Investigation of Advanced Oxidation Process for the Removal of Residual Carbaryl from Drinking Water Resources

Ali Reza Rahmani, Mohamad Taghi Samadi and Maryam Khodadadi

Abstract—A laboratory set-up was designed to survey the effectiveness of UV/O_3 advanced oxidation process (AOP) for the removal of Carbaryl from polluted water in batch reactor. The study was carried out by UV/O_3 process for water samples containing 1 to 20 mg/L of Carbaryl in distilled water. Also the range of drinking water resources adjusted in synthetic water and effects of contact time, pH and Carbaryl concentration were studied. The residual pesticide concentration was determined by applying high performance liquid chromatography (HPLC). The results indicated that increasing of retention time and pH, enhances pesticide removal efficiency. The removal efficiency has been affected by pesticide initial concentration. Samples with low pesticide concentration showed a remarkable removal efficiency compared to the samples with high pesticide concentration. AOP method showed the removal efficiencies of 80% to 100%. Although process showed high performance for removal of pesticide from water samples, this process has different disadvantages including complication, intolerability, difficulty of maintenance and equipmental and structural requirements.

Keywords— AOP, Carbaryl, Pesticides, Water treatment.

I. INTRODUCTION

THE extensive use of pesticides in agriculture for protecting plant and crop, as well as easier introduction of different generations of chemical pesticides onto the market have dramatically increased the variety and quantities of agrochemicals present in the environment in recent years [1]. Pesticides are divided into several types depending on their usage, including herbicides, insecticides, fungicides, rodenticides, nematicides, microbicide, and plant as well as insect growth regulators [2]. These substances have been also categorized based on their unique chemical structures into organochlorines, organophosphorous, carbamates and pyrethoides [2]. Organophosphorus pesticides are very toxic when absorbed by human organisms because of acetyl-cholinesterase deactivation [3] and organochlorines are more persistent, suspected to be bioaccumulated in the food chain [4]. In Iran, about 20,000 tons of pesticides are annually

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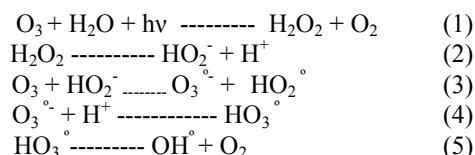
applied in the country, of which, about 1000 tons allocate to Hamadan province [5]. The pesticides are released into the environment from manufacturing, transportation and agriculture applications [6]. Many pesticides are found in urban streams. Therefore, the human populations are exposed to pesticides and other organic micro pollutants either by drinking water or via the food supplies [7]. Some pesticides have been identified to be potential chemical mutagens. Pesticide residues such as diazinon and parathion are also extensively concerned because of their potential long-term adverse affects [8]. Organophosphorus pesticides have a higher acute toxicity than organochlorines [9]. As inhibitors of cholinesterase activity, organophosphorus pesticides produce overstimulation of cholinergic neurotransmission, and producing symptoms such as increased salivation, sweating, changes in blood pressure and heart rate, nausea, diarrhea, headache, muscle tremor, and in high-dose situations, breathing difficulty, convulsions and death [10]. Moreover, toxicology studies have demonstrated specific neuro-degenerative effects from exposure to certain pesticides. Human case reports have also suggested causal relations between pesticide exposure and Parkinson disease [11]. The limits and guideline values for pesticides in drinking water have been issued by the World Health Organization (WHO), European Unions (EU), and many countries. The EU has set pesticide standards for drinking water at a maximum permissible concentration (MCL) for any particular pesticide of 0.1 and 0.5 μg/L for the sum of all pesticides, including their degradation products (Directive 98/83/EC of the council). The Iranian regulation for pesticides in drinking water, MCL, ranged from 0.2 μg/L to 100 μg/L [12]. Therefore, it is important to develop techniques and processes for the removal of pesticides from agricultural runoffs, industrial wastewater and water resources. Several treatment alternatives have been proposed for the removal of pesticides and their derivatives from aquatic solutions, such as electrochemical oxidation [13], biological treatment [14], UV irradiation [15], ozone and GAC [16], UV/H_2O_2 oxidation [15], coagulants [17]-[18], membrane technology [19], O_3/H_2O_2 [20] and UV/O_3 and UV/TiO_2 [21]. Chemical oxidation processes are more effective to reduce or completely destroy of pesticide contamination from water and wastewater. Previous studies have indicated the effectiveness of advanced oxidation processes (AOPS) to destroy refractory micro-pollutants such as pesticides. In advanced oxidation process, a combination of

World Academy of Science, Engineering and Technology
International Journal of Environmental and Ecological Engineering
Vol:5, No:12, 2011

