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ODSTRAŇOVANIE METRIBUZÍNU POMOCOU VYBRANÝCH POKROČILÝCH OXIDAČNÝCH PROCESOV (AOPs)

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REMOVAL OF METRIBUZIN BY USING SELECTED ADVANCED OXIDATION PROCESSES (AOPs)

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ABSTRAKT

Tento príspevok sa zameriava odstraňovaniu herbicídu metribuzínu z vody s využitím vybraných pokročilých oxidačných procesov (AOP). Metribuzín, ako významný kontaminant podzemných vôd kvôli jeho rozšírenému využívaniu a dlhodobej perzistencii, predstavuje hrozbu pre zdravie človeka a vodné ekosystémy. Hodnotená bola účinnosť foto-Fentonovej reakcie, Fentonovej reakcie a ferrioxalátový systém, pričom foto-Fentonova reakcia sa ukázala byť najefektívnejšou technikou, dosahujúcou kompletné odstránenie metribuzínu v rôznych koncentráciách za niekoľko minút. Porovnanie oxidácie vzduchom a oxidácie ozónom ďalej odhalilo výrazne lepšie výsledky ozónovej oxidácie v degradácii metribuzínu, čo naznačuje jeho významný potenciál pre aplikácie v čistení vody.

Kľúčové slová: *metribuzín, AOPs, Fentonová reakcia, HPLC-UV*

ABSTRACT

This study focuses on the removal of the herbicide metribuzin from water using selected advanced oxidation processes (AOPs). Metribuzin, as a significant groundwater contaminant due to its widespread use and long-term persistence, poses a threat to human health and aquatic ecosystems. The photo-Fenton reaction, Fenton reaction and ferrioxalate system were evaluated, with the photo-Fenton reaction proving to be the most effective technique, achieving complete removal of metribuzin at various concentrations in a matter of minutes. Comparison of aeration and ozone oxidation further revealed significantly better performance of ozone oxidation in degradation of metribuzin, indicating its significant potential for applications in water purification.

Key words: *Metribuzin, AOPs, Fenton reaction, HPLC-UV*

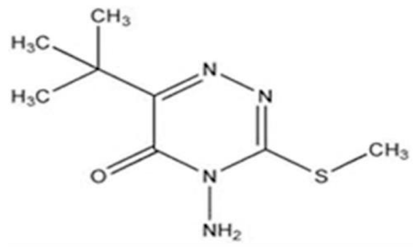
INTRODUCTION

Metribuzin, functioning as both a pre and post-emergence herbicide, inhibits photosynthesis. This synthetic triazinone compound is the key ingredient in Sencor 480 SC, BUZZIN or Keeper liquid [1] and it is the second most used herbicide in Slovakia [2].

The effect of metribuzin is directed at dicotyledonous weeds and grasses in various crops such as cereals, potatoes, tomatoes or carrots. Noted for its persistence and high soil mobility, metribuzin poses a risk of reaching and contaminating groundwater, though it breaks down into less toxic by-products over time. It's hazardous when ingested and poses a significant threat to aquatic life, potentially leading to enduring damage to water ecosystems. Consequently, metribuzin is flagged as a likely groundwater pollutant [3].

Metribuzin has demonstrated various toxic effects across different organisms and exposure routes. In rats, oral administration during pregnancy led to adverse effects on embryonic structures like the placenta and umbilical cord. Acute toxicity studies reveal that metribuzin is lethal to mice, rats, cats, guinea pigs, and quail at varying doses, with inhalation and oral routes being particularly significant. Continuous and intermittent dosing over periods ranging from weeks to years has shown to cause significant damage to the liver, kidneys, and other metabolic changes in dogs, mice, and rats, including weight loss and changes in organ weights. Notably, it also affects the reproductive system and immune response in rats, indicating its potential for widespread biological impact [4].

Tab. 1 - Structure and basic properties of metribuzin [5, 6]

	Molecular mass	214.29 g mol^{-1}
	Chemical formula	$C_8H_{14}N_4OS$
	CAS RN	21087-64-9
	Dissociation constant pKa at 25°C	1.3
	Henry´s law constant at 25°C	1.7110^{-05} Pa m^3 mol^{-1}
	Surface tension at 20°C	63.1 mN m^{-1}
	Maximum UV-VIS absorption	294 nm
	General biodegradability	Not readily biodegradable

Advanced Oxidation Processes (AOPs) stand out as appealing substitutes for biological methods and non-destructive physical treatments of water, thanks to their capability to break down organic pollutants completely. AOPs deploy potent oxidants (like O_3, H_2O_2) and catalysts (such as Fe, Mn,

TiO_2), often in combination with high-energy sources, for instance, UV light. The essence of AOP technology is the production of highly reactive and non-selective oxidizing agents, specifically hydroxyl radicals (HO•), which are capable of eliminating persistent and toxic contaminants, including many organic pollutants [7,8]. Ozone is effectively used to remove pesticides in the water purification process due to its oxidizing and disinfecting properties, targeting electron-rich functional groups such as double bonds and aromatic rings, making it a selective oxidant. This selective reactivity towards specific pollutants, including microbes and organic contaminants, highlights its role in advanced oxidation processes (AOP) where it can initiate the formation of hydroxyl radicals. Applications of ozonation include pesticide removal, decolourisation, and elimination of undesirable tastes and odors [9]. Despite its effectiveness, the formation of oxidation by-products requires efforts to minimize their formation. Implementation of ozonation requires several units including ozone generators, refrigeration systems, air pre-treatment for dehumidification, and post-treatment reactors to handle excess ozone, adding to the complexity and efficiency of this method [10].

The Fenton reaction occurs when ferrous iron (Fe^{2+}) reacts with hydrogen peroxide (H_2O_2). During this reaction, the ferrous iron is oxidized to ferric iron (Fe^{3+}), and hydrogen peroxide is broken down to produce a hydroxyl radical (HO•) and a hydroxide ion (HO^-). This process is significant because the hydroxyl radical is a very powerful oxidant capable of breaking down many types of organic pollutants in water [11].

The efficiency of the Fenton reaction depends on the concentrations of hydrogen peroxide (H_2O_2) and ferrous (Fe^{2+}) ions, where the ideal concentration ratio approaches 1:1. Additionally, the Fenton reaction is environmentally friendly, does not burden the ecosystem, and the optimal conditions for its implementation are at pH = 3 and temperature 30 °C [8].

The photo-Fenton reaction involves shining UV light on a mixture containing iron (Fe^{3+}) and water (H_2O). When the UV light (labelled '*hv*') hits this mixture, it causes the iron (Fe^{3+}) to be reduced to iron (Fe^{2+}). This activation leads to the formation of hydroxyl radicals (HO•) [11].

The inclusion of hydrogen peroxide in the photo-Fenton reaction significantly increases the efficiency of the pollutant decomposition, as additional hydroxyl radicals (HO•) are formed in addition to those produced by the splitting of water molecules, making the photo-Fenton reaction even more efficient [8].

The ferrioxalate system is a modified Fenton process using oxalate ions to create ferrioxalate complexes, improving hydroxyl radical (HO•) production. These complexes, efficiently convert Fe^{3+} to Fe^{2+} and are effective at neutral pH. This system not only increases HO• radical generation but also produces superoxide radicals and hydrogen peroxide (H_2O_2), enhancing the breakdown of tough pollutants. Additionally, it boosts water mineralization by breaking down ferrioxalate complexes and forming reactive species with dissolved oxygen, leading to effective pollutant degradation [12].

MATERIALS AND METHODS

Chemicals and instruments

Acetonitrile of HPLC grade was obtained from Fisher Slovakia, and a 99 % pure metribuzin standard was obtained from Thermo Scientific Chemicals, hydrogen peroxide, dihydrate of oxalic acid, heptahydrate of ferrous sulfate and sulfuric acid was obtained from mikroCHEM, s.r.o., Slovakia with p.a. grade. Ultrapure water was generated using Crystal Water equipment. a UV-C reactor constructed at the UIBE MTF was used for the photo-Fenton reaction. The plant consists of a Köttermann metal chamber with external dimensions of 450 x 450 x 480 mm and an internal volume of approximately 95 dm^3. Four Phillips TUV 15W SLV germicidal UV-C lamps with parallel wiring and a power of 4.9 W each at a wavelength of 250 nm are used for water and air disinfection. The surface of the chamber is matt-finished and a 1 mm thick aluminium foil is used to increase the reflectivity of the UV-C radiation. The lamps are powered by a Philips HF-S 3/4 18 TL-D II electronic ballast, allowing all four UV-C lamps to be powered simultaneously. Cooling by a pair of fans prevents temperature rise during photo-oxidation processes, contributing to stable and efficient operation of the device. For the HPLC analysis, an Agilent Infinity II system equipped with a quaternary pump (capable of 400 bar), an autosampler, and a UV detector managed by OpenLab CDS software was used.

An Agilent Infinity Lab Poroshell 120 Eclipse EC-C18 column with a pore size of 4 μm, an inner diameter of 4.6 mm and a length of 150 mm was used.

Preparation of solutions

To prepare three standard metribuzin solutions, 25 μg of the substance was weighed, transferred to a 250 mL volumetric flask, and diluted to volume with ultrapure water. Calibration solutions at concentrations of 25, 50 and 100 mg/L were then prepared from these stock solutions using ultrapure water in triplicate for verification of the results. The solutions were degassed and the metribuzin thoroughly dissolved using an ultrasonic bath for 10 minutes, then evaporated and stored at room temperature. All the experiments were carried out on solutions of concentrations 20, 50 and 100 mg/L and volume 100 mL prepared from stock solution by the same procedure. The linear regression equation for the detection of metribuzin was $y = 18.889x + 22.106$ with a reliability factor $R^2 = 1$.

Experimental procedure

The Fenton reaction was applied to 100 mL of aqueous solutions with concentrations of 20, 50 and 100 mg/L of metribuzin. Sulphuric acid was used to adjust the pH of the solutions to 3. All solutions were stirred with a magnetic stirrer throughout the course of the experiment and samples were taken at specified time intervals and then filtered through a 0.45 μm PTFE filter for subsequent analysis. At the beginning and also after each 10 mL sample was taken, a 0.04 mg of ferrous sulfate heptahydrate and 0.04 mLof hydrogen peroxide was added.

The ferrioxalate Fenton reaction was realised on 100 mL water samples containing metribuzin at concentrations of 20, 50, and 100 mg/L. Throughout the study, the samples were consistently stirred with a magnetic stirrer and taken out at set intervals for analysis, following filtration through a 0.45 μm PTFE filter. Initially, and after every 10 mL sample was collected, 0.04 mg of ferrous sulfate heