Original Article

Effectiveness of Ultrasound and Ultraviolet Irradiation on Degradation of Carbaryl from Aqueous Solutions

M Khoobdel[1], *M Shayeghi[2], S Golsorkhi[2], M Abtahi[2], H Vatandoost[2], H Zeraatii[3], S Bazrafkan[2]

[1]Health Research Center, Baqiyatallah University of Medical Sciences, Tehran, Iran
[2]Department of Medical Entomology, School of Public Health, Tehran University of Medical Sciences, Iran
[3]Department of Biostatistics, School of Public Health, Tehran University of Medical Sciences, Iran

(Received 16 Dec 2009; accepted 19 Apr 2010)

Abstract

Background: Carbaryl (1-naphthyl-N-methyl carbamate) is a chemical in the carbamate family used chiefly as an insecticide. It is a cholinesterase inhibitor and is toxic to humans and classified as a likely human carcinogen. In the present study, the degradation of the carbaryl pesticide was investigated in the laboratory synthetic samples of tap water, in the effect of sonolysis and photolysis processes.

Methods: This study was conducted during 2006–7 in Chemistry and Biochemistry of Pesticides Laboratory in Tehran University of Medical Sciences (TUMS) in Iran. The carbaryl (80%) was used for preparing samples. First concentration of all samples were 4 mg/l. Sonochemical examinations in ultrasound reactor was done in two 35, 130 Hz, and 100 w, and three time. Photolysis examinations has done in the effect of 400 w lamp and moderate pressure and 6 time, then the amount of pesticide in the samples has been measured by the High Performance Thin Layer Chromatography (HPTLC) method.

Results: The highest degradation in photolysis process after 1 hour in the 35 KHz was 35%, and in the 130 KHz was 63%. Degradation of carbaryl at 130 KHz is higher than 35 KHz at the same time. Carbaryl elimination was increased by arise frequency and exposure time. After 8 min in photolysis, 100% omitting has been showed.

Conclusion: Degradation of carbaryl in high frequency ultrasound wavelength was more than low frequency. Degradation of carbaryl in water, combination of high frequency ultrasound wave length and UV irradiation was considerably more effective than ultrasound or ultraviolet irradiation alone.

Keywords: Ultrasound, Ultraviolet, Degradation, Pesticide, Carbaryl

Introduction

Pesticides are an important potential component of chemical pollutants used extensively for agriculture and sanitation purposes and released into the environment (Howard 1991). However, most of them are highly toxic, can exhibit chemical stability and resistance to biodegradation and continuously contaminated the aquatic and soil ecosystems (Tomlin 1995, Hardesen and Wratten 1998). From theatrical point the amount of synthetic pesticides in endless, and the entrance of each of these compounds to drinking water and wastewater that is ejected to the acceptor waters, causes some hygienic problems (Varshney 1998).

Carbaryl (1-naphthyl-N-methylcarbamate) is a broad spectrum carbamate insecticide with a variety of agricultural, garden and domestic application. Due to its wide use, human may be exposed to its residues through food and other routes (Gunasekara et al. 2008). Although moderately water soluble, it neither vaporizes nor volatilizes readily. It is demon-

*Corresponding Author: Dr Mansoureh Shayeghi, E-mail:mansorehshayeghi@yahoo.com

strated that even a weakly sorbed and easily degradable pesticide as carbaryl, is effectively sequestrated in soil with time, rendering it partly inaccessible to microorganisms and affecting the bioavailability of the compound (Ahmed et al. 2004).

Carbaryl is a cholinesterase inhibitor and is toxic to humans. It is classified as a likely human carcinogen by the United States Environmental Protection Agency (EPA 2004). It kills various beneficial insect and crustacean species along with intended pest victims, so care must be taken when spraying where beneficial non target species are present (Koskinin et al. 1994, Back 2002). Carbaryl is highly toxic to honey bees and very highly toxic to fresh water invertebrates as water fleas (*Dafnia*), shrimp, stonefly and other aquatic community. Carbaryl has been detected in many of surface water of USA at µg/L concentration (Gunasekara et al. 2008). This insecticide can be highly to slightly toxic to fish, depending upon the species (Vonesh and Kraus 2009, EPA 2010).

Carbaryl consists of 2-nephtyl carbamate that has carcinogenic effects, and is produced in industrial processes (Petrier et al. 1996). By the entrance of this insecticide to water sources and biological cycles, a lot of people are at risk of cancer so the protection of limited watery sources are very important (Branch and Jacoz 1999, Back 2002).

Carbaryl is detected in water at ppb concentrations but degradation is relatively rapid, with 1-naphthol identified as the major degradation product (Gunasekara et al. 2008). In Iran was done some study about phosphorus insecticide residue in drinking water and rivers, but there is no study among carbarly residues in water or wastewater (Shayeghi et al. 2007, 2008).

The application of power ultrasound to chemical processes is one of number intensification technologies that have undergone serious and wide-ranging development over the past 10-15 yr (Matouq et al. 2008). Many reports for ultrasound treatment of water and wastewater have been considered (Norwood 1990, Somich 1990, Suslick and Price 1999, Joyce 2002, Gogate et al. 2003, Benito et al. 2005, Dehghani et al. 2007a, Dehghani et al. 2007b, Asakura et al. 2008, Dehghani et al. 2008a, Dehghani et al. 2008b, Mahvi et al. 2009, Dehghani et al. 2010). Ultrasonic irradiation has been investigated in the degradation of some pesticide such as atrazine, parathion, carbofuran, Dichlorvos (Kotronarou et al. 1992, Koskinen et al. 1994, Petrier et al. 1996, Pfalzer and Hua 1998, Schramm and Hua 2001).

The high frequency ultrasound technique was also used to degradation of dissolved diazinon pesticide in water as a clean technology to protect environment (Motouq et al. 2008). In another study, the sonochemical photodegradation of fenitrotion in aqueous solution was investigated by Ultrasonic/UV system (Katsumata et al. 2009). Also degradation of carboforan in aqueous solution by ultrasound and was studied (Ma et al. 2010). A combination of UVA radiation and ozone, in presence of titanium dioxide has been investigated for carbaryl degradation as a potential destructive technology for the treatment of pesticide wastewater (Rajeswari and Kanmani 2009).

The photoinduced degradation of carbaryl was studied in surface water (Miller and Chin 2002). Degradation of carbaryl in mixture with other pesticide was also done by combined photo-fenton and biological oxidation (Balleseros et al. 2009).

Today more economical methods like using the ultrasound and ultra violate ray methods are noticed. Previous studies were not performed sonochemical and photolysis declaration of carbamat. In this study the effects of ultrasonic and photolysis methods in the degradation and eliminating of carbaryl from drinking water were assessed.

Materials and Methods

All solvents which were used in this study provided from Merck Co. Standard of

carbaryl were obtained from Switzerland Accustandard Ltd. Silica gel HPTLC plates (SiO_4, $60F_{254}$) which were used as stationary phase, were bought from Merck Co in 20×20 cm dimensions. Capillary tubes with 1, 2 and 5 µl capacity which was used for spotting purchased from CAMAG Ltd.

This study was conducted during 2006-7 in Chemistry and Biochemistry of Pesticides Laboratory in Tehran University of Medical Sciences (TUMS) in Iran.

UV lamp characteristics: medium power, 125.5 mm length, 20mm diameter, voltage 130±15 V, intensity 3.25 A, radiation intensity 90 Mw/cm^2, half life 1000 h, manufactured by France.

Ultrasound irradiation system characteristic: capacity 3.7 lit, power 90 and 100 W, 2.5 W/cm, altered number 2, manufactured by Germany.

Sonochemical and photochemical experiments were carried out by use of a bath sonicator (100W) working at 35 and 130 KHz frequencies and by a 400W medium pressure UV lamp.

Samples of this study are synthetic and from Tehran pipe water. The concentration of carbaryl in all of samples was 4 mg/lit (4ppm) and used the 80% insecticides. The samples were adjusted in reactor in 3 time of remaining (20, 40 and 60 minutes) and at of 35 and 130 KHz frequencies and 100 w. In the photolysis process samples with 4 ppm concentration were affected in 6 remaining time (1, 2, 4, 6, 8, 10 min) and the 250 nm wavelength. Reaction temperature in ultrasonic and ultraviolet process was kept at 20±1 ċ. The pH of the sample solution was adjusted with HCL and/or NaOH at 7.1.

After the fixed time the amount of insecticide in samples were determined by using the HPTLC methods. For this reason insecticide in samples were extracted by using dichloromethane. Five µl loading of each standard and sample solution was spotted on the HPTLC plate. In each plate, 15 spots were performed which contained 3 standard spots and 12 samples (from the solution which were prepared with repellents). Distance between tracks was 1 cm. In this study, the multiple levels spotting method was used.

Plates were developed using a mobile phase consisting of hexane-acetone (60/40 v/v). Liner ascending was carried out in a twin-trough glass chamber (CAMAG, Switzerland) equilibrated with mobile phase (Hatrik and Take 2001).

The developed plate was air-dried for 10 min and then the spots were seen in UV cabinet with 254 nm. The slit dimension was set at 10.0×0.40 mm. The monochromatic bandwidth was set at 20 nm and a scanning speed 20 mm/s was employed. Densitometry scanning was performed on CAMAG TLC scanner III at 290 nm and operated by CATS4 software. The source of radiation utilized was the deuterium lamp.

The spot migration distance (MD) for the developed spots was defined by the distance between the solvent front and the starting line during the developing period. Spots developing rate or R_f values (Retardation factor) were determined. The position of a substance zone (spot) in a thin layer chromatogram can be described by R_f. This is defined as the quotient obtained by dividing the distance between the substance zone from the starting line (Z_S) by the distance between the solvent front (Z_f) and the starting line (Z_0) (Denistrop 2000).

$$R_f = Z_S / Z_f - Z_0$$

Where:

Z_S: distance of the substance zone from the starting line [mm]

Z_f : distance of the solvent front from the solvent line [mm]

Z_0 : distance between the solvent level and the starting line [mm]

Data analysis, which included average amount of materials in each spot, was automatically done by CATS4 software.

This study was done in accordance with Helsinki Declaration and guideline of Iranian Ministry of Health and Medical Education and was approved by Ethics Committee of Tehran University of Medical Sciences.

Results

The effects of ultrasound wave for carbaryl degradation at 35 and 130 KHz with increasing time have a faster rate and the concentration of pesticide was decreased.

In the sonochemical process, carbaryl undergoes degradation at 130 KHz have a faster rate than 35KHz, like that at 35 KHz, after 60 min the maximum output of elimination is 35% , whereas at 135 KHz, after the same time is 63% (Table 1).

Also ultraviolet irradiation technique was considerably more effective than ultrasound. In UV technique, 100% of insecticide was eliminated from water in the 8 min. (Fig. 1). The photochemical degradation of carbaryl in 8 min was complete (Fig. 2). According to the results ultraviolet irradiation technique was considerably more effective than ultrasound. In UV technique, 100% of insecticide was eliminated from water in the 8 min (Table 1).

Table 1. Degradation percentage of carbaryl

Process	Exposure time(min)	Degradation percentage
Ultrasound Frequency (35khz)	20	9
	40	22.15
	60	35
Ultrasound Frequency (130khz)	20	25
	40	49
	60	63
Ultraviolet Irradiation	1	80.27
	2	85.6
	4	90
	6	95.4
	8	100

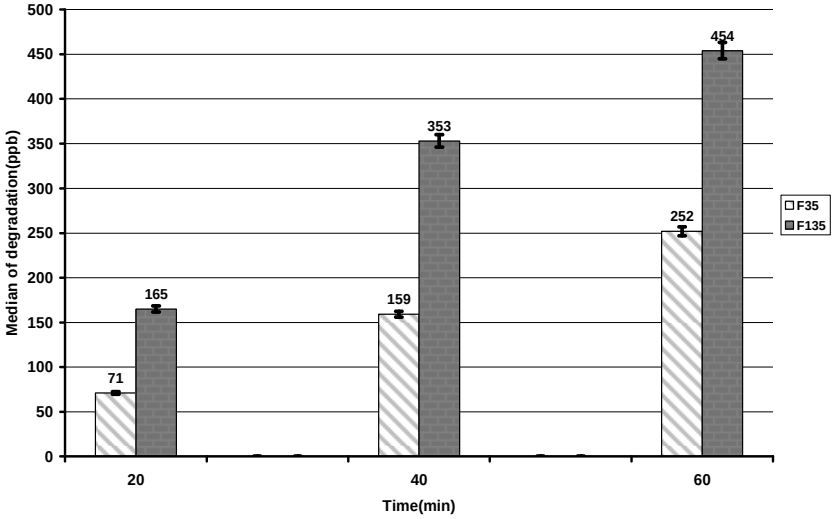

Fig. 1. Declaration percentage of carbaryl in sonochemical treatment

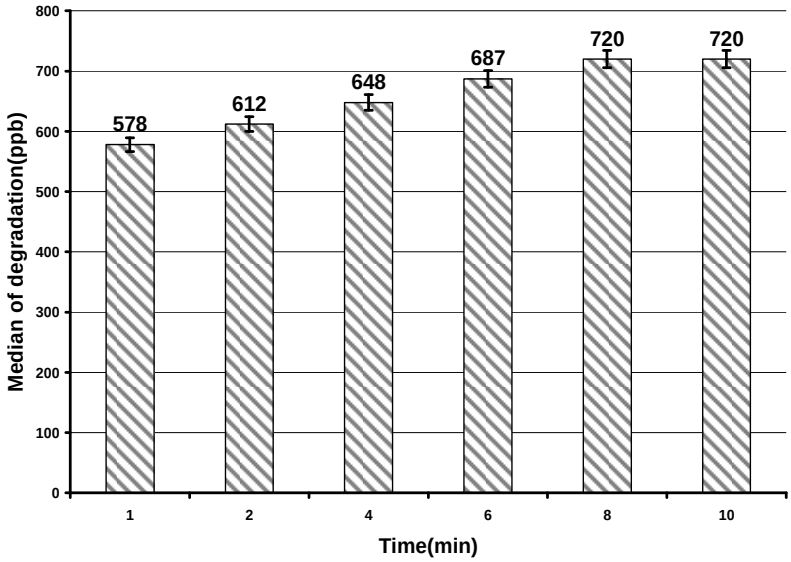

Fig. 2. Declaration median of carbaryl in photolysis process

Discussion

According to the Results, in sonochemical degradation, elimination of carbaryl at 130 KHz is higher than 35 KHz at the same time. Carbaryl elimination was increased by arise wave length frequency and contact time. In another study, degradation of diazinon was successful performed using 1.7 MHz wavelength of ultrasound in 5 min (Matouq et al. 2008).

Carbaryl in natural waters rapidly hydrolyzed to 1- naphtol, which is identified as a general and primary degradation product of carbaryl. Degradation was mediated by hydroxyl radical oxidation (Gunasekara et al. 2008). Carbaryl was photolyzed into 1,2 naphthoquinone, 1,4- naphthoquinone, 2-hydroxy-1, 4- naphthoquinone and 7-hydroxy-1,4-naphthoquinone (Brahimia and Richard 2003).

