

Removal of the Herbicide Molinate by Drinking Water Treatment Processes

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Abstract. The removal of molinate efficiency as an organic contaminant was evaluated by applying drinking water treatment processes. Water treatment processes viz., chlorination, ozonation and activated carbon treatment were applied separately to water system. The level of molinate in water reduced to 33% when it was treated with sodium hypochlorite. In water system, 47 and 73% of this herbicide was dissipated by treatments of ozone and ozone combined with hydrogen peroxide, respectively. Powdered activated carbon (PAC) exhibited a better performance for the removal of molinate as compared to granular activated carbon (GAC) and activated carbon removed this herbicide effectively. The association of ozonation with sodium hypochlorite and activated carbon treatments were considered to be the best-tested treatment for the removal of molinate from water. Therefore, if molinate enters water as an organic contaminant, it could be removed effectively by drinking water treatment processes.

Keywords: herbicide molinate, drinking water, chlorination, activated carbon, ozonation

Introduction

The use of herbicides in agriculture has undoubtedly contributed to increased crop yields but off-site migration may cause contamination of nearby natural waterways. The herbicide molinate (*S*-ethyl hexahydro-1*H*-azepine-1-carbithioate) is used extensively to control germinating broad-leaved plant and grass weeds during rice production. It is highly soluble (solubility - 880 mg/l) herbicide (Hartley and Kidd, 1983) that is often detected as a contaminant in surface water (Cerejeira *et al.*, 2003; Sudo *et al.*, 2002; Coupe *et al.*, 1998; Paune *et al.*, 1998). It is one of the most frequently detected herbicides exceeding drinking water guidelines. Surface water contamination may have toxicological effects for human health if used for public consumption (Leonard, 1988). Now a days, surface water is used as water resource for drinking purpose. The contamination of drinking water supplies by agrochemical compound is an urgent problem for which remedial measures need to be found. In recent years, several processes such as coagulation followed by filtration, activated carbon adsorption and advanced oxidation process (AOP) are being used not only for waste-water treatments but also for the production of drinking water. Recently, water chlorination is the most widely used method for water purification (Abia *et al.*, 1998). In this treatment, the chlorinating agents react with different organic chemicals and can remove organic contaminants by oxidation with simultaneous disinfection (Mascolo *et al.*, 1995).

Various treatment technologies such as adsorption and ozonation have been developed to remove or degrade organic

compounds from water system. Activated carbon is commonly used in drinking water treatment for the removal of organic contaminants because of their porous structure and large internal surface area. Among these processes, the application of ozone as AOP is considered as a potential treatment for various organic contaminants in drinking water throughout the world. Ozone is a powerful oxidizing agent and hence is applied for the purification of drinking water as well as wastewater (Masschelin, 1982). Ozone may react with solutes either by direct oxidation or by indirect reaction, whereby OH radicals resulting from the decomposition of O₃ serve as oxidant in advanced oxidation process (AOP). Due to its high oxidation potential, ozone has been widely used during the past few years (Langlais *et al.*, 1991). Drinking water should be free from molinate to reduce the risk of undesirable long-term effects. Hence, it is important to assess drinking water treatment processes with regard to their potential for removing organic contaminants. The objective of this study was to compare the drinking water treatments in terms of the removal efficiency for this organic contaminant.

Materials and Methods

Agrochemicals and chemicals. The herbicide molinate (99.7% purity) was collected from Zeneca Agrochemicals (Syngenta). Sodium hypochlorite (NaOCl) was obtained from Yakuri Pure Chemicals Co., Japan. Granular activated carbon (20-40 mesh) and powdered activated carbon (100 mesh) were purchased from Aldrich Chemical Co., USA. All other chemicals were of reagent grade supplied by Sigma Chemical Co., USA and Kanto Chemical Co., Japan.

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Sodium hypochlorite treatment. In this treatment, the aqueous solution containing molinate (1 mg/l) was treated with sodium hypochlorite solution at concentrations of 5, 10 and 20 mg/l Cl_2 separately and then mixed at 100 rpm. After 0.5, 1, 2 and 4 h, the treated water samples were collected and the remaining concentration of molinate was analyzed by gas chromatograph (GC).

