Analysis of Organochlorine Pesticides in Drinking Water and their Degradation by Synthesized Iron oxide Nanoparticles

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This study reports the analysis of drinking water sources of river Krishni catchment, contaminated by organochlorine pesticides. Iron oxide nanoparticles had been synthesized through co-precipitation method and utilized for the degradation of organochlorine pesticides using advanced oxidation processes. The sharp and narrow peaks of X-ray diffraction patterns revealed the crystalline nature of synthesized iron oxide nanoparticles having size less than 100 nm. The nanoparticles were also characterized using TEM, UV-Vis and IR spectral analysis. Liquid-liquid extraction and GC-MS were used for the detection analysis of pesticides. GC-MS technique was used for further quantitative analysis of 19 pesticides. The degradation analysis showed the maximum amount of degradation (up to 98.38 %) of organochlorine pesticides.

Keywords: Pesticides, Liquid-liquid extraction, Iron oxide nanoparticles, GC-MS, Degradation.

INTRODUCTION

According to the Stockholm convention, pesticides are listed as persistent organic pollutants. Some pesticides because of their toxic nature banned by the government, but due to the persistency they remain in the environment for years. Thus, they can be entering in aquatic environment *via* soil percolation or surface runoff [1]. Some of the banned pesticides are consistently found in water, sediments and soil [2]. They end up with the food chain and pose potential hazards in living beings [3]. Only a small percentage (0.3%) of applied pesticides goes into target pest while 99.7% go somewhere else into environment [4]. Their presence also has been reported in many developing as well as developed countries. India ranked as 10th major pesticides consumption country with a consumption amount of 500 million tonnes. India is the country where ground water aquifer constitutes the main drinking water resource for rural and adjacent urban area. Drinking water from many parts of India has been reported with the presence of pesticides residues [5]. As water is the second natural resource without which the survival of living creature are not possible after air, it should be clean and potable. So many treatment methods have been reported for the removal of pesticide from surface and ground

water. Among these techniques, advanced oxidation process (AOP) is most effective, cheap and convenient. Nanomaterials like titanium dioxide, zinc oxide and iron oxides were used as photocatalyst for the heterogeneous degradation of different pesticides [6]. Organochlorine pesticides *e.g.*, methyl parathion and lindane degradation have been reported by using TiO_2 nanoparticles [7]. Apart this, iron containing compound showed an application in the field of soil sedimentation as well as ground water remediation. High efficiency of iron containing compound reported in the process of adsorption and co-precipitation of arsenic. An extra advantage of using iron oxide nanoparticle is, they can easily remove from the aqueous medium after the remediation process by using a magnet [8]. Among the various form of iron oxides, hematite (α-Fe_2O_3) form special property for remediation of drinking water by photochemical reaction while the maghemite (γ-Fe_2O_3) used in commercial magnetic data storage device [9].

The objective of this work was to carry out a systemic study regarding the level of various organochlorine pesticides residue in drinking water and the synthesis of iron oxides nanoparticles for the photocatalytic degradation of organochlorine pesticides.

EXPERIMENTAL

The pesticides analytical standards mixture (EPA-625) was purchased from Sigma-Aldrich, U.S.A. Pesticides standard solutions were prepared in *n*-hexane. Analytical grade of highest purity chemicals, solvents and reagents were purchased from Merck, India.

Study area: The present study was carried out in Krishni river waterway catchment region of Saharanpur, Shamli and Baghpat districts of western U.P., India. Krishni river is an intermittent in nature, which flow only during monsoons. In the absence of fresh water, river carries mostly partially treated or untreated wastes from various huge, medium and small scale industries like sugar and refineries as well as domestic wastes from nearby town of Saharanpur, Shamli and Baghpat districts [10]. It is a tributary of Hindon river and cover 78 km stretch along side industrial as well as agricultural intensive area. The water level of Krishni river fluctuates from season to season, furthermore relies on upon the industries arranged in its catchment city or town. The shading and smell additionally may differ with season, in monson it conveys muddy water, however in other season its shading absolutely changes to dark with a terrible smell. Individuals living in the towns or villages of the catchment of Krishni river are constrained to live with such unsuitable smell [11]. Five villages were chosen for the present study *i.e.* Bhnera khemchand, Thana bhawan, Kabraut, Gangnauli and Barnawa. Sampling locations along with their latitude and longitude are listed in Table-1. India Mark-II hand pumps installed by Department of Irrigation, Government of India were chosen for sampling.

TABLE-1
LATITUDE AND LONGITUDE OF THE SELECTED VILLAGES

Village name	District	Latitude (N)	Longitude (E)
Bhnera Khemchand	Saharanpur	29.6770	77.4444
Thana Bhawan	Shamli	29.5875	77.4168
Kabraut	Shamli	29.4025	77.3483
Gangnauli	Baghpat	29.2042	77.3274
Barnawa	Baghpat	29.0654	77.3712

Collection of samples: A total of 5 ground water samples (1 L each) collected from different sites of Krishni river catchment. The samples were collected in 1 L of cleaned, washed and dried amber coloured glass bottles. All the samples were immediately transferred to the laboratory in an ice-packed cool box and stored at 4 ºC until extraction was done. The water samples were extracted within 48 h of collection. All the glassware were rinsed with acetone and heated at 200 ºC in a laboratory oven to avoid contamination.

Extraction and analysis: Before the extraction procedure, all the water samples were filtered to remove the suspended impurities. Liquid-liquid extraction procedure was followed for the analysis [12]. 1 L water sample transferred to a 2 L separating funnel and 100 g NaCl was added and mixed by inverting the funnel several time until NaCl dissolved. A total 200 mL DCM was used for extracting each sample (100:50:50). This 200 mL of organic solvent was filtered and passed through anhydrous sodium sulphate layer in order to remove the moisture content. This organic solvent then concentrated with the help

of vacuum rotary evaporator until 5 mL of solvent was left in the round bottom flask. This organic solvent further concentrated under a gentle stream of nitrogen in a turbovap. The solvent change phenomenon was done with *n*-hexane.

The qualitative and quantitative studies of pesticide residue were done by using a Trace GC Ultra DSQ, GC-MS equipped with capillary column. A 1 μL of extracted solvent was injected using an auto sampler. The ovan temperature program for the analysis was as follow: Initial temperature: 80 ºC (hold for 2 min). Increased the temperature at the rate of 5 ºC/min till 200 ºC (hold for 5 min). Further increased the temperature at 5 ºC per minute till 280 ºC (hold 5 min).

The results of water samples analysis are shown in Table-2, which strongly indicated the presence of organochlorine pesticides in all the water samples.

Catalyst synthesis: Iron nitrate nonahydrate (3.35 g) was dissolved in 50 mL of distilled water with a continuous stirring to make homogenous solution, then 0.5M NaOH solution was added dropwise with a constant stirring until pH of solution reached at 10 and a reddish brown precipitate formed. Rest apart the reaction vessels for 2.5 h with a set rate of stirring. The precipitate was filtered and washed with distilled water several times until excess NaOH was eluted. The precipitate finally washed with ethanol and distilled water in a 50:50 ratio. The washed precipitate was dried overnight at 110 ºC. After crushing the precipitate, placed them into a muffle furnace at 500 ºC for 5 h [13,14]. Grind the precipitate further to obtained the fine powder of iron oxide nanoparticles and stored for further characterization and use.

Advance oxidation process (AOP): A known amount of iron oxide nanoparticles added in the vessel containing 250 mL aqueous solution of known pesticides and placed the vessel under UV irradiation into a photochemical reactor chamber. The aqueous solution was continuous stirred at a rate of 400 rpm by using a magnetic stirrer and for a fixed period of time. A 10-15 mL of aliquot was taken at a regular interval of time *i.e.* 1, 3, 6, 12 h and follows the extraction process as described earlier. These samples were concentrated with the help of nitrogen purging and further analysis was done using GC-MS. All AOP experiments were performed in triplet.

The percent removal efficiency was quantified by the following expression:

$$\text{Removal efficiency (\%)} = \frac{C_o - C}{C_o} \times 100 \tag{1}$$

where C_o and C are initial and final concentration of pollutants (pesticides), respectively.

RESULTS AND DISCUSSION

XRD analysis: The X-ray diffraction pattern was recorded on Rikagu Ultima IV X-Ray diffractometer using Cu*K*α radiation (λ = 1.54 Å) at 40 kV. The scanning rate was 4/min in 2θ scale. The XRD spectrum of synthesized iron oxide nanoparticles is shown in Fig. 1. Perfect size and crystalline nature was confirmed by the sharp and narrow peak of diffraction. These sharp and narrow peaks appeared at 2θ = 24.16º, 33.28º, 35.74º, 40.99º, 49.49º, 54.23º, 57.55º, 62.26º and 64.17º with the h k l values (012), (104), (110), (113), (024), (116), (122),

TABLE-2
CONCENTRATION OF PESTICIDE DETECTED IN THE GROUND WATER SAMPLES IN THE STUDY AREA

Pesticides	Concentrations (ppb)				
	Bhnera Khemchand	Thana Bhawan	Kabraut	Gangnauli	Barnawa
α-HCH	0.019	0.011	0.015	0.380	0.095
β-HCH	0.024	0.089	0.033	0.079	0.034
γ-HCH (Lindane)	0.351	0.258	0.641	0.948	0.925
δ-HCH	0.018	0.009	0.012	0.022	0.012
Aldrin	0.07	Not detected	0.010	0.09	Not detected
Dieldrin	Not detected	Not detected	0.032	0.045	0.038
Endrin	0.018	0.004	Not detected	0.031	0.025
Endrin aldehyde	Not detected	0.052	0.044	0.063	0.058
α-Endosulfan	0.921	Not detected	0.412	1.818	0.810
β-Endosulfan	Not detected	Not detected	0.213	0.620	0.123
Endosulfan sulphate	Not detected	Not detected	0.628	0.135	0.049
o,p'-DDT	0.131	0.105	Not detected	0.918	0.114
p,p'-DDT	0.095	Not detected	Not detected	0.932	Not detected
o,p'-DDE	0.009	0.033	0.046	0.031	Not detected
p,p'-DDE	0.053	0.015	0.051	0.068	Not detected
o,p'-DDD	0.110	0.412	Not detected	0.013	0.086
p,p'-DDD	Not detected	Not detected	Not detected	0.019	0.002
Heptachlor	0.197	0.090	0.018	0.086	0.021
Heptachlor epoxide	0.026	0.069	0.081	0.102	Not detected

Fig. 1. XRD spectra of synthesized Fe_2O_3 nanoparticles
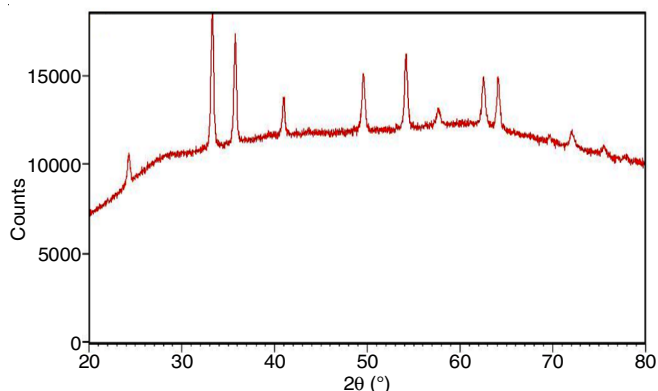

Fig. 2. SEM image of synthesized Fe_2O_3 nanoparticles

(214) and (300), respectively. Crystal structure of iron oxide nanoparticles was rhombohedral with R-3C (167) space group which was in agreement with the reference code 00-001-1053 [15].

SEM analysis: The SEM analysis was performed by using MIRA3 TESCAN with an operating voltage of 10Kv. Freshly prepared iron oxide nanoparticles undergo SEM analysis for the study of morphology of their surface. The SEM images (Fig. 2) of iron oxide nanoparticles having size less than 100 nm.

TEM analysis: The size of prepared iron oxide nanoparticles was confirmed by the TEM analysis using JEM-1011 microscope. Fig. 3 has shown the formation of spherical aggregate of iron oxide nanoparticles having the mean dimension of 38 nm.

