POLISH JOURNAL OF SOIL SCIENCE
VOL. XLVII/2 2014 PL ISSN 0079-2985

Soil Chemistry

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MCPA DECOMPOSITION METHOD IN SOIL MATRIX USING OZONE AS AN OXIDANT***

Abstract. In presented research a method for remediation of MCPA contaminated soil based on the combination of fluidization process technique and ozone was utilized. Exposition of soil contaminated with MCPA at the concentration of 0,1 % w/w on the a mixture of air and ozone allowed for removal of over 90% of MCPA in form of MCPA 2-ethylhexanol-ester (MCPA 2-EHE) in laboratory conditions. The efficacy of the method was proven by GC-MS analysis of MCPA concentration profile during soil remediation procedure and by comparing of kinetic data, such as half life time, with the natural half life time of MCPA in the soil.

Modern agriculture involves the use of chemical agents of anthropogenic origin, without which the production on the current scale is virtually impossible. An important group of these substances are pesticides – chemical compounds – that can be detected in the environment, even at locations far from agricultural activity. Due to their persistence in the environment, toxicity and high biological activity they also pose a threat to humans.

As a result of international and internal legislative regulations of the European Union, Polish administration obliged itself to fulfill the obligations of the Stockholm Convention on Persistent Organic Pollutants [10]. Another problem

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*** Research has been funded by the National Science Centre, Cracow, Poland, by research grant No. N523 556038.

that is particularly important and present in Poland are the pesticide landfills. According to the National Plan of waste Management there is a plan that by 2018 all contamination of land caused by these landfills should be eliminated. Therefore development of an effective method for remediation of pesticide contaminated soil is a must.

A common group of pesticides used in the agriculture is based on the 2-methyl-4-chlorophenoxyacetic acid (MCPA), which is a herbicide classified as a class of phenoxyacetic acid derivatives. This compound is not very stable in the environment, but depending on the chemical form it is characterized by a significant mobility. Particularly dangerous are the forms highly soluble in water such as ammonium salts which are transported along with groundwater. Depending on the form of the compound the toxicity of MCPA varies [12].

It was found that exposure to MCPA can have an impact on vertebrates, especially on the level of reproductive hormones and the reproduction itself, as demonstrated on the example of toxicological studies in rats and rabbits [8]. In addition, this toxicity can increase due to accumulation of these compounds in fatty tissue [13], which is important during the long exposure to small amounts of the compound, i.e. uptake with food.

If these substances are applied in accordance with the canons of good agricultural practice their negative effect is limited because the modern plant protection agents are biodegradable. However, still there are issues of contamination when those compounds are utilized or stored incorrectly [11, 14].

Degradation of MCPA can be based on advanced oxidation methods (Advanced Oxidation Process-AOP). Utilization of these methods can be efficient method degradation of the pesticide residues on such a complex matrix as food [2, 5]. Ozone is an excellent oxidant that can be successfully utilized for degradation of various toxic compounds [7], it can be also utilized for indirect oxidation of highly resistant substances such as DDT [3]. However, the problem with soil remediation is the feeding of the oxidant to a soil due to limitation of maximum exchange. The solution of this issue may be the use of fluidized bed technology which provides optimal conditions for the mass transfer coefficient [4, 6].

In the presented research on the use of ozone for the remediation of soil contaminated with MCPA 2-ethylhexanol-ester (MCPA 2-EHE) technique using a laboratory scale fluidized bed was adapted. The tests provided the necessary kinetic data, which indicate the effectiveness of the method.

MATERIALS AND METHODS

Basic chemicals and solvents:

- Dichloromethane p.a., Chempur (Piekary śląskie)
- Acetone, p.a., Chempur (Piekary śląskie)

- Magnesium sulfate anhydrous p.a., Chempur (Piekary śląskie)
- MCPA technical , 96%, Organika-Sarzyna (Nowa Sarzyna)
- 2-Ethyl-Hexanol p.a., Fluka
- Toluen, p.a., Chempur (Piekary śląskie)
- Sulfuric acid, 95%, Chempur (Piekary śląskie)
- Sodium bicarbonate p.a., Chempur (Piekary śląskie)

Analytical Equipment

- Gas chromatograph Varian GC – 450 coupled with MS – 240 mass spectrometry

Synthesis of 2-ethyl-1-hexanol-ester MCPA

Direct determination of MCPA in acidic form is practically impossible by GC. However, it can be made in the form of 2-ethyl-1-hexanol-ester. Therefore, the MCPA was transformed using the azeotropic esterification method.

For this purpose, a 0.5 mol of MCPA (i.e., 100.31 g), 0.4 mol of 2-ethyl-1-hexanol (i.e. 52 g), 175 cm^3 of toluene and a few drops of sulfuric acid (VI) were placed in a round bottom flask equipped with a reflux condenser. The flask was placed in a heating mantle and kept gentle reflux (MCPA ester boiling point> 150 ˚C) for about 1 hour. Then, the heating mantle was removed and the reaction mixture was cooled to room temperature. After the esterification, a solution of sodium bicarbonate in water (50 ml of water 4 g of sodium bicarbonate) was added to the mixture to remove the remaining acid, also a portion of NaCl was added to the mixture. The mixture was transferred to a separatory funnel where the organic phase was separated from the aqueous phase. Than the organic phase was transferred into a small conical flask and dried with anhydrous magnesium sulfate. The drying agent was separated by filtration on a filter at elevated temperature (at room temperature a crystallization phenomenon occurred). After filtration, the solution was placed in a vacuum evaporator to remove the toluene. The purity of the final solution was 98% and the yield of the process was 90%.

Experimental set up

A fluidized bed reactor (reactor cross-section of 5 cm, bed height of 20 cm) was fed with ozone by Korona 02/10 ozone generator (maximum ozone yield was 10 g⁄h) C.S.I EKOTECH, Piotrków Trybunalski, Poland). The scheme of this apparatus is presented in Fig 1. Ozone concentration was analyzed with a medium range Ozone Analyzer UV – 106M (0–1000 ppm) (Ozone Solutions, Hull, IA, USA).

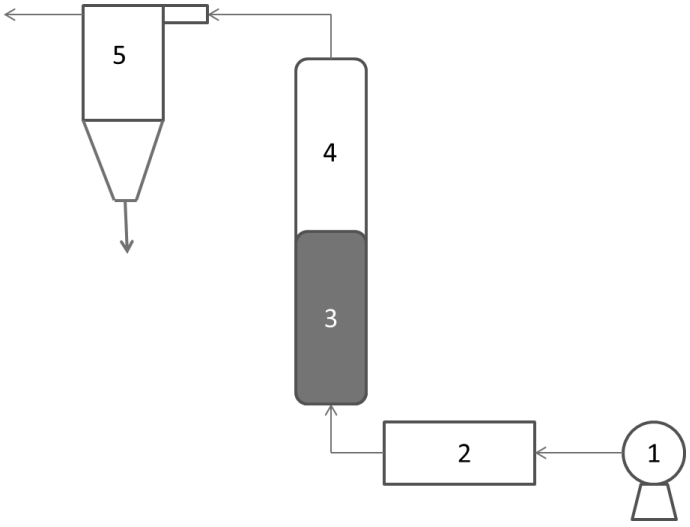

Fig.1. Scheme of fluidized bed reactor: 1. – pump, 2. – ozone generator, 3. – soil layer, 4. – reactor, 5. – cyclone.

Determination of MCPA desorption

To exclude or determine if there was an impact on the efficacy of remediation process due to desorption of MCPA under the impact of the air stream, the soil contaminated with MCPA at concentration of 0.1% w/w was placed in a fluid bed reactor (construction described above). Then, air was pumped into the reactor at the flow rate of 18 dm^3/min. In order to determine the concentration of the herbicide in the soil, samples (10 g) were collected at scheduled intervals.

Remediation experiment

A sample of 210 g of MCPA contaminated soil (MCPA concentration was 0.1% w/w) was placed in a fluidized bed reactor. Then, a mixture of air and ozone at concentration of 2,55 – 3,0 ppm was pumped into reactor. The flow rate of the air and ozone mixture was 18 dm^3/min. In order to determine the reduction of MCPA concentration in the soil during the ozonation, soil samples (10 g) were collected at scheduled intervals.

The pesticide analyses and soil properties were determined according to Balawejder *et. al*. [3]

RESULTS AND DISCUSSION

MCPA is the main ingredient in many herbicidal formulations used on commercial scale in agriculture. Its utilization leads to pollution of soil, which is

a great ecotoxic problem. Also, large quantities of this herbicide are or have been deposed in the pesticide landfills, which resulted in a consecutive contamination of the soil in the vicinity of these sites. In this study, attempts were made to develop effective methods for remediation of the soil contaminated with pesticides. The tests were performed using a laboratory-scale reactor with a diameter of 5 cm.

The experiment was conducted for 144 hours and during that period the mixture of air and ozone at concentration of ~ 3 ppm was fed to the reactor. By the end of this experiment, about 90% of the analyte has been degraded. The analysis of the experiment results, which was made of three replications, allowed conclude that after about 44 hours a satisfactory result had been achieved. Further ozonation did not yield any results.

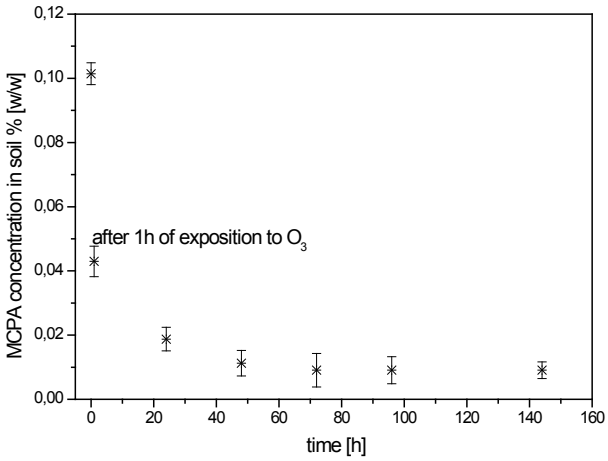

Fig 2. Course of MCPA concentration during exposition on the stream of gazeous ozone. The presented results are mean values ±SD.

In order to describe the kinetics of MCPA degradation, a kinetic equation describing first order kinetics was used. This approach is common for descriptions of the kinetics of the degradation experiments [9]:

$$-\frac{dc}{dt} = kc \tag{1}$$

where:
c – concentration, t – time, k – reaction rate constant

$$k=\frac{1}{t}\ln\frac{c_0}{c} \tag{2}$$

$$t_{0,5} = \frac{ln2}{k} \tag{3}$$

However, considering the course of ln C/C_0, it should be noted that this reaction is certainly of a different order (no linear course of this relationship). This may be a result of the coexistence of two mechanisms i.e., herbicide desorption and degradation under the influence of ozone. This assumption is supported by the observation of about 10% of the desorption of the pesticide under the influence of the air itself.

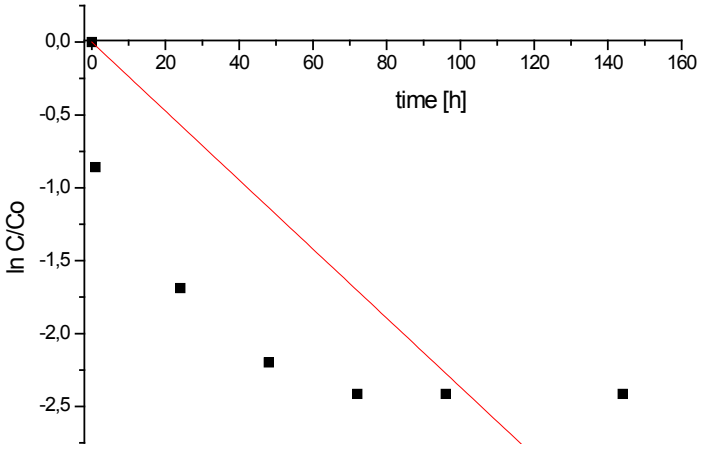

Fig. 3. Dependents of ln C/C_0 versus time during the experiment.

It was concluded that this relationship was exponential and an empirical equation was utilized to describe the relation of pesticide concentration during the experiment:

$$y = A1 * \exp\left(-\frac{x}{t1}\right) + y0 \tag{4}$$

where: time [h], concentration [%] w/w, $A1$, $t1$, $y0$ – equation parameters that were found with the help of the Origin 8.0 software.

Using this equation resulted in achieving of the determination coefficient $R^2 = 0.9864$, which demonstrates a good fit of the model used for the empirical data.

Solving this equation by substitution of $y = 0.5 * C_0$ MCPA allowed for determination of half-life time $t_{0,5} = 0.79$ h. This result is highly satisfactory because the half-life of the pesticide in the soil during natural degradation processes ranges from 15 to 50 days.

The analysis of the chromatograms of the soil samples after ozonation showed that there were no intermediates of MCPA degradation. This demon-

strates a very fast pace of transformation of these products to end products such as CO_2, H_2O and HCl. This observation corresponds with the literature reporting the photo catalytic degradation of MCPA [1].

CONCLUSIONS

1. The conducted study confirmed that ozone can effectively degrade MCPA in soil. The utilization of fluidized bed technology has enabled the removal of more than 90% of the pesticides at the time of tens of hours.

2. The determined half-life time of less than one hour during the process confirms the effectiveness of the proposed method since MCPA decomposes in nature for hundreds of days.

3. The results of the experiments conducted on the laboratory scale lead to the conclusion that it is reasonable to scale up the process with the perspective of utilization in environmental protection.

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METODA ROZKŁADU MCPA W MATRYCY GLEBOWEJ Z UŻYCIEM OZONU JAKO UTLENIACZA

Przedstawiono sposób rekultywacji gleby zanieczyszczonej pestycydem MCPA za pomocą kombinacji technik procesu fluidyzacji i procesu ozonowania. Ekspozycja gleby zanieczyszczonej MCPA w postaci estru z 2-metyloheksanolem (MCPA-2-EHE) w stężeniu 0,1% w/w na mieszaninę powietrza i ozonu pozwoliła na usunięcie ponad 90% MCPA w warunkach laboratoryjnych. Skuteczność metody została sprawdzona na drodze analitycznych analiz ilościowych wykonanych techniką GC-MS (analiza pików chromatogramu gazowego) podczas prowadzonej procedury remediacji, oraz przez porównanie danych kinetycznych, jak wyznaczony czas połowicznego rozkładu z czasem połowicznego rozkładu MCPA w glebie w warunkach naturalnych.