutant concentration, irradiation time on the process efficiency was investigated. Based on the results obtained, we proposed a technological solution for advanced degradation of Lindane from tens of μg/L to MAC for surface water (≤0.02 μg/L).

EXPERIMENTAL SETUP

Solar pilot installation for water treatment by photocatalysis

The experiments were conducted in pilot installation with recirculation (V_{total}=6.4L). Water to be treated was continuously pumped at 90L/h through the feeding /recirculation column, solar reactor and heat exchangers, after Fenton reagents (H_2O_2 and $FeSO_4$) were added. The main element of solar reactor is the battery collector (V_{ir}=5.4L, A_{ir}= 1.53 m^2) with 26 borosilicate glass tubes connected in series. These components were mounted on the plain surface of the reflector made of aluminum foil on glass fiber. To insure the proper irradiance throughout the experiment, the reflector was installed on a frame coupled to a computer-based - two axes automatic system which follows the sun according to the astronomic algorithm. The equation for calculation of solar energy accumulated at different irradiation times is:

$$E_n = E_{n-1} + \Delta t_n \times I_{med\,n} \times \frac{A_{ir}}{V_{total}}$$

where:
$E_{n,\,n-1}$ = solar energy accumulated at different irradiation times n and n-1, [kJ/L];
Δt_n = irradiation period = $t_n - t_{n-1}$, s;
$I_{med\,n}$ = average irradiance during Δt_n, [W/m^2]:
A_{ir} = irradiated area, [m^2].

Characteristics of polluted water

The experiments of advanced oxidation were conducted on groundwater samples from a monitoring well belonging to SC OLTQUINI SA, a company processing Lindane. For physical-chemical characterization of water samples were applied the following analytical methods: gas-chromatography (Lindane, Σ HCH), ion- chromatography (Cl^-, SO_4^{2-}), molecular absorption spectrometry (Fe^{2+}), gravimetry (suspended solids) and COD-Cr.
Characterization data showed in table 1 emphasize a high level of HCH isomers of tens of µg/L ($MAC_{\Sigma HCH}$ = 0.042 µg/L). Lindane is present at concentrations 1700 x higher than MAC for surface water (0.02 µg/L).

Tabel 1 Physical -chemical characterization of groundwater

Indicator	UM	Variation domains
pH	-	6.97-7.27
Cl^-	mg/L	170-196
SO_4^{2-}	mg/L	35-52
Fe	mg/L	0.09-0.1
Suspended solids	mg/L	44-52
COD	mgO_2/L	70.4-78.8
γHCH(Lindane)	µg/L	18.01-34.01
ΣHCH	µg/L	52.25-68.68

RESULTS AND DISCUSSIONS

Organic pollutants degradation by solar-Fenton process is based on the oxidizing effect of OH• radicals, in-situ generated by decomposing H_2O_2, under catalytic action of Fe^{2+}:

$Fe^{2+} + H_2O_2 \rightarrow Fe(OH)^{2+} + OH\bullet$

In the presence of sun light, the photoreduction of $Fe(OH)^{2+}$ species assures Fe^{2+} regeneration and supplementary OH• radicals, which accelerates the process of pollutant degradation.

$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + OH\bullet + OH^-$

Influence of Fe^{2+} concentration and irradiation time

Considering that Fe^{2+} is the photocatalyst for generation of OH• radicals, this parameter was studied on Lindane turnover in order to establish the optimum degradation conditions.

The experiments were performed under certain operating conditions: pH=2.5-3; $[Lindane]_0$ = 34 µg/L; ΣHCH=68.68 µg/L; $[Fe^{2+}]$ = 15-50 mg/L; $[Fe^{2+}]:[H_2O_2]$ = 1:8; t_{irr} = 50-200 min; I_{med} = 30W/m^2. The analysis of the results, presented in table 2 reveals the following aspects:

- increasing photocatalyst concentration and irradiation time had a positive effect on Lindane degradation as well as on other HCH isomers, due to increasing absorbance of light which intensified the in-situ generation of free OH• radicals;
- degradation of other HCH isomers is higher than Lindane due to its high resistance of this isomer to oxidation;
- the highest degradation efficiencies of 96-98% of HCH were recorded at $[Fe^{2+}]$ = 50mg/L si t_{irr} = 200min.