UV, oxidants and catalysts such as TiO_2 has been applied to generate hydroxyl radicals (OH^o). Also ozonation is recognized to be an effective treatment process to achieve degradation of organic contamination of drinking water [2]-[20]. However, it has been shown that the photocatalytic oxidation process of UV/O_3 can be producing more hydroxyl radicals [21]. The organic pollutants such as pesticides are oxidized by free hydroxyl radicals and products are carbon dioxide and mineral salts [7]. In this process the main reactions occurring can be defined as follows:
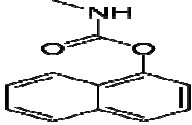
$$O_3 + H_2O + h\nu \text{ --------- } H_2O_2 + O_2 \qquad (1)$$
$$H_2O_2 \text{ ---------- } HO_2^- + H^+ \qquad (2)$$
$$O_3 + HO_2^- \text{ .... } O_3^{\circ-} + HO_2^{\circ} \qquad (3)$$
$$O_3^{\circ-} + H^+ \text{ ------------ } HO_3^{\circ} \qquad (4)$$
$$HO_3^{\circ} \text{ --------- } OH^{\circ} + O_2 \qquad (5)$$

The objective of this research was determination of the efficiency of UV/O_3, as an advanced oxidation process (AOP) to remove Carbaryl (carbamates) from drinking water resources. Also the effects of main parameters such as water pH, retention time and initial pesticide concentration were investigated.

II. EXPERIMENTAL

A. Reagents and Materials

All chemical reagents used in this study were obtained from Merck (Hohenbrunn, Germany). The pure Carbaryl pesticide purchased from Sigma Aldrich (Spain) (Table 1). The carbaryl was selected based upon it's toxicity, persistence and wide uses in Hamadan (The Hamadan city is the capital of Hamadan province, west of Iran) farmlands. Pesticide standard stock solution was prepared in methanol (1000 mg/L). The pH of the solution was controlled by pH meter (Suntex model sp-701, Taiwan). Distillated water was prepared by Fater Electronic water distiller model 2104 (Tehran, Iran). For all batch experiments, glassware and bottles were washed and rinsed with HNO_3 before the use and then by distilled water.

TABLE I
CHEMICAL CHARACTERISTICS OF CARBARYL

Pesticide	Chemical structure	Formula and molecular structure	Molecular Weight (gr/mol)	Purity
Carbaryl	carbamates	$C_{12}H_{12}NO_2$:63-25-2	201.23	99%

B. Ozone / UV Pilot

Ozone gas produced by ARDA (model COG-OM, type 1A) (France) ozonizer was bubbled into glass cylindrical reactor with 2.0 L volume which immersed in a cooling water jacket with 10 L volume of cold water. An oxygen concentrator ARDA (model 7F-3) (France), conducted the concentrated oxygen to the ozonizer. The rate of ozone generation was 1.0 gr/hr (at atmospheric pressure 1.0 atm, 25°C) and generated ozone continuously conducted to the pilot reactor by silicon pipes and diffused in deionized water by using a disperser. The initial dissolved ozone was 4.0 mg/L. A low-pressure lamp (ARDA 125 W) (France) with quartz cortex, was used as the UV emitter (UV-C, λ= 247 nm). The UV lamp was immersed centrally in the glass reactor. The schematic diagram of the used AOP system was shown in Fig. 1.
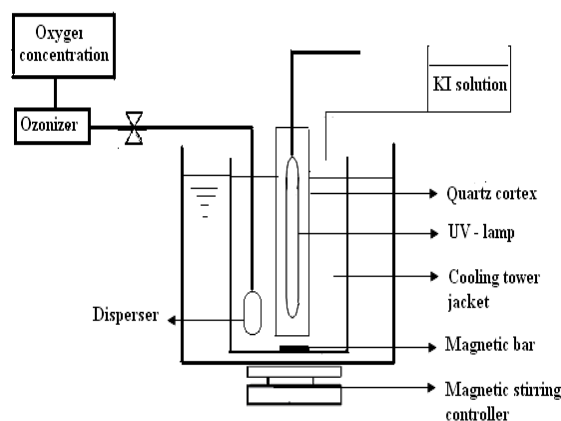

Fig. 1 Schematic diagram of UV/O_3 system experimental set-up

C. Set-up and Procedures

Experimental determination of removal efficiency for carbaryl was carried out by preparation of pesticide synthetic solutions with concentrations of 1, 5, 10, 15 and 20 mg/L in distilled water from 1000 mg/L stock solution (to simulate high–loaded pesticide containing agricultural run-offs in Hamadan). Also the pH values in the range of drinking water resources (6, 7, and 9) adjusted in synthetic water with nitric acid 1% and sodium hydroxide 1%. The UV/O_3 glass reactor was filled separately with synthetic solutions and UV lamp and ozonizer were turned on. The experiments were carried out at 20 ±1°C. A magnetic stirrer steadily mixed the solution in the reactor to achieve complete homogeneity, in the reaction time of 30, 60, 90 and 120 min. The excessive ozone was trapped in 2% potassium iodide (KI). Then, the collected samples analyzed for Carbaryl by HPLC method and the removal efficiency of UV/O_3 was determined.