IR analysis: IR spectra revealed the bond structure and identification of functional group. Infrared spectra of iron oxide nanoparticles performed at Perkin-Elmer IR spectrophotometer using KBr pallets. The absorption bands at 460 and 527 cm^{-1} were due to the presence of Fe-O group (Fig. 4), which appeared due to the formation of rhombohedral crystal lattice of hematite form of iron oxide [16].
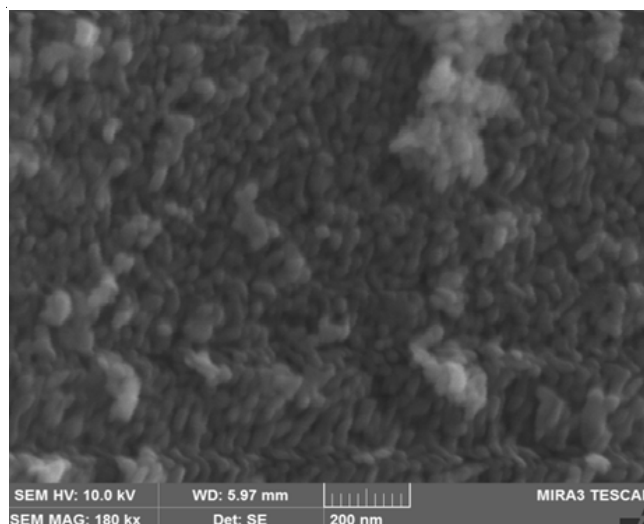

Fig. 3. TEM image of synthesized Fe_2O_3 nanoparticles

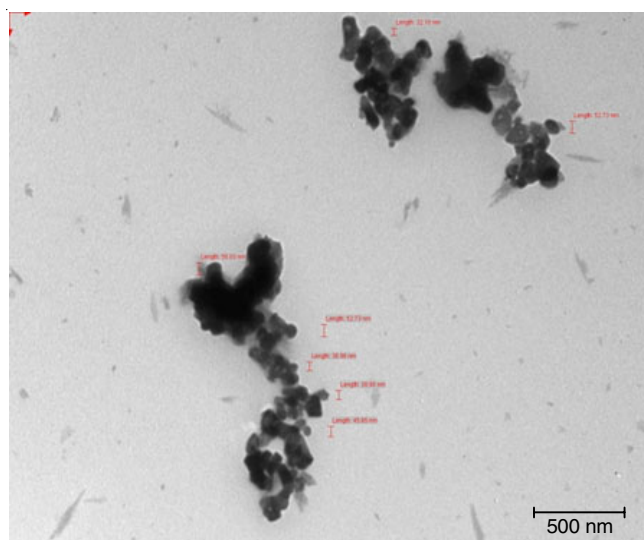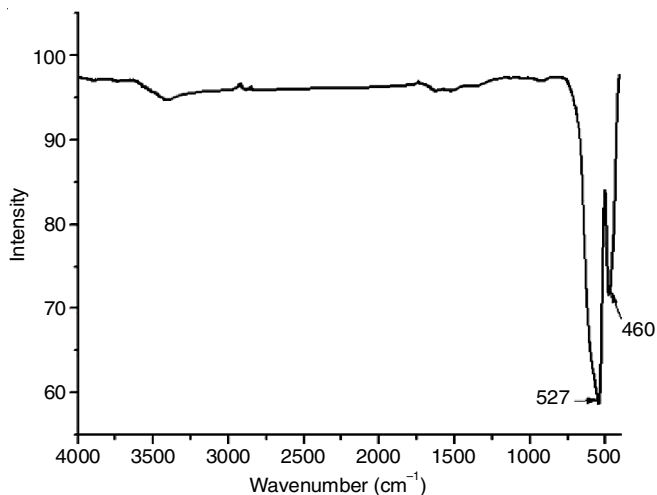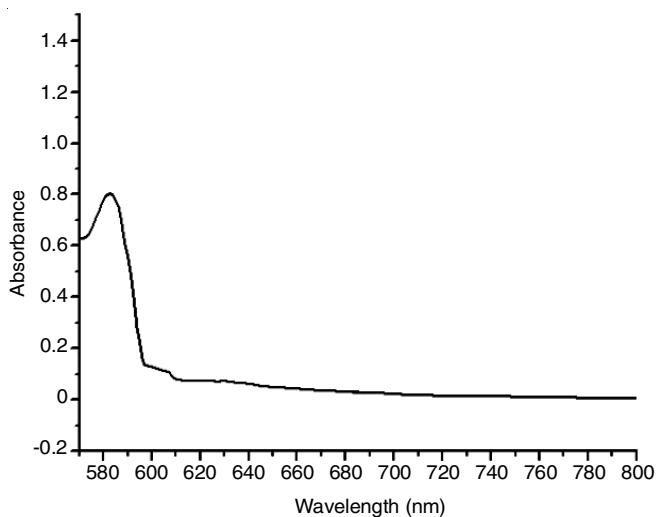Fig. 4. IR spectra of synthesized Fe$_2$O$_3$ nanoparticles