Table 2. The influence of photocatalyst concentration and irradiation time on the Lindane degradation efficiency. $[Lindane]_0$ = 34.01µg/L; $[Fe^{2+}]:[H_2O_2]$ = 1:8

$t_{ir.}$, min	Fe^{2+}, mg/L	H_2O_2, mg/L	Lindan, µg/L	ΣHCH, µg/L	E, kJ/L	η_{Lindan}, %	$\eta_{\Sigma HCH}$, %	η_{H2O2}, %
0	**15**	**70**	**34.01**	**68.68**	-	-	-	-
50		<1	10.15	11.32	22.22	70.16	83.52	>98.57
100		<1	9.01	9.76	51.29	73.52	85.79	>98.57
150		<1	8.74	9.12	82.28	74.31	86.72	>98.57
200		<1	8.67	8.86	105.59	74.52	87.10	>98.57
0	**25**	**125**	**34.01**	**68.68**	-	-	-	-
50		3.50	5.91	6.9	20.83	82.62	89.95	97.20
100		2.33	2.61	3.22	51.00	92.31	95.31	98.14
150		1.62	2.40	2.72	84.96	92.94	96.04	98.70
200		<1	2.24	2.40	115.16	93.41	96.51	>99.20
0	**50**	**250**	**34.01**	**68.68**	-	-	-	-
50		11.51	3.48	4.04	24.88	89.77	94.12	95.40
100		7.43	1.41	1.69	55.80	95.84	97.54	97.03
150		4.38	1.25	1.37	93.60	96.33	98.00	98.25
200		2.15	1.18	1.23	126.45	96.52	98.21	99.14

Influence of H_2O_2 concentration and irradiation time

Taking into account that the level of OH• radicals depends on hydrogen peroxide concentration, the influence of H_2O_2 variation on Lindane and others HCH isomers degradation was studied.

For advanced oxidation of HCH isomers (tens µg/L) different doses of H_2O_2 were applied according to the molar ratio $[Fe^{2+}]:[H_2O_2]$ = 1:8-1:25 and also different irradiation times = 50-200 min at the optimal photocatalyst dose established in previous experiments and I_{med} = 30 W/m^2.
The experimental results presented in table 3 and 4 are emphasizing the following aspects:

- the increases of H_2O_2 concentration and Fe^{2+} concentration have similar effect on pollutant degradation;
- extension of samples irradiation time between 50 and 150 min. has a positive effect on pollutants degradation; this is more pronounced in the first 50 min. of irradiation and is significantly diminishing later, due to decrease of substrate;
- at identical conditions of operation the degradation efficiencies of pollutants decrease with increasing of their concentration and [Lindane]/[ΣHCH] ratio; this is due to formation of degradation intermediates which compete with HCH isomers for OH• radicals consume, as well as higher resistance of Lindane to oxidation, compared to the other HCH isomers;
- Involvement of •OH in secondary reactions is sustained by the evolution of H_2O_2 consumption, which increases with pollutant concentration; this effect is pronounce for prolonged irradiation;
- Advanced degradation of HCH isomers with more than 99.9% efficiency is recorded after applying doses of H_2O_2 between 500-750mg/L and irradiation times of 150min., the remanent pollutants concentrations complying with discharging limits for surface water (Lindane ≤ 0.02 µg/L, ΣHCH ≤ 0.042 µg/L).