D. Analytical Methods

Dissolved ozone levels were determined by potassium iodide (KI) standard titrimetry in samples [22]. The standard curve for Carbaryl pesticide was plotted using serial concentrations of the pesticide standard solution from 0.1 to 25 mg/L. The linearity relative coefficient (r^2) from calibration curve was 0.999. Extraction of Carbaryl pesticide from water samples were done by using the liquid-liquid extraction by dichloromethane and chloroform. The general extraction procedure included: transferred 500 ml of filtered water sample (Wattman, 0.45 μm pore diameter Teflon filter) to a decanter cone, adding 30 ml dichloromethane and 15 gr pure grade of NaCl, well shaking for 30 min, transferred through

World Academy of Science, Engineering and Technology
International Journal of Environmental and Ecological Engineering
Vol:5, No:12, 2011

the sodium sulfate (NaSO$_4$) column to remove moisture, re-adding 30 ml dichloromethane, evaporated to dryness by rotary evaporator (Heidol, type VV1; Germany) [23], and reconstituted in 1 ml chloroform. The extracted samples residual ozone was expelled by bubbling with ultra pure nitrogen. The samples were analyzed by high performance liquid chromatography (HPLC) for carbaryl. HPLC analyses were carried out using an HP 1200-MSD (Agillent: USA) with UV-Vis detector and auto sampler. The chromatographic part was composed of an HP 1200 chromatograph equipped with a C18 (μ Bond PakTM; Water, USA) column (250 mm × 4.6 mm). The mobile phase was composed of water, methanol and acetonitrile (15:45:40) and flow rate of 1 mL/min. The peak of carbaryl detected at 12.7 min after injection of samples. The UV detector was set at λ=140 nm. The obtained data were processed with Chem Station (Agillent Technologies; USA) software.

III. RESULTS AND DISCUSSION

In the present study, the efficacy of UV/O$_3$ advanced oxidation process coagulation in removing of pesticide was investigated. Also the impact of important parameters including water pH, retention time and initial pesticide concentration on the effectiveness of the removal processes were evaluated.

A. Effect of pH

The hydroxyl radicals produced by AOPs have a higher oxidation potential (2.8 V) than molecular ozone and can attack organic and inorganic molecules with very high reaction rates [2]-[24]. The carbaryl degradation by UV/O$_3$ process as a function of pH is shown in Figures 2-4. The experiments were carried out in pH values of 6, 7 and 9 (minimum, average and maximum pH values of drinking water resources). The results indicated that, increasing of pH significantly increased the removal efficiencies of pesticide ($p<0.05$). A maximum removal efficiency of 100% was obtained with the UV/O$_3$ process within 120 min, 1 mg/L initial pesticides concentration at pH 9. Pesticide degradation efficiency with 20 mg/L initial pesticide concentration within 120 min at pH 9 was 97%. At pH 6, with the same experimental conditions (initial pesticide concentration of 20 mg/L and 120 min) degradation efficiencies decreased to 95%. Increasing in pH (>8) causes a predominant decomposition of ozone molecules into hydroxyl radicals and subsequently a rapid reaction between the radicals and pesticides as organic molecules [2]. Neutral pH 7 showed similar removal efficiency to basic pH (96% removal at mentioned experimental conditions). This is consistent with the previous study for the removal of organophosphorus pesticides by APO process [2]-[7].
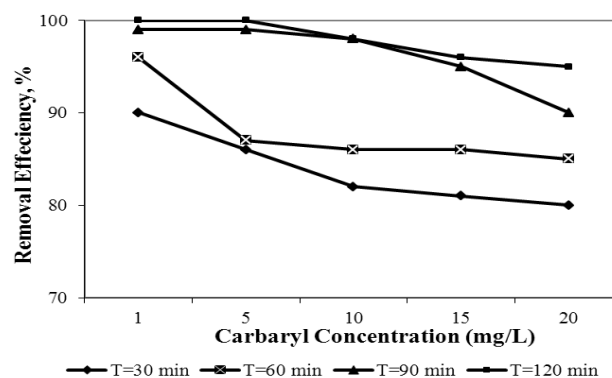

Fig. 2 Effect of initial Carbaryl concentration onto removal efficiency by UV/O$_3$ process at various retention times: pH=6
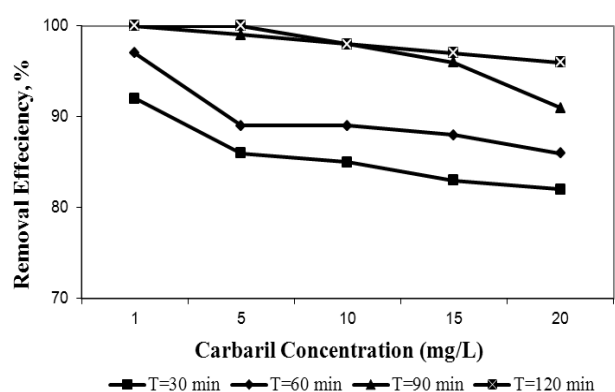

Fig. 3 Effect of initial Carbaryl concentration onto removal efficiency by UV/O$_3$ process at various retention times: pH=7
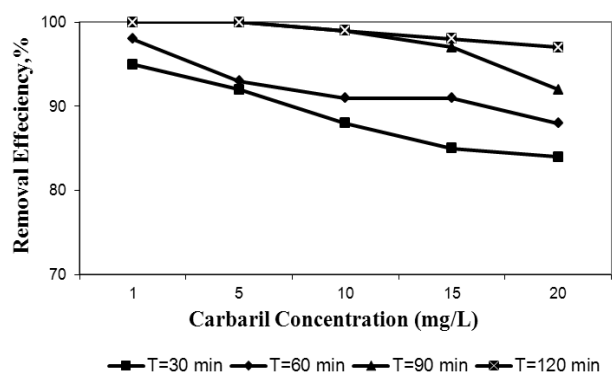

Fig. 4 Effect of initial Carbaryl concentration onto removal efficiency by UV/O$_3$ process at various retention times: pH=9

B. Effects of Pesticide Initial Concentration

The results showed that the initial concentration of Carbaryl has significantly affected the removal efficiency ($p<0.05$). Presented data in Figures 2-4 shows that in UV/O$_3$ system at pH 7 with pesticide initial concentration of 20 mg/L, 82.5% of carbaryl was removed in 30 min. However, at the same level of pH and retention time, with 1 mg/L of selected pesticide, the removal efficiency increased to 91.8%. Maldonado et al. and Ikehata et. al. reported that high initial concentration of pesticides in AOP reactor decreased the removal efficiency [2,

World Academy of Science, Engineering and Technology
International Journal of Environmental and Ecological Engineering
Vol:5, No:12, 2011

25]. Also Daneshvar et al., (2005) showed that increase in diazinon concentration decreased the removal efficiency in a nano particles and UV combined system [26]. The mechanism can be explained by constant concentrations of dissolved ozone and UV irradiation with limited production of hydroxyl radical production (as the main reaction agent) in all samples. Therefore, in the samples with low initial concentration of pesticide, the removal efficiency was significantly higher than the samples with high initial concentration of pesticide.

C. Effects of Pesticide Initial Concentration

Our results showed that increase in retention time significantly enhances the Carbaryl removal efficiency ($p < 0.05$). As shows in Figures 2-4, within 30 min at pH 7 and 20 mg/L of pesticides concentrations, the removal efficiency was 82.5%. At the same experimental conditions, increasing of retention time to 90 min improved the removal efficiencies to 91%. Increasing of retention time to 120 min, had a venial effect on removal efficiencies (increased removal efficiencies 5.5%). Longer retention time caused to produce higher concentration of pesticide degradation metabolites as well as hydroxide radicals produced by UV/O_3 utilized for metabolites degradation. Daneshvar et al. (2005) reported the increasing of organophosphorus pesticides removal efficiency in a UV/ZnO pilot plant by increasing in the retention time [26]. Our results were consistent with the previous study on halogenated lambda-cyhalothrin and non halogenated deltamethrin pesticides removal by AOP process [27].

IV. CONCLUSION

The results of this study showed that UV/O_3 advanced oxidation process (AOP) has high performance for removal of Carbaryl (carbamates) residual pesticide from polluted water. The process was influenced by factors such as pH, pesticide initial concentration and retention time. At basic pH, higher removal efficiencies have been observed. By this process removal efficiency of 100% was obtained within 120 min, 1 mg/L initial pesticides concentration at pH 9. At acidic pH values, the removal efficiencies were significantly decreased. Decline of retention time and increment of pesticide initial concentration significantly decreased the pesticide removal efficiency. The removal efficiency of UV/O_3 ranged 80%-100% for carbaryl. Although AOP process showed high performance for removal of pesticide from water samples, this process has different disadvantages including complication, intolerability, difficulty of maintenance and equipmental and structural requirements.

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