UV-visible analysis: This spectrum recorded on Shimadzu UV-1800 UV-Vis spectrophotometer. The concentration of Fe$_2$O$_3$ measured at maximum absorbance using Lambert-Beer's law. An absorption peak around 600 nm confirmed the formation of iron oxide nanoparticles as shown in Fig. 5 [8].

Fig. 5. UV spectra of synthesized Fe$_2$O$_3$ nanoparticles

Efficiency of nanoparticles for pesticides degradation: The degradation studies of pesticides were achieved by mixing the mixed pesticides standard into deionized water in the presence of 3% v/v surfactant Triton X-100. Sonicated this mixture for 2 h, so that the pesticides should mix in water. In this batch experiment samples were taken after a fixed period of time and extracted with n-hexane. Vortex this extracted mixture for 10 min and separated the hexane layer. This hexane layer leached through the anhydrous sodium sulphate, so that the moisture removed completely. Nitrogen purging was used for further concentration. Finally, 2 µL of aliquot was subjected to GC-MS analysis. The degradation efficiency (percent) of synthesized nanoparticle having 1 g/250 mL optimum dose with irradiation time are listed in Table-3.

The results of the present study showed that iron oxide nanoparticles were capable of degrading organochlorine pesticides. In present treatment process, it had been observed that

TABLE-3
DEGRADATION EFFICIENCY (%) OF SYNTHESIZED
NANOPARTICLE OPTIMUM DOSE WITH IRRADIATION TIME

Pesticides	Degradation efficiency (%)			
	After 1 h	After 3 h	After 6 h	After 12 h
α-HCH	26.83	76.03	99.61	BDL
β-HCH	51.33	91.02	96.11	BDL
γ-HCH (Lindane)	38.96	64.69	83.92	94.23
δ-HCH	39.00	61.94	80.82	BDL
Aldrin	18.95	73.81	97.64	BDL
Dieldrin	BDL	–	–	–
Endrin	99.47	BDL	–	–
Endrin aldehyde	39.16	70.05	99.26	BDL
α-Endosulfan	97.16	BDL	–	–
β-Endosulfan	73.17	99.17	BDL	–
Endosulfan sulphate	BDL	–	–	–
o,p'-DDT	52.12	91.02	98.61	BDL
p,p'-DDT	52.80	93.36	BDL	–
o,p'-DDE	BDL	–	–	–
p,p'-DDE	26.09	85.34	97.60	BDL
o,p'-DDD	72.74	96.58	BDL	–
p,p'-DDD	68.40	94.72	BDL	–
Heptachlor	BDL	–	–	–
Heptachlor epoxide	31.09	87.59	BDL	–

BDL = Below detection limit

in the absence of iron oxide nanoparticles, there were no significant changes in the concentrations of organochlorine pesticides during the entire process of UV irradiation. Thus, iron oxide nanoparticles were clearly responsible for the degradation of detected organochlorine pesticides. It was observed that after 12 h of photocatalytic process higher degradation percentage of organochlorine pesticides were obtained.

