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The Comparison of Advanced Oxidation Process and Chemical Coagulation for the Removal of Residual Pesticides from Water

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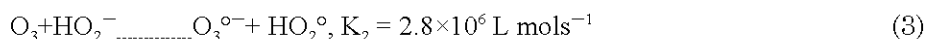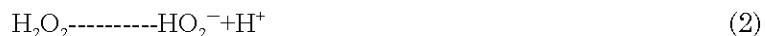
ABSTRACT

The pesticide pollution of water resources is a pervasive problem. A laboratory set-up was designed to compare the effectiveness of UV/O_3 Advanced Oxidation Process (AOP) with coagulation using Polyaluminum Chloride (PACl) for the removal of three widely used pesticides, Chlorpyrifos, Diazinon and Carbaryl from water resources. The study was carried out for water samples containing 1 to 20 mg L^{-1} of pesticides. Also the impact of important parameters including initial pesticides concentration and retention time were investigated. The residual pesticide concentration was determined by applying Gas Chromatography-Mass Spectrometry (GC-MS) and High Performance Liquid Chromatography (HPLC). In AOP process, samples with low pesticide concentration (1 mg L^{-1}) showed a significant removal efficiency compared to the samples with high pesticide concentration (20 mg L^{-1}). Also prolonged retention time caused a significant increase in the efficiency of the selected pesticides removal. Variation in the doses of PACl has significant effect on the pesticides removal efficiency. Both methods showed the removal efficiencies for diazinon, chlorpyrifos and carbaryl. Although AOP method showed higher performance for removal of selected pesticides, at similar condition, coagulation by PACl demonstrated acceptable performance without any need to the special equipment and structural requirements.
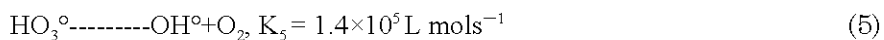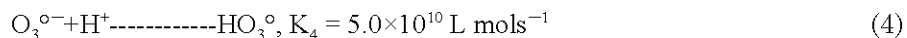
Key words: Pesticides, water treatment, AOP, PACl

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 (Kralj, 2007). Pesticides are divided into several types depending on their usage, including herbicides, insecticides, fungicides, rodenticides, nematicides, microbicides and plant as well as insect growth regulators (Ikehata and El-Din, 2005). These substances have been also categorized based on their unique chemical structures into organochlorines, organophosphorous, carbamates and pyrethoides (Ikehata and El-Din, 2005). Organophosphorus pesticides are very toxic when absorbed by human organisms because of acetyl-cholinesterase deactivation (Berijani *et al.*, 2006) and organochlorines are more persistent, suspected to be bioaccumulated in the food chain

(Lartiges and Garrigues, 1995). The pesticides are released into the environment from manufacturing, transportation and agriculture applications (Honeycutt and Schabcker, 1994). 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 (Badawy *et al.*, 2006). 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 (Bolognesi and Morasso, 2000). Organophosphorus pesticides have a higher acute toxicity than organochlorines (Zohair, 2001). As inhibitors of cholinesterase activity, organophosphorus pesticides produce over stimulation 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 (Padilla *et al.*, 2005). Moreover, toxicology studies have demonstrated specific neurodegenerative effects from exposure to certain pesticides. Human case reports have also suggested causal relations between pesticide exposure and Parkinson disease (Firestone *et al.*, 2005). 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 $\mu g\ L^{-1}$ for the sum of all pesticides, including their degradation products (Directive 98/83/EC of the council). 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 (Arapoglou *et al.*, 2003), biological treatment (Liu *et al.*, 2004), UV irradiation (Real *et al.*, 2007), ozone and GAC (Kim *et al.*, 2005), UV/H_2O_2 oxidation (Real *et al.*, 2007), coagulants (Exall and Vanloon, 2000; Seiichi *et al.*, 2006), membrane technology (Boussahel *et al.*, 2000), O_3/H_2O_2 (Chen *et al.*, 2008) and O_3/UV and UV/TiO_2 (Kuo, 2002). Chemical oxidation processes are more effective to reduce or completely destroy the pesticide contamination from water and wastewater. Previous studies have indicated the effectiveness of Advanced Oxidation Processes (AOP_S) to destroy refractory micro-pollutants such as pesticides. In advanced oxidation process, a combination of UV, oxidants and catalysts such as TiO_2 has been applied to generate hydroxyl radicals ($OH°$). Also ozonation is recognized to be an effective treatment process to achieve degradation of organic contamination of drinking water (Chen *et al.*, 2008; Ikehata and El-Din, 2005). However, it has been shown that the photocatalytic oxidation process of UV/O_3 can be producing more hydroxyl radicals (Kuo, 2002). 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 (Ikehata and El-Din, 2005; Andreozzi *et al.*, 1999). The organic pollutants such as pesticides are oxidized by free hydroxyl radicals and products are carbon dioxide and mineral salts (Badawy *et al.*, 2006). In this process the main reactions occurring are shown in Eq. 1-5:
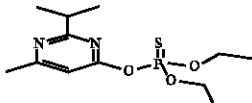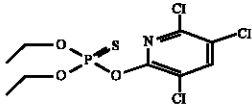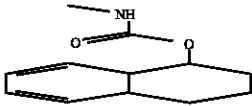
$$O_3 + H_2O + h\nu \text{---------} H_2O_2 + O_2 \tag{1}$$

$$H_2O_2 \text{---------} HO_2^- + H^+ \tag{2}$$

$$O_3 + HO_2^- \text{.............} O_3^{°-} + HO_2^{°}, K_2 = 2.8 \times 10^6\ L\ mols^{-1} \tag{3}$$

$$O_3^{\circ-}+H^+\text{------------}HO_3^{\circ}, K_4 = 5.0\times10^{10}\ L\ mols^{-1} \tag{4}$$

$$HO_3^{\circ}\text{---------}OH^{\circ}+O_2, K_5 = 1.4\times10^{5}\ L\ mols^{-1} \tag{5}$$

The objective of this research was comparison of the efficiency of two important methods including UV/O_3 as an Advanced Oxidation Process (AOP) and Poly Aluminum Chloride (PACl), as a coagulant that is applied in conventional water treatment plants to remove three widely used pesticides, Chlorpyrifos (halogenated organophosphorus), Diazinon (non-halogenated organophosphorus) and Carbaryl (carbamates) from drinking water resources. Also the effects of main parameters such as retention time and initial pesticide concentration were investigated.

MATERIALS AND METHODS

Reagents and materials: The pesticides used in this research (chlorpyrifos, diazinon and carbaryl), were at least 98% purity and purchased from Sigma Aldrich (Spain). The chemical characteristics of selected pesticides are listed in Table 1. These pesticides were selected based upon their toxicity, persistence and wide uses in farmlands. Chloroform, sodium sulfate, nitric acid, Poly Aluminum Chloride (PACl) and manganese sulfate were from Merck Company (Germany) and dichloromethane was purchased from Scharlau Inc. (Germany). Deionized water was also used throughout the examinations. Pesticides standard stock solutions were prepared in methanol (1000 mg L^{-1}). 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.

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 g h^{-1} (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

Table 1: Chemical characteristics of selected pesticides

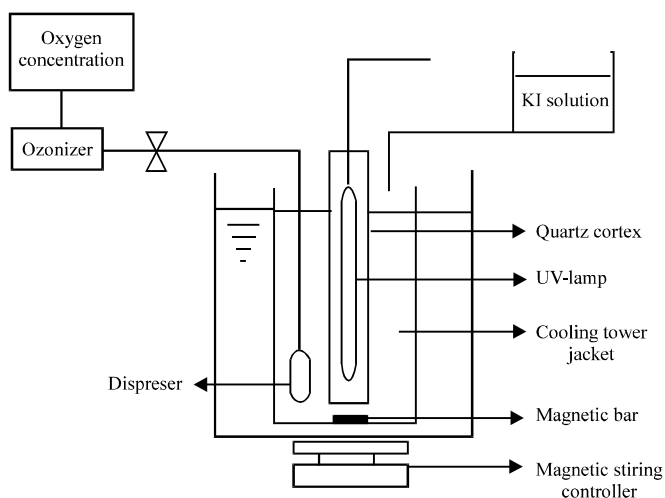| Pesticide	Chemical structure	Formula and molecular structure	Molecular weight (g mol^{-1})	Purity (%)
Diazinon	Non-halogenated organophosphorus	$C_{12}H_{21}N_2O_3PS$: 333-41-5	304.35	98
Chlorpyrifos	Halogenated organophosphorus	$C_9H_{11}Cl_3NO_3PS$: 2921-88-2	305.60	99.5
Carbaryl	Carbamates	$C_{12}H_{12}NO_2$:63-25-2	201.23	99

Fig. 1: Schematic diagram of UV/O$_3$ system experimental set-up

4.0 mg L^{-1}. 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.