The best yield observed at 130 KHz for carbaryl degradation may be the result of much more hydroxyl availability at the out of the bubble of cavitations. It was found that out put of elimination of carbaryl at photochemical degradation was higher than sonochemical destruction because in photolysis process, in addition of hydroxyl radical production, there is direct effect of ultraviolet energy on breaking down of the carbon-carbon bounds of carbaryl molecules (Wu et al. 2001).

Degradation of fenitrothion by ultrasound/UV system was effective and achieved complete elimination after 30 min (Katsumata et al. 2009). In another study, photolytic ozonation (O3/UV) had a synergistic effect on carbaryl degradation (Rajeswari and Kanmani 2009).

In conclusion, based on the results, probably to elimination the carbaryl in water, combination of high frequency ultrasound wave length and UV irradiation was considerably more effective than ultrasound or ultraviolet light alone.

Acknowledgements

The authors would like to thank Mrs. Azar Ghasri for their kind cooperation in Environmental Health Engineering laboratory. This study was financially supported by School of Public Health, Tehran University of Medical Sciences.

References

Asakura Y, Nishida T, Koda S (2008) Effects of ultrasonic frequency and liquid height on sonochemical efficiency of large-scale sonochemical reactors. Ultrason Sonochem. 15: 244–250.

Back RC (2002) Significant developments in eight years with sevin insecticide. J Ager Food Chem. 13(3): 198–199.

Ahmad R, Kookana RS, Megharaj M, Alston AM (2004) Aging reduces the bioavailability of even a weakly sorbed pesticide (carbaryl) in soil. Environ Toxicol Chem. 23(9): 2084–2089.

Benito Y, Arrojo S, Vidal P (2005) Hydrodynamic cavitations as a low-cost AOP for wastewater treatment: Preliminary results and a new design approach. Wessex Institute of Technology, pp. 495–504.

Branch RA, Jacoz E (1999) Is carbaryl as safe as its reputation? Am J Med. 80: 659–664.

Brahimia O, Richard C (2003) Phototransformatiom of carbaryl in aqueous solution Laser-as photolysis and steady-state studies. J Photoch Photobia A. 156: 9–14.

Denistrop EH (2000) Applied thin layer chromatography: Best practice and avoidance of mistakes. Wiley-VCH, Weinheim. pp. 1-304.

Dehghani MH, Najafpoor AA, Azam K (2010) Using sonochemical reactor for degradation of LAS from effluent of wastewater treatment plant. Desalination. 250: 82–86.

Dehghani MH, Jahed Gh R, Mesdaghinia A, Nasseri S (2008 a) Using irradiation treatment for reduction of anaerobic bacteria from a wastewater treatment plant. Environ Technol. 29(11): 1145–1148.

Dehghani MH, Mesdaghinia AR, Nasseri S, Mahvi AH, Azam K (2008 b) Application of sonochemical reactor technology for degradation of reactive yellow dye in aqueous solution. Water Qual Res J Canada. 43(2/3): 183–187.

Dehghani MH, Mahvi AH, Jahed Gh R, Sheikhi R (2007a) Investigation and evaluation of ultrasound reactor for reduction of fungi from sewage. Zhejiang Univ Sci B. 8(7): 493–497.

Dehghani MH, Mahvi AH, Najafpoor AA, Azam K (2007b) Investigating the potential of using acoustic frequency on the degradation of linear alkylbenzen sulfonates from aqueous solution. Zhejiang Univ Sci A. 8(9): 1462–1468.

EPA (2004). Interim reregistration eligbility decision for carbaril. Carbaryl IRED facts. P.289.

EPA (2010) Carbaryl IRED facts. Pp:1-6.

Gogate PR, Wilhelm AM, Pandit AB (2003) Some Aspects of the design of sonochemical reactors. Ultrason Sonochem. 10: 325–330.

Gunasekara AS, Rubin AL, Goh KS, Spurlock FC, Tjeerdema RS (2008) Environmental fate and toxicology of carbaryl. Rev Environ Contam Toxicol. 196: 95–121.

Hatrik S, Take J (2001) Extraction methodology and chromatography for determination of residual pesticides in water. J Chromatogr. 733: 217–233.

Howard PH (1991) Handbook of Environmental Fate and Exposure Data for Organic Chemicals. Volume III. Pesticides, Lewis Publishers, Chelsea, MI. 76–85.

Joyce E (2002) The development and evaluation of ultrasound for the treatment of bacterial suspension. Ultrason Sonochem. 10: 315–318.

Katsumata H, Okada T, Kaneco S, Suzuki T, Ohta K (2010) Deagradation of fenitrothion by ultrasound/ferrioxalate/ UV system. Ultrason Sonochem, 17(1): 200–206.

Koskinen WC, Sellung KE, Baker JM, Barber BL, Dowdy RH (1994) Ultrasonic deg-

radation of atrazine and alachlor in water. J Environ Sci Health B. 29(3): 581–590.

Kotronarou A, Mills G, Hoffmann MR (1992) Decomposition of parathion in aqueous solution by ultrasonic irriadiation. Environ Sci Technol. 26(7): 1460–1462.

Mahvi AH (2009) Application of ultrasonic technology for water and wastewater treatment. Iran J Public Health. 38(2): 1–17.

Mastovska K (2005) Food and nutritional analysis pesticide residues. Encyclopedia of Analytical Science, pp. 251–261.

Matouq AM, Al-Anber ZA, Tagawa T, Aljbour S, Al-Shannag M (2008) Degradation of dissolved diazinon pesticide in water using the high frequency of ultrasound wave. Ultrason Sonochem. 15: 869–74.

Norwood VM (1990) A literature review of waste treatment technologies which may be applicable to wastes generated at fertilizer/agrichemical dealer sites. Bulletin Y-214. NFERC. Tennessee Valley Authority. Muscle Shoals. AL

Petrier C, David B, Laguian S (1996) Ultrasonic degradation at 20 Hkz and 500 Hkz of atrazine and pentachlorophenol in aqueous solution: preliminary results. Chemosphere. 32(9): 1709–1718.

Pfalzer TU, Hua I (1998) The use of acoustic cavitations for the destruction of the carbamate pesticide carbofuran. 215th American Chemical Society (ACS) National meeting., Dallas,TX, 29 Apr. Paper no 117.

Rajeswari R, Kanmani S (2009) A study on synergistic effect of photocatalytic ozonation for carbaryl degradation. Desalination. 242(1–3): 277–85.

Somich CJ, Muldoon MT, Kearney PC (1990) On-site treatment of pesticide waste and rinsate using ozone and biologically active soil. Environ Sci Technol. 24: 745–749.

Suslick KS, Price G (1999) Applications of Ultrasound to Materials Chemistry. Annu Rev Matl Sci. 29: 295–326.

Schramm JD, Hua I (2001) Ultrasonic Irradiation of Dichlorvos: Decomposition Mechanism Water Res. 35(3): 665–674.

Shayeghi M, Khoobdel M, Bagheri F, Abtahi M (2008) The residues of azinphos-methyl and diazinon in Garaso and Gorganrood rivers in Golestan Province. J School Public Health and Institute Public Health Res. 1(6): 75–82.

Shayeghi M, Khoobdel M, Vatandoost H (2007) Determination of organophosphorus insecticides (Malathion and Diazinon) residue in the drinking water. Pak J Bio Sci. 10(17): 2900–2904.

Tomlin C (1995) The pesticide manual, 10th ed. Crop Protection Publication, The Royal Society of Chemistry. pp. 435–436.

Varshney CK (1998) Water pollution and management India publisher Company. 17: 883–887.

Vonesh JR, Kraus JM (2009) Pesticide alters habitat selection and aquatic community composition. Oecologia. 160(2): 379–85.

Wu C, Liu X, Wei D, Fan J (2001) Phtosonochemical degradation of organic mater in water. Water Res. 35(16): 3927–3933.