Optimization: To achieve a maximum degradation, catalytic degradation conditions were optimized as follows:

Effect of catalyst dose: The optimum dosage was achieved by using 0.5, 1, 2 and 5 g of catalyst during the process. The results are shown in Fig. 6. It was clear that maximum degradation of organochlorine pesticides were achieved with 1 g of nanocatalyst. When nanocatalyst was added in bulk amount *i.e.* 5 g/250 mL, two factors were responsible for a decrease in degradation process. First was higher dose of catalyst increase turbidity of the suspension which leads to decrease the penetration of UV light and second was maximum adsorption site on the surface of nanocatalyst, which become unoccupied and minimum adsorption take place and hence degradation decrease.
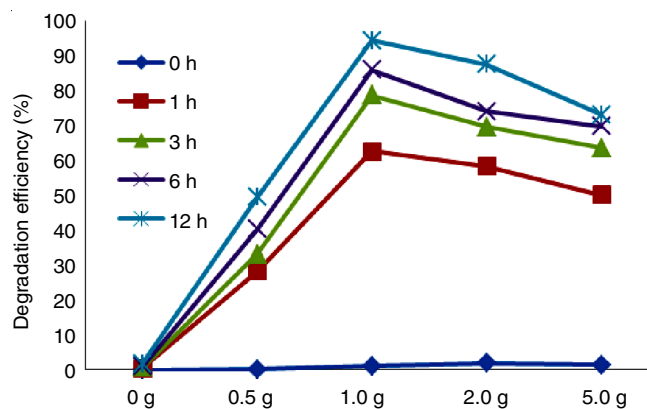

Fig. 6. Effect of nanocatalyst dose on degradation efficiency

In the absence of nanocatalyst negligible degradation takes place.

Effect of stirring rate: The degradation efficiency of nano catalyst depends upon the available adsorption site on the surface of catalyst for organochlorine pesticides, which is control by stirring rate up to a good extent. The results of stirring rate variation on the percentage degradation efficiency for organo-chlorine pesticides are shown in Fig. 7. It was clear that the maximum degradation efficiency of nanocatalyst was achieved at a stirring rate of 400 rpm, when maximum site of catalyst are available for degradation. It seems that at a rate of 600 rpm speed, the aqueous solution started spilling and the degradation process disturbed and further stirring not takes place. At a speed of 0 rpm minor degradation achieved. Maximum degradation of pesticides were achieved in order of 400 rpm > 200 rpm > 100 rpm > 0 rpm > 600 rpm, when the catalyst quantity taken 1 g/250 mL of sample.
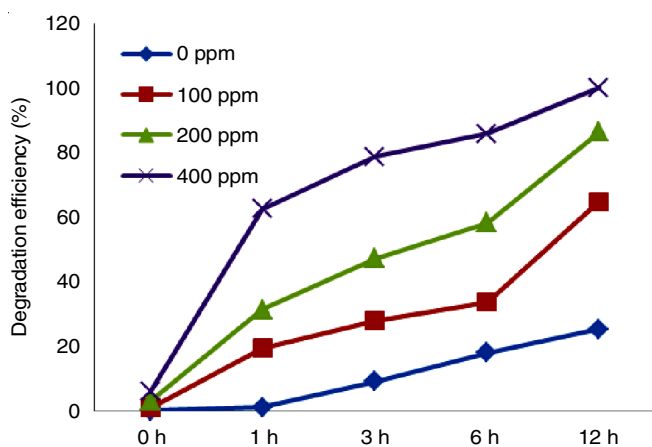

Fig. 7. Effect of stirring speed on the degradation efficiency

Effect of UV irradiation time: The degradation efficiency of nanocatalyst also depend upon the time of UV irradiation under the batch experiment carried out. The optimization achieved by using 1, 3, 6 and 12 h of irradiation time. It is clear from Fig. 8 that a maximum efficiency of nanocatalyst was in order 12 h > 6 h > 3 h > 1 h > 0 h, when the nanocatalyst dose was 1g/250mL of sample. It seemed that after 12 h of irradiation time, nanocatalyst showed a maximum degradation efficiency towards organochlorine pesticides and least degrad-ation at 0 h.
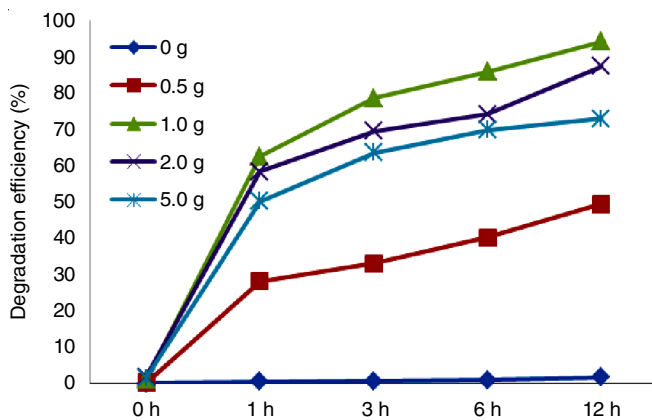