Set-up and procedures: Experimental determination of removal efficiency for selected pesticides was carried out by preparation of pesticides synthetic solutions with concentrations of 1, 5, 10, 15 and 20 mg L^{-1} in deionized water from 1000 mg L^{-1} stock solution (to simulate high-loaded pesticide containing agricultural run-offs). Also the desired pH = 7 value in the range of drinking water resources adjusted in synthetic water with nitric acid 1% and sodium hydroxide 1%. The O$_3$/UV glass reactor was filled separately with synthetic solutions; 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. At the end of the predetermined reaction time (30, 60, 90 and 120 min), the samples were analyzed for residual pesticides. The excessive ozone was trapped in 2% potassium iodide (KI).

The PACl solution with concentration of 12, 24 and 36 mg L^{-1} was used for determination of removal efficiency for chemical coagulation process. The PACl with desired concentration was added to 2 L jars which were filled of pesticides synthetic solutions with up-mentioned concentration and pH = 7. The steps of chemical coagulation were included; 1 min rapid mixing with stirring rate of 100 rpm, 15 min slow mixing (coagulation and flocculation) with stirring rate of 30 rpm and 30 min settling time.

Analytical methods: Dissolved ozone levels were determined by potassium iodide (KI) standard titrimetry in samples (APHA, AWWA, WEF, 2005). The standard curve for selected pesticides was plotted using serial concentrations of the pesticides standard solution from 0.1 to 25 mg L^{-1}. The linearity relative coefficient (R^2) from calibration curves were 0.999, 0.998 and 0.999 for diazinon, chlorpyrifos and carbaryl, respectively. Extraction of pesticides from water samples were done by using the solid phase extraction method on 180 mg Strata C$_{18}$ cartridges for diazinon and liquid-liquid extraction by dichloromethane and chloroform for chlorpyrifos and carbaryl. 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 g pure grade of NaCl, well shaked for 30 min, transferred through the sodium sulfate ($NaSO_4$) column to remove moisture, re-adding 30 mL dichloromethane, evaporated to dryness by rotary evaporator (Heidol, type VV1; Germany) (Wu *et al.*, 2007) and reconstituted in 1 mL chloroform. The extracted samples residual ozone was expelled by bubbling with ultra pure nitrogen. The samples were analyzed by Gas Chromatography-Mass Spectrometry (GC-MS) for diazinon and High Performance Liquid Chromatography (HPLC) for chlorpyrifos and carbaryl.

Gas chromatography-mass spectrometry analysis was carried out on Varian Saturn CP-3800 (Holland) GC-MS, equipped with DB-5 fused silica capillary column (30 m×0.25 mm I.D.×0.25 µm thickness). The temperature program was set as follows: Initial temperature at 110°C, for 1 min, ramped to 188°C at 25°C min^{-1}, for 4 min, increased to 193°C at 20°C min^{-1}, then ramped to 244°C at 25°C min^{-1}, for 6.21 min and read the samples concentration. Helium gas with >99% purity was used as carrier gas with constant flow rate of 0.7 Cm sec^{-1}. The peak of diazinon detected at 9.21 min after injection of samples and splitless injection was 1 µL.

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 C_{18} (µ Bond Pak™; Water, USA) column (250×4.6 mm). The mobile phase was composed of water, methanol and acetonitrile (15:45:40) and flow rate of 1 mL min^{-1}. The peaks of chlorpyrifos and carbaryl detected at 14.9 and 12.7 min after injection of samples, respectively. The UV detector was set at λ =140 nm. The obtained data were processed with Chem Station (Agillent Technologies; USA) software.

RESULTS AND DISCUSSION

In the present study, the efficacy of both UV/O_3 advanced oxidation process and PACl chemical coagulation in removing of three widely used pesticides was compared. Also the impact of important parameters including retention time, initial pesticide concentration and chemical structure on the effectiveness of the removal processes were investigated.

Effects of pesticide initial concentration on removal efficacy: The pesticide initial concentration variations in water samples were significantly affected the removal efficiency ($p<0.05$). The selected pesticides degradation by UV/O_3 process as a function of pesticide initial concentration is shown in Fig. 2-4. Presented data shows that with pesticide initial concentration of 20 mg L^{-1}, 75, 35 and 82.5% of diazinon, chlorpyrifos and carbaryl were removed in 30 min. However, at the same level of pH and retention time, with 1 mg L^{-1} of selected pesticides, the