Table 3.The influence of H_2O_2 concentration and irradation time on the Lindane degradation efficiency. $[Lindane]_0$ = 18.01µg/L;$[Fe^{2+}]$=50mg/L

$t_{ir.}$, min	$[Fe^{2+}]/[H_2O_2]$	H_2O_2, mg/L	Lindan, µg/L	ΣHCH, µg/L	E, kJ/L	η_{Lindan}, %	$\eta_{ΣHCH}$, %	η_{H2O2}, %
0	**1/8**	**250**	**18.01**	**52.25**	-	-	-	-
50		16.15	1.16	1.58	24.23	93.57	96.98	93.54
100		12.30	1.04	1.25	56.18	94.12	97.61	95.08
150		10.90	0.98	1.07	90.72	94.52	97.95	95.64
200		9.97	0.95	0.98	118.72	94.72	98.12	96.01
0	**1/16**	**500**	**18.01**	**52.25**	-	-	-	-
50		38.15	0.16	0.33	22.73	99.10	99.37	92.37
100		31.25	0.07	0.12	51.93	99.60	99.77	93.75
150		28.60	0.02	0.02	77.79	99.89	99.96	94.28

Table 4. The influence of H_2O_2 and irradation time on the Lindane degradation efficiency. $[Lindane]_0$ = 34.01µg/L;$[Fe^{2+}]$=50mg/L

$t_{ir.}$, min	$[Fe^{2+}]/[H_2O_2]$	H_2O_2, mg/L	Lindan, µg/L	ΣHCH, µg/L	E, kJ/L	η_{Lindan}, %	$\eta_{\Sigma HCH}$, %	η_{H2O2}, %
0	**1/8**	**250**	**34.01**	**68.68**	-	-	-	-
50		11.51	3.48	4.04	24.88	89.77	94.12	95.40
100		7.43	1.41	1.69	55.80	95.84	97.54	97.03
150		4.38	1.25	1.37	93.60	96.33	98.00	98.25
200		2.15	1.18	1.23	126.45	96.52	98.21	99.14
0	**1/16**	**500**	**34.01**	**68.68**	-	-	-	-
50		29.00	0.96	1.29	29.01	97.18	98.12	94.20
100		17.05	0.57	0.69	66.47	98.31	99.00	96.59
150		9.15	0.32	0.37	93.75	99.07	99.46	98.17
200		6.40	0.13	0.13	117.22	99.62	99.81	98.72
0	**1/25**	**750**	**34.01**	**68.68**	-	-	-	-
50		50.14	0.46	0.73	28.32	98.65	98.93	93.34
100		37.54	0.03	0.16	52.17	99.92	99.78	94.99
150		26.25	0.02	0.03	87.76	99.94	99.96	96.50

Technological solution for advanced degradation of Lindane from water

Based on the experimental results in solar photocatalytic pilot installation ($V_{irr.}$= 5.4L), it was established `the technological flow sheet and the optimal operating parameters for efficient degradation of Lindane and other HCH isomers from tens of µg/L to concentrations under MAC.
The proposed technological flow sheet has the following steps:

- pretreatment through settling, applied optionally to remove solid suspensions over 60mg/L;
- solar photocatalysis (pH=2.5-3; Fe^{2+} = 50 mg/L; H_2O_2 = 500-750 mg/L; t_{irr}/ µg HCH removed = 6 min; I_{med} = 30W/m^2);
- photocatalyst precipitation (pH=7-7.5) and filtration.

CONCLUSIONS

- the solar-Fenton process can be considered an efficient and cost effective method for advanced degradation of organochlorinated insecticides from water;
- high visible light absorbance of ferrihydroxo species, allows the replacement of UV sources with solar natural light. Use of solar light ensures the Fe^{2+} photocatalyst continuously regeneration in the OH• generation process,

which has positive influence on pollutant degradation efficiency and it is a cost effective technology;

- photodegradation of Lindane from tens µg /L levels up to discharging limit into surface water can be performed by applying the following treatment flow: pretreatment (optional applied) – advanced oxidation (solar Fenton system) - precipitation-filtration.

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