Fig. 8. Effect of irradiation time on degradation efficiency

Thus, the results of the present studies showed that the optimum conditions for the better degradation were 1 g nano-catalyst dose at 400 rpm stirring rate with maximum 12 h of irradiation time. It was also observed that after 1 h of irradiation, concentration of four pesticides *viz.* dieldrin, endosulfan sulphate, *o,p′*-DDE and heptachlor reached below the detection limit. The optimum irradiation time for endrin, α- and β-endosulfan was 3 h, when their concentration reached at below detection limit. Five pesticides named α-HCH, *o,p′*-DDT, *o,p′*-DDD, *p,p′*-DDD and heptachlor epoxide concentration decreased to the minimum level after 6 h of irradiation. The results also showed that seven pesticides *viz.* β-HCH, γ-HCH (lindane), δ-HCH, aldrin, endrin aldehyde, *o,p′*-DDT and *p,p′*-DDE degradation continued till 12 h of irradiation time. This could be due to slow degradation rate of most of these pesticides [17].

Kinetic studies: The kinetics of AOP was studied in order to understand the rate of reaction during degradation. The organo-chlorine standard contains a mixture of various pesticides, therefore, it is quite difficult to perform a detail analysis of individual pesticides. To study such a combinational process, the rate of reaction can be studied in terms of slowest degrading pesticide δ-HCH, hence the slowest step is the rate determine step for a reaction. The experimental data obtained with time in the presence of Fe_2O_3 nanocatalyst was modelled by assum-ption of pseudo-first order kinetics where the progressive degradation of pesticides can be presented as follows:

$$-\frac{d[\delta\text{-HCH}]}{dt} = k[\delta\text{-HCH}]$$

$$-\frac{d[\delta\text{-HCH}]}{[\delta\text{-HCH}]} = k_1 dt$$

By integrating both sides of the equation we get:

$$\ln\frac{[\delta\text{-HCH}]_o}{[\delta\text{-HCH}]} = k_1 t$$

The experimental data fitted to pseudo-first order kinetics, as a straight line with an R^2 value of 0.978 was obtained (Fig. 9).
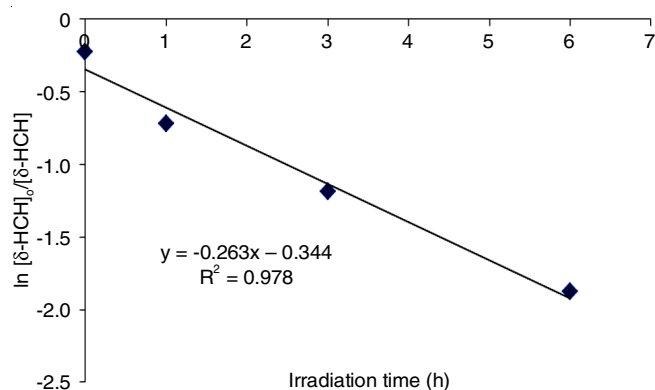

Fig. 9. Linear fitting of ln [δ-HCH]$_o$/[δ-HCH] as a function of irradiation time

Conclusion

In this study, the presence of organochlorine pesticides in drinking water samples from the selected site of western Uttar

pradesh were analyzed using GC-MS analysis. In addition, monodisperse iron oxide nanoparticles were synthesized, characterized and utilized for the degradation of detected organochlorine pesticides in water samples. Present studies showed that the degradation efficiency of synthesized nanoparticles towards mixed organochlorine pesticides was satisfactory.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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