Ozone treatment. Ozonation was performed on water solution containing 1 mg/l of molinate at 10°C by ozone generator (Nexo NE 210 SX, Korea) that was cooled in an ice bath (Bader and Hoigne, 1981). In control treatment, only air was passed through water samples by air-pump (LP-80A, Korea). The water sample was treated with O_3 and O_3 combined with 50 and 100 mM H_2O_2 in which O_3 dosage used was 0.75 mg/l per min. The concentration of ozone in aqueous solution was measured by the indigo colorimetric method (APHA, 1995). The treated water samples were collected at 5, 15, 30 and 60 min. Afterwards, the remaining amount of molinate was analyzed by GC.

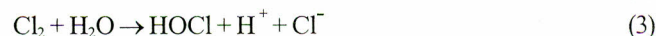
Activated carbon treatment. In adsorption experiment, the aqueous solution of molinate (1 mg/l) was treated with 0.2, 0.5 and 1% wt. of granulated activated carbon and powdered activated carbon with surface area of $1500\text{ m}^2/\text{g}$ and uniform pore volume of $1.5\text{ cm}^3/\text{g}$ separately and it was mixed well at 100 rpm. After 15, 30, 60 and 120 min, the treated water samples were collected and then filtered with Buckner funnel containing celite and filter paper using vacuum filter. After a specified time, the analysis of remaining molinate was performed by GC.

Analytical method. The collected samples were partitioned by hexane. After the collection of hexane layer, the dehydration of sample was done by anhydrous sodium sulfate. The sample was condensed by rotary evaporator and further analyzed in a gas chromatograph (GC) equipped with a thermionic specific detector (Varian CP-3800, USA) following the method as outlined by Carson *et al.* (1994). Analytical conditions for GC were as follows: column, $30\text{ m} \times 0.25\text{ mm i.d.}$, J and W Scientific DB-1; temperature, column oven at 100°C (1 min) $\rightarrow 20^\circ\text{C per min} \rightarrow 230^\circ\text{C}$ (5 min); carrier gas flow rate, N_2 -25 ml/min, H_2 -4.25 ml/min and air-160 ml/min; detector block at 300°C and injection volume, $1.0\ \mu\text{l}$.

Results and Discussion

Disappearance of molinate by sodium hypochlorite treatment. In the experiment, water sample was treated with Cl_2 at the rate of 5, 10 and 20 mg/l from 30 min to 4 h contact time. The highest disappearance rate of molinate (33%) was obtained from the treated water sample, when it was treated with 20 mg/l Cl_2 as

NaOCl after 4 h as shown in Fig. 1. The molinate degradation by aqueous chlorine probably took place via chlorine transfer from the NaOCl (Abia *et al.*, 1998). The mechanism of electro-generation in basic solution containing chloride ions was as follows:



Among the chlorinated species, HOCl is much more reactive than OCl^- and therefore, it is the main attacking chlorinated agent (Morris, 1978). The addition of sodium hypochlorite to the treated water resulted in organic oxidation due to the participation of electrogenerated hypochlorite ions in this process. Similar observation was also reported by Panizza *et al.* (2000). In addition, water chlorination may be used as water disinfection in drinking water system for the control of water-transmitted disease.

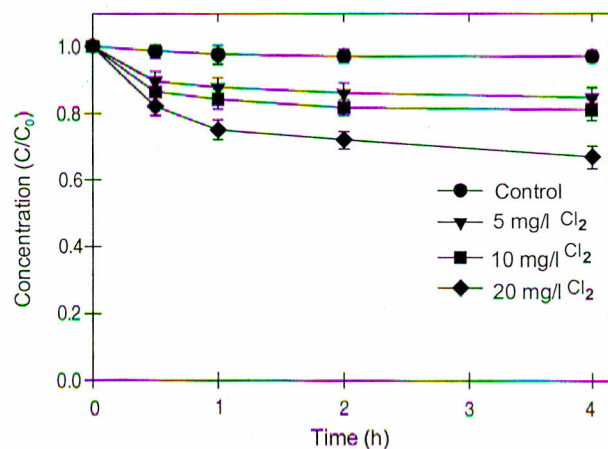


Fig. 1. Removal of molinate by sodium hypochlorite treatment. Error bars indicate standard deviation of mean ($n = 4$).

Disappearance of molinate by ozone treatment. The water was treated with ozone and ozone combined with hydrogen peroxide between 5 and 60 min. The elimination of 47 and 73% of the initial concentration of molinate was obtained within 60 min from water sample by treatments of ozone and ozone combined with hydrogen peroxide, respectively (Fig. 2). In order to assess the ozonation process with respect to oxidation by ozone and OH radicals, the mechanisms and the kinetics of the elementary reactions involved in ozone decomposition have been investigated in numerous studies (Tomiyasu *et al.*, 1985; Staehelin and Hoigne, 1982). In water system, hydroxyl ions (OH^-) are described as being respon-

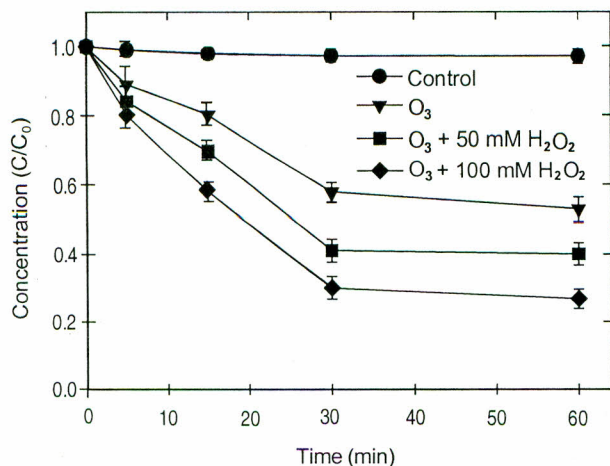
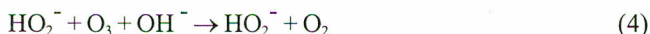


Fig. 2. Disappearance of molinate by ozone and ozone combined with hydrogen peroxide treatment. Error bars indicate standard deviation of mean ($n = 4$).

sible for the initial decomposition of ozone involved in the following reactions (Elliot and McCracken, 1989; Sehested *et al.*, 1984):



The ozonide anion radical ($\text{O}_3^{\cdot -}$), formed by the reaction between ozone and the oxide anion radical $\text{O}_2^{\cdot -}$, decomposes immediately into an OH^- radical.



This OH^- reacts with ozone in the following way:



According to eqs. (4) and (5), the initiation of ozone decomposition is accelerated by the addition of hydrogen peroxide, leading to the advanced oxidation process (AOP). AOP involved the generation of hydroxyl radicals in an amount that is able to affect water purification. Hydrogen peroxide reacts with ozone when it is present as an anion, HO_2^- . The reaction rate of the system $\text{O}_3/\text{H}_2\text{O}_2$ is based on the initial concentration of both oxidants:



The combination of eqs. (11) and (12) shows that two ozone molecules produce two OH^- as follows:



Eq. (9) is a fast process leading to the consumption of ozone molecules and OH^- radicals. In order to dissipate this organic contaminant, the capability of exploiting the high reactivity of OH^- radicals in oxidation process may develop through the formation of OH^- radicals after the decomposition of ozone within an aqueous medium. The mechanism also elucidates the role exerted by H_2O_2 since it is formed during ozone decomposition in an aqueous phase. It is clear that the addition of H_2O_2 to ozone in aqueous solution allowed a better molinate removal probably due the formation of OH^- radicals.

Removal of molinate by activated carbon treatment. The experimental results in Fig. 3 reflected that GAC removed up to 74 and 81% of the initial concentration of molinate from water system when it was applied at rates of 0.5 and 1%, respectively. The maximum removal of molinate efficiency by 1% of GAC was found during 120 min. Molinate was removed efficiently from water by the treatment of 1% of PAC after 30 min (Fig. 4). In retrospect to the adsorptive capacity of PAC, it exhibited a better performance in the adsorption of molinate as compared to GAC (Fig. 5). Powder and granular activated carbons have been used in drinking water treatment for the removal of organic contaminant because of their porous structure and large surface area (Hopman *et al.*, 1995). Considering the effect of activated carbon on the adsorption of organic contaminant from aqueous solution, PAC exhibited a larger adsorption capacity over GAC, indicating that PAC had greatly improved contact efficiency with the media leading to greater rate of adsorption due to higher surface area (1500-1600 m^2/g). Martin-Gullon and Font (2001), and Hopman *et al.* (1995), studied the pesticide adsorption of activated carbons and reported that activated carbon with higher surface area

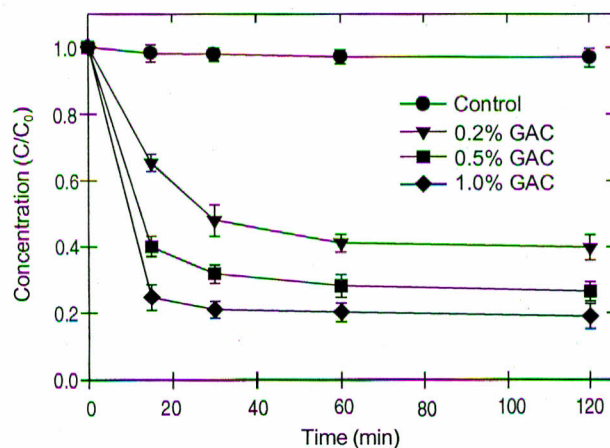


Fig. 3. Effect of granular activated carbon on the removal of molinate. Error bars indicate standard deviation of mean ($n = 4$).

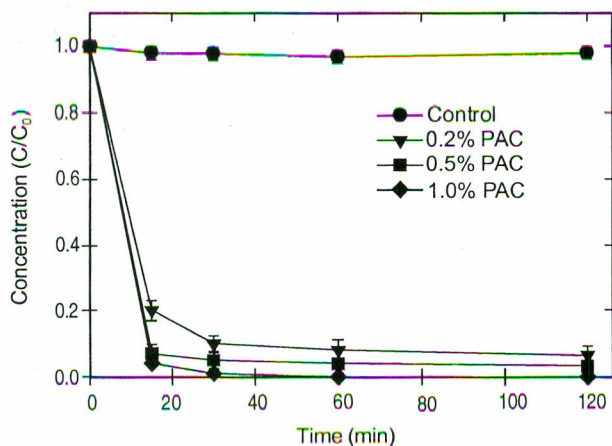


Fig. 4. Effect of powdered activated carbon on the removal of molinate. Error bars indicate standard deviation of mean ($n = 4$).

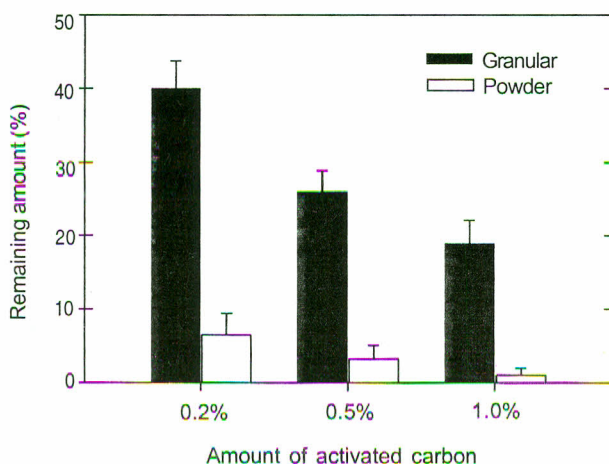


Fig. 5. Effect of powder and granulated form and amount of activated carbon on the removal of molinate. Error bars indicate standard deviation of mean ($n = 4$).

gave the best performance for the removal of pesticide as organic contaminant. In addition, a good understanding of the impact of pore size distribution on competitive adsorption is required as basis for selecting the best activated carbon and applying it in an optimal way. At least 90% of the total surface area of activated carbon corresponded to surface area within micropores (Sontheimer *et al.*, 1988). As a result, activated carbons are particularly suitable to elucidate pore size effects on organic pollutant adsorption from aqueous solution (Pelekani and Snoeyink, 2001; Chen *et al.*, 1997).

From these findings, it can be concluded that two treatment approaches viz., ozonation and activated carbon treatment were found to be suitable for removing the herbicide molinate in aqueous solution as compared to sodium hypochlorite

treatment. The chemical oxidation may lead to the formation of degradation product of molinate. Therefore, if molinate enters to waters system as an organic contaminant, it could be removed effectively by drinking water treatment processes.

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