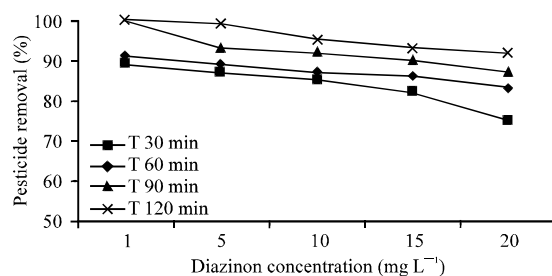Fig. 2: Effect of initial Diazinon concentration versus UV/O_3 removal efficiencies at various retention times, pH = 7, temperature= 20±1°C
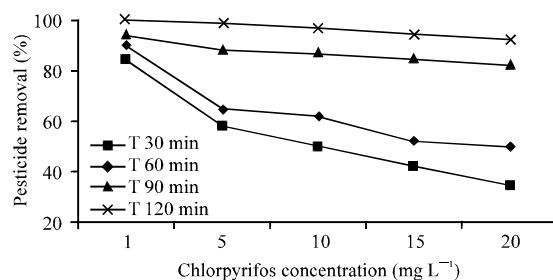
Fig. 3: Effect of initial Chlorpyrifos concentration versus UV/O$_3$ removal efficiencies at various retention times, pH = 7, temperature = 20±1°C
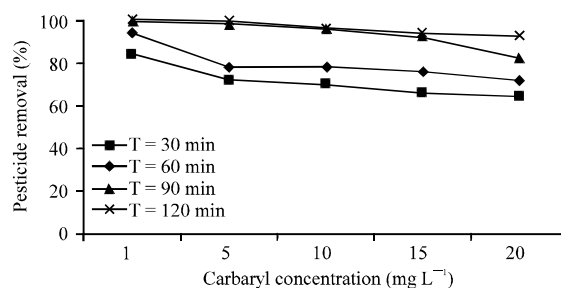

Fig. 4: Effect of initial Carbaryl concentration versus UV/O$_3$ removal efficiencies at various retention times, pH = 7, temperature = 20±1°C

removal efficiency increased to 89.2, 84.5 and 91.8%, respectively. Maximum increase in removal efficiency was in chloropyrifos (49.5%). Maldonado *et al.* (2006) and Ikehata and El-Din (2005) reported that high initial concentration of pesticides in AOP reactor decreased the removal efficiency (Maldonado *et al.*, 2006; Ikehata and El-Din, 2005). Also Daneshvar *et al.* (2005) showed that increase in diazinon concentration decreased the removal efficiency in a nanoparticles and UV combinated system (Daneshvar *et al.*, 2005). 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. In the present study, chlorpyrifos showed the highest impact of pesticide initial concentration on its removal efficiency, with various retention times (average 27.7%) and diazinon revealed the least effect (average 7.1%).

Also in the case of chemical coagulation with PACl, the pesticide removal efficiency significantly affected by the variations in pesticide initial concentration (p<0.05) (Fig. 5-7). The results showed that at pH = 7 and 12 mg L^{-1} of PACl concentration, increasing of pesticides initial concentration from 1 to 20 mg L^{-1} can decrease removal efficiency from 95 to 45%, 90 to 46% and 100 to 86.5% for diazinon, chlorpyrifos and carbaryl, respectively. The most effect of pesticide initial concentration on its removal efficiency by PACl coagulation shown in diazinon (average 48.77%) and the least effect shown in chlorpyrifos (average 12.1%) (Inverse of AOP system). Humbert *et al.* (2008), Kim *et al.* (2005) and Seiichi *et al.* (2006) reported the adverse effect of pesticide initial concentrations on its removal efficiency.
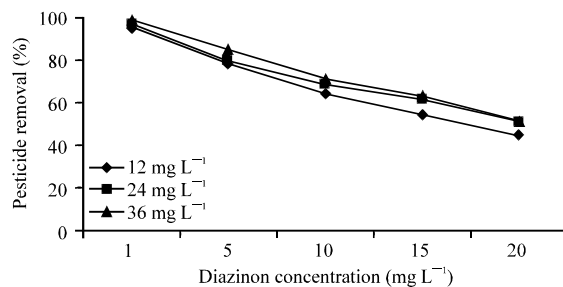
Fig. 5: Effect of PACl variation on diazinon removal efficiencies in chemical coagulation system; pH = 7, temperature = 20±1°C
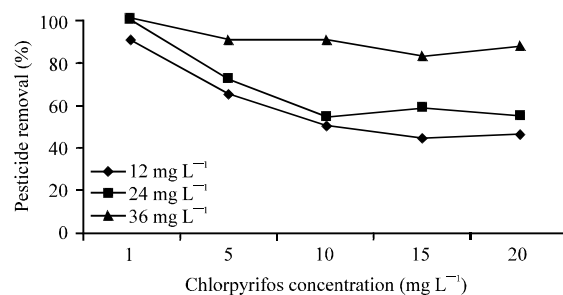

Fig. 6: Effect of PACl variation on chlorpyrifos removal efficiencies in chemical coagulation system; pH = 7, temperature = 20±1°C
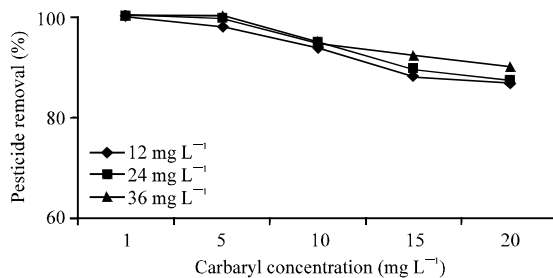

Fig. 7: Effect of PACl variation on carbaryl removal efficiencies in chemical coagulation system; pH = 7, temperature = 20±1°C

Effect of retention time on removal efficacy: Our results showed that increase in retention time significantly enhances the selected pesticides removal efficiency ($p < 0.05$). As shows in Fig. 2-4, within 30 min at pH = 7 and 20 mg L^{-1} of pesticides concentrations, the removal efficiencies for diazinon, chlorpyrifos and carbaryl were 75, 35 and 82.5%, respectively. At the same experimental conditions, increasing of retention time to 90 min improved the removal efficiencies to 87.1, 82.2 and 91%. Increasing of retention time to 120 min, had a venial effect on removal efficiencies (increased removal efficiencies 4.9, 10.3 and 5.5%, respectively). Longer retention time caused to produce higher concentration of pesticides degradation metabolites as well as hydroxide radicals produced by UV/O_3 utilized for metabolites degradation. The highest effect of retention time on pesticides removal efficiency with pH = 7 and initial concentrations showed in chlorpyrifos

(average 55%), however diazinon showed the lowest impact (average 13.3%). Different activation of benzene rings (heterocyclic or hemicyclic) in chemical structure of selected pesticides may be the reason of various behavior of pesticides removal efficiency by UV/O_3. Based on chemical structure, carbayl and chlorpyrifos need least and most retention time for degradation, respectively. Daneshvar *et al.* (2005) reported that, the increasing of organophosphorus pesticide removal efficiency in a UV/ZnO pilot plant improved by increasing the retention time. Our results were consistent with the previous study on halogenated lambda-cyhalothrin and non halogenated deltamethrin pesticides removal by AOP process (Lafi and Al-Qoda, 2006).

In chemical coagulation process using PACl, three subsequent stages (rapid mixing, slow mixing and settling step) have similar longtime in all samples.

Effect of PACl dose on removal efficacy: As shown in Fig. 5-7, variation of PACl doses has significant effect on halogenated organophosphorus (chloropyrifos) and carbamate (carbaryl) pesticides removal efficiency ($p<0.05$) but its effect on removal of non-halogenated organophosphorus (diazinon), was not significant ($p = 0.7543$). As showed in these Fig. 5-7, with 12 mg L^{-1} PACl and 20 mg L^{-1} initial pesticides concentration at $pH = 7$, removal efficiency for diazinon, chlorpyrifos and carbaryl was 45, 46 and 86.5%, respectively. Increasing of coagulant concentration to 36 mg L^{-1} increased removal efficiencies to 51.4, 87.5 and 90%. Therefore, chlorpyrifos and carbaryl effectively can be removed from water samples by applying PACl plus. Halogenated organophosphorus and carbamate pesticides have more polarity then more tendency to adsorb on surface of positive multivalent metal ions (Al^{+3}), annihilate zeta potential and production of floc, as well as high molecular weight and large density of chloropyrifos (molecular weight 350.57 g mol^{-1} and density 1.398 kg L^{-1}). It would be most likely to settle by coagulation-flocculation process due to gravity effects. Cheng *et al.* (2006) reported effective removal of atrazin from industrial wastewater using 0.5 g L^{-1} PACl.

CONCLUSION

The results of this study showed that UV/O_3 advanced oxidation process and chemical coagulation by PACl have high performance for removal of selected pesticides from water samples:

- Advanced oxidation process by UV/O_3 was influenced by factors such as pesticide initial concentration and retention time. Decline of retention time and increment of pesticides initial concentration significantly decreased the pesticides removal efficiency
- Chemical coagulation by PACl had acceptable performance for removal of pesticides. The removal efficacy of chlorpyrifos and carbaryl were more than diazinon. PACl dose played a key role in the removal of pesticides. Increasing of coagulant dose caused a significant increase in the removal efficiency
- Although AOP process showed higher performance for removal of selected pesticides from water samples but this process has disadvantages including complication, intolerability, difficulty of maintenance and equipment and structural requirements. Applying PACl even within the usage range, based on chemical composition of treated water may causes significant pesticides removal

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