Removal of Herbicide Mecoprop from Surface Water Using Advanced Oxidation Processes (AOPS)

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ABSTRACT: In the last twenty years, due to a number of natural and anthropogenic reasons, many water sources have become poorer in quality with respect to micropollutants. An example of a micropollutant that needs to be removed is the chlorophenoxypropionic herbicide mecoprop (MCPP). MCPP is one of the nine pesticides used as an indicator to monitor pesticide concentrations in rivers because it is frequently found to exceed the 0.1 µg L-1 limit in England and Wales. The aim of this study was to investigate the effectiveness of different AOPs for the degradation of the herbicide Mecoprop (MCPP) in both deionised water (DW) and in surface water using different UV_{254} intensities and concentrations of reagents. For an initial MCPP concentration of 10 mg/L, Photo-Fenton at neutral pH using 20 mg/L of H_2O_2 and 20 mg/L Fe^{2+} proved to be the most effective process in terms of degradation rate in both DW and surface water. When using an environmentally relevant concentration (1 µg/L) and neutral pH, if optimized, Photo-Fenton and UV/H_2O_2 processes achieved the best degradation results.

Key words: Mecoprop, removal, Advanced Oxidation Processes, surface water

INTRODUCTION

In the last twenty years, due to a number of neutral and anthropogenic reasons, many water sources have become poorer in quality with respect to micropollutants. An example of a micropollutant that needs to be removed is the chlorophenoxypropionic herbicide mecoprop (MCPP). MCPP is one of the nine pesticides used as an indicator to monitor pesticide concentrations in rivers because it is frequently found to exceed the 0.1 µg/L limit in England and Wales (Topalov et al., 2000; Topalov et al., 2004; Clarke, 2006; Flox et al., 2007). It bioaccumulates to some extent in mammals, birds and fish (PPDB 2014). Hence removal and degradation of this herbicide is needed. AOPs include the ultraviolet/ hydrogen peroxide process (UV/H_2O_2), the Fenton process, Photo-Fenton, semiconductor photocatalysis (TiO_2) and photoactivation of persulphate with UV (PS). In order to overcome the ineffectiveness of conventional treatments, there has been an increasing interest in these promising technologies. While the latest studies regarding AOPs and MCPP removal were carried out using effluent coming from a municipal wastewater treatment plant (De la Cruz et al., 2012), the aim of this study was to investigate the effectiveness of different AOPs for the degradation of the herbicide MCPP in both deionised water (DW) and in surface water. The operating condition for each AOP which resulted in the fastest degradation in DW was then assessed in surface water. Additionally, the effect of these AOPs was also tested using an environmentally relevant concentration of MCPP in both DW and surface water.

MATERIALS & METHODS

A high-purity mecoprop (99.5% purity) standard was provided by Sigma-Aldrich (Germany). Iron sulfate heptahydrate (FeSO4·7H2O), reagent-grade hydrogen peroxide (35 % w/w) and sodium persulfate (99.9%) were acquired from Fisher Scientific (Loughborough, UK). Titanium dioxide (Aeroxide®

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TiO2 P25 Degussa) was purchased from Lawrence Industries (Tamworth, UK). For chromatographic analysis, the following were used: HPLC-grade acetonitrile was supplied by Sigma-Aldrich (Poole, UK), laboratory grade water (LGW) was produced by a Purelab Option-S7/15 system (Elga process water, Buckinghamshire, UK) and orthophosphoric acid (HPLC electrochemical grade) from Fisher Scientific (Loughborough, UK).

Two MCPP concentrations were investigated. A stock solution of 100 mg/L of Mecoprop was prepared in deionised water (DW). It was then used for the preparation of 10 mg/L test solutions. Such high concentration was used in order to accurately monitor the kinetics of MCPP degradation. Another stock solution of 100 μg L^{-1} was also prepared to obtain a 1 μg/L test solution.

UV experiments were all conducted in a Wedeco AG laboratory scale quasi-collimated beam apparatus (Herford, Germany) equipped with three 30 W UV-C low pressure lamps emitting monochromatic light at 254 nm. A volume of 250 mL of test solution was placed in a Petri dish at different distances from the light source and stirred. All experiments were carried out at neutral pH (6.8-7.0) and room temperature (20-22ºC).

Two sets of experiments were run. Firstly, AOPs performance for the degradation of MCPP was studied with an initial concentration of 10 mg/L. A comparison between two UV intensities was carried out in DW. One of the intensities and the most suitable operating condition for MCPP degradation was then assessed in surface water from a Scottish region (pH 6.9 at 20ºC, DOC 4.55 mg/L, UV254 0.18 cm^{-1} and turbidity 0.38 NTU). Another experiment was carried out to test MCPP degradation with a lower initial concentration (1 μg/L) in DW and then in surface water. In this way, a more relevant approach for MCPP removal using AOPs could be evaluated. When assaying Photo-Fenton, a first attempt using a low concentration of iron was performed to minimize the usage of iron, as its presence could affect the taste, smell or colour of the water. However, the effect of precipitation lead to an increase of iron usage in order to optimize the process. Samples were collected and filtered through 0.22 μm diameter nylon filters. Samples were immediately quenched by adding acetonitrile to scanvenge ·OH. All of the experiments were duplicated. The course of MCPP degradation was followed by direct injection in a high performance liquid chromatography Shimadzu HPLC equipped with a UV-visible detector (serie SPD). For the purpose of the herbicide analysis this was equipped with a reverse phase C18 column (Phenomenex® Gemini 5u C18 110A, UK) and the injection volume of each sample was 10 μL. An isocratic

method was used with 0.05% orthophosphoric acid: acetonitrile (40:60) with a flow rate of 1 mL/min at =200 nm. The limit of quantification for mecoprop was 0.5 mg/L. The HPLC chromatograms showed that MCPP had a retention time of 3.95 minutes. In the second part of the work water was spiked with a MCPP concentration of 1 μg/L. These samples were analysed at ALS Environmental in Conventry, UK. The method consisted on the extraction of the free acid compounds from acidified aqueous solution using styrene-divinyl benzene (SDVP) solid phase extraction (SPE) cartridges. The compounds were eluted from the cartridges with ethyl acetate and reacted with diazomethane to form the methyl derivatives. The derivatives were then quantified by gas chromatography with mass spectrometry detection (GC-MS). The limit of detection in this case was 0.04 μg/L.

RESULTS & DISCUSSION

Data on the degradation of MCPP were processed using the integral method for pseudo-first order kinetic equation. In the first place, to optimize the AOPs, three UV intensities were assayed, 12, 15 and 23 W/m^2. Using these intensities, pseudo-first-order degradation rate constants (k) were calculated in DW using only UV$_{254}$ radiation (photolysis) for a reaction time of 60 minutes. In the second place, a comparison between two optimized intensities was also carried out in DW using different AOPs and concentration of reagents (Table 1). From these degradation rate values, another set of tests were conducted in surface water using this time the most suitable parameters (concentration of reagents from each AOP and UV intensity). The final experiments consisted of applying the AOPs with the most suitable parameters in both DW and surface water using 1 μg/L as a first attempt to obtain results with an environmentally relevant concentration of MCPP.

Results of the photolysis tests showed that at 23 W/m^2, k was 0.113 min^{-1}, compared to 0.101 min^{-1} and 0.062 min^{-1} for 15 and 12 W/m^2, respectively. The time it took for the herbicide to be removed to a concentration below the detection limit was similar in the three cases and it was achieved in 60 minutes. Between 15 and 23 W/m^2, the difference in their degradation rates was small. This means that the increase in UV irradiation did not linearly increase the degradation rate. At 23 W/m^2 the maximum production of hydroxyl radicals was likely to have been achieved and so it was close to irradiance saturation. Therefore, increasing the UV irradiation intensity would not make the reaction go faster and would not improve MCPP degradation. Given the limited removal benefit of operating at the highest UV intensity, intensities 12 and 15 W/m^2 were used to compare the AOPs performance in DW.

Table 1. MCPP pseudo-first-order degradation constants in DW for each operating condition

AOP	Operating condition		Intensity 15 W/m^2		Intensity 12 W/m^2	
			K (min^{-1})	r^2	K (min^{-1})	r^2
UV			0.101	0.991	0.062	0.998
UV/TiO2	TiO2 (mg/L)	100	0.51	0.972	0.301	0.987
		150	0.534	0.981	0.379	0.996
		200	0.542	0.991	0.397	0.99
UV/H$_2$O$_2$	H$_2$O$_2$ (mg/L)	100	0.81	0.989	0.626	0.98
		150	0.815	0.989	0.652	0.987
		200	1.203	0.991	0.689	0.993
		300	1.43	0.993	0.821	0.998
		400	1.373	0.994	0.816	0.999
UV/PS	PS (mg/L)	100	0.311	0.989	0.147	0.984
		150	0.36	0.993	0.314	0.979
		200	0.445	0.989	0.412	0.985
		300	0.637	0.995	0.62	0.962
		400	0.629	0.996	0.593	0.994
Photo-Fenton	Fe (mg/L)	H$_2$O$_2$ (mg L^{-1})				
	10	10	1.381	0.968	0.908	0.96
	10	20	2.263	0.971	1.338	0.986
	20	10	3.013	0.985	1.542	0.982
	20	20	4.817	0.998	3.644	0.999
Fenton	Fe (mg/L)	H$_2$O$_2$ (mg L^{-1})				
	10	10	0.39	0.978		
	10	20	0.458	0.974		
	20	10	0.828	0.981		
	20	20	1.106	0.983		

The following results were obtained performing tests using different AOPs and concentration of reagents applying UV intensities of 15 W/m^2 and then 12 W/m^2 (Table 1). Examining each AOP at 15 W/m^2, it was found out that as the concentration of persulfate (PS) increased from 100 to 400 mg/L, MCPP removal increased. However, it can be observed that increasing the reagent concentration from 300 to 400 mg/L does not increase the *k*, as it decreases 0.008 min^{-1}. This is due to a scavenging effect of the SO$_4^-$ radicals (Benitez et al., 2011; Autin et al., 2013). According to the *k,* the same tendency as with PS could be observed for hydrogen peroxide until 300 mg/L. For 400 mg/L the degradation rate constant was lower than for 300 mg/L due to an excess of H$_2$O$_2$, which has the same scavenging effect as the SO$_4^-$ radicals. TiO$_2$ photocatalysis was also assayed. No significant

differences were observed in relation to MCPP degradation rate constants applying the different concentrations. In relation to the photoassisted Fenton process (UV/H$_2$O$_2$/Fe), four conditions were tested at neutral pH. The concentrations were combinations of 10 and 20 mg/L of H$_2$O$_2$ and Fe, similar to those used in other studies (MacAdam and Parsons, 2009). Although 10 mg/L of H$_2$O$_2$ and 10 mg/L Fe was the slowest combination removing MCPP, it still had a quite high degradation rate constant of 1.381 min^{-1} in comparison to the other AOPs. In relation to the reagents, the highest influence in MCPP removal in this process was the iron. Adding a higher concentration of iron increased more the *k* than adding a higher concentration of H$_2$O$_2$ (Martínez et al., 2005). This fact is shown by the *k* values, which were higher for 10 mg/L of H$_2$O$_2$ and 20 mg/L Fe than for 20 mg/L of H$_2$O$_2$ and

10 mg/L Fe. A very good performance was observed when adding 20 mg/L of H_2O_2 and 20 mg/L Fe, obtaining a fast degradation of the herbicide (4.817 min^{-1}).

Having assayed the AOPs using 15 W/m^2, the degradation of MCPP using a UV intensity of 12 W/m^2 in DW was also obtained. AOP performance with this intensity followed a similar tendency as with 15 W/m^2. The comparison of AOPs in DW between the intensity of 12 and 15 W/m^2 demonstrated that the AOPs took approximately the same time to remove MCPP from the water. Therefore, from an economical point of view, it would be more favorable to use the lower intensity for the same reaction time. For that reason, in further tests the intensity of 12 W/m^2 was used. To evaluate the performance of the AOPs in water containing organic matter and other contaminants, the optimum conditions obtained in DW were applied to surface water. As expected, MCPP degradation was slower in surface water than in DW (Fig.1). In DW, MCPP was the only organic compound present and so the radicals $SO_4^{-\cdot}$ and $\cdot OH$ were always able to react with the herbicide. However, in the presence of other compounds it was observed to some extent an inhibition of MCPPs degradation (Konstantinou et al., 2001; De la Cruz et al., 2012; Autin et al., 2013). Although Photo-Fenton experienced the biggest difference between DW and surface water, it still remained the most effective process for MCPP removal. On the other hand, the background dissolved organic matter had a smaller impact on the inhibition of MCPP degradation during UV/PS and UV/TiO$_2$.

A lower initial concentration of herbicide was tested to evaluate the AOPs performance in DW and surface water using 12 W/m^2. Firstly, in DW it was observed that the AOPs assayed, with the exception of the Fenton process, were able to remove MCPP to below the permitted limit of 0.1 µg/L (Fig.2). One of the fastest process was UV/PS, which was successful at removing 96% within the first minute. UV/TiO$_2$, Photo-Fenton and UV/H$_2$O$_2$, all had similar degradation rates and showed a similar behavior to UV/PS. The fact that Photo-Fenton with 1 mg/L of Fe^{2+} and UV/H$_2$O$_2$ exhibited a similar performance may have been due to precipitation of Fe^{2+} and it was therefore not acting as a catalyst. When increasing the Fe^{2+} concentration to 5 mg/L, precipitation did not take place and Photo-Fenton was observed to be the fastest process. On the other hand, when the AOPs were applied to surface water, the same effect as with a higher initial concentration was observed. The degradation rates in DW were higher than the ones obtained in surface water for all the AOPs (Table 2). The UV/H$_2$O$_2$ process and Photo-Fenton with 5 mg/L of Fe^{2+} were the least affected by the presence of natural organic matter and other ions and at the same time they proved to remove MCPP with the highest degradation rates of the five processes (Fig.3).
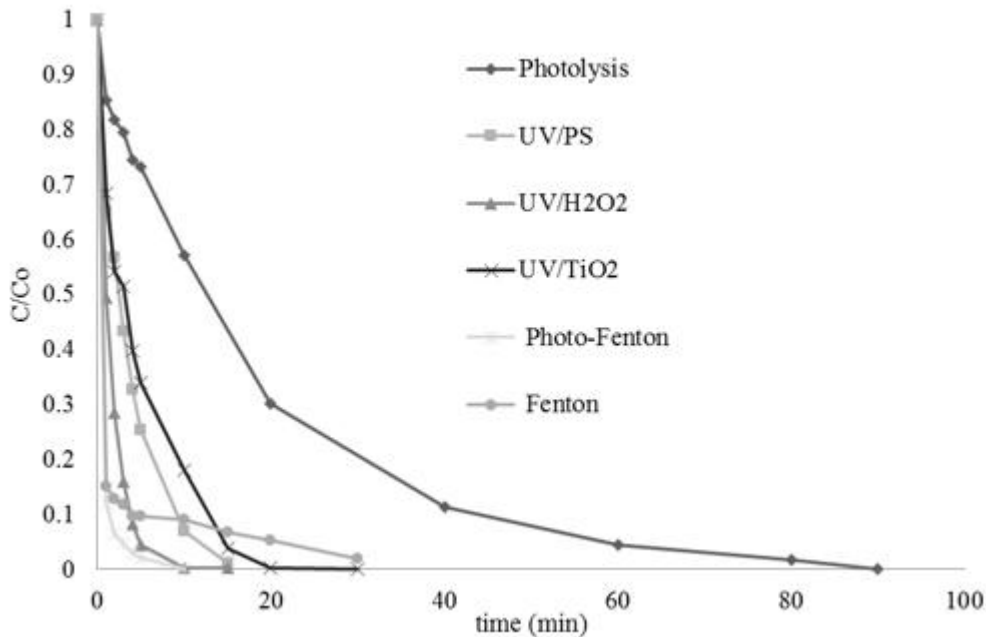
Fig. 1. MCPP degradation in surface water by UV (12 W/m²), UV/PS (300 mg/L), UV/H$_2$O$_2$ (300 mg/L), UV/ TiO$_2$ (150 mg/L), Photo-Fenton (20 mg/L of H$_2$O$_2$ and 20 mg/L Fe), Fenton (20 mg/L of H$_2$O$_2$ and 20 mg/L Fe) using an initial MCPP concentration of 10 mg/L
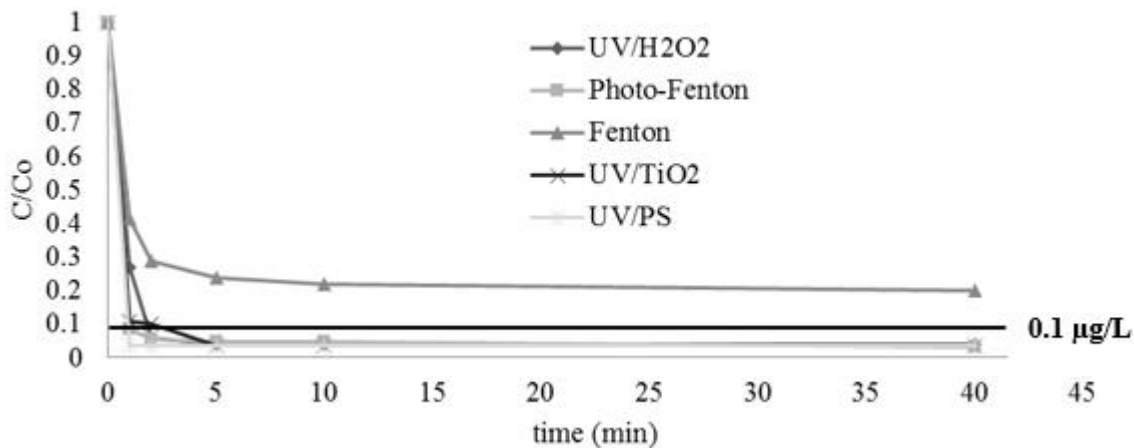
Fig. 2. MCPP degradation in DW by UV/PS (100 mg/L), UV/H$_2$O$_2$ (50 mg/L), UV/TiO$_2$ (50 mg/L), Photo-Fenton (50 mg/L of H$_2$O$_2$ and 1 mg/L Fe), Fenton (50 mg/L of H$_2$O$_2$ and 1 mg/L Fe) using an initial concentration of 1 μg/L

Table 2. MCPP pseudo-first-order degradation rate in DW and surface water using an initial concentration of 1 μg/L under different operating conditions

AOP	Operating condition		DW K (min^{-1})	surface water K (min^{-1})
UV/TiO$_2$	TiO$_2$ (mg/L)	50	0.109	0.067
UV/H$_2$O$_2$	H$_2$O$_2$ (mg/L)	50	0.106	0.104
UV/PS	PS (mg/L)	100	0.113	0.085
Photo-Fenton	H$_2$O$_2$ (mg/L) Fe^{2+}(mg/L)	50 1	0.11	0.091
Photo-Fenton	H$_2$O$_2$ (mg/L) Fe^{2+}(mg/L)	20 5	0.127	0.109
Fenton	H$_2$O$_2$ (mg/L) Fe^{2+}(mg/L)	50 1	0.052	0.024

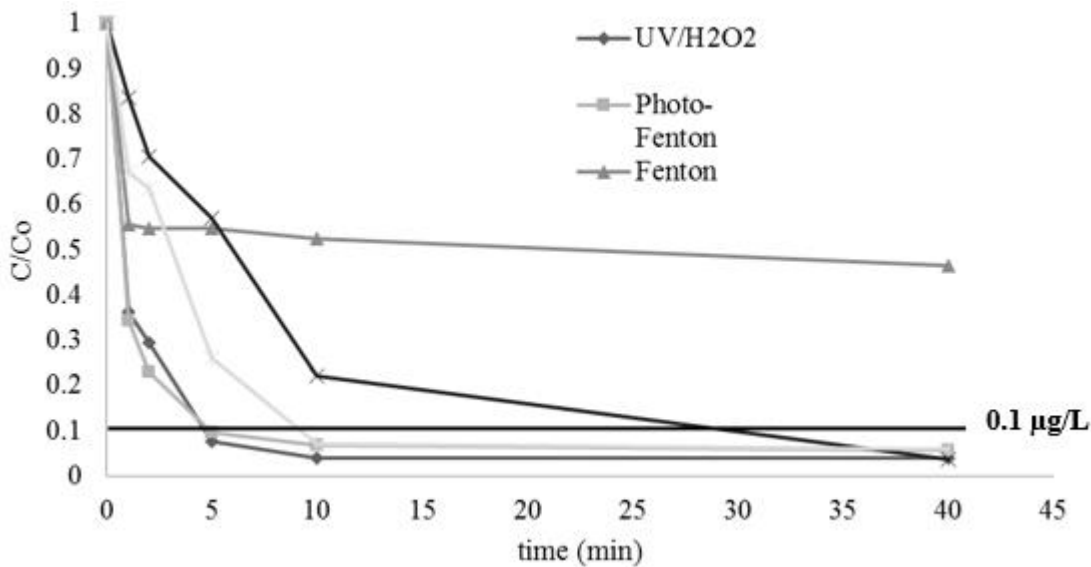**Fig. 3. MCPP degradation in surface water by UV/PS (100 mg/L), UV/H2O2 (50 mg/L), UV/TiO2 (50 mg/L), Photo-Fenton (5 mg/L of H2O2 and 1 mg/L Fe), Fenton (50 mg/L of H2O2 and 1 mg/L Fe) using an initial MCPP concentration of 1 μg/L**

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CONCLUSIONS

The performance of different AOPs has been assayed for the treatment of MCPP in DW and surface water. Pseudo first-order kinetic behaviour was observed for the degradation of this herbicide. This experimental study evidences that MCPP is capable of being degraded by UVC light due to its high reactivity towards hydroxyl radicals.

The presence of dissolved organic matter and other ions in surface water inhibited to some extent the AOPs performance, decreasing their degradation rate constant with respect to DW. It is possible that the organic matter was filtering and scattering the UV light reducing the irradiance efficiency. Other compounds in the water were reacting with the hydroxyl radicals, not just the MCPP as happened in DW.

Attending to results in DW using a high initial MCPP concentration, UV/H_2O_2, Fenton and Photo-Fenton processes were able to degrade MCPP effectively within 5 minutes. Indeed, with a higher initial concentration of MCPP Photo-Fenton was the fastest process in terms of the degradation rate constant and took 15 minutes for MCPP removal below limit of detection in surface water. However, when using an environmentally relevant concentration (1 µg/ L) and natural pH, the iron precipitated and did not act as catalyst. The UV/H_2O_2 process appeared to be the best option because it showed a fast removal of MCPP and it can be applied at full-scale.

In conclusion, AOPs are capable of degrading MCPP in surface waters under optimal conditions. It would be interesting to study the application of AOPs at pilot scale and the different combinations of processes, such as GAC filtration, ozonation processes and UV processes. Further tests are also required in order to assess the impact of different water constituents (alkalinity, DOC, SO_4^{2-}, NO_3^-, PO_4^{3-}) on the effectiveness of these processes and the formation of by-products from pesticide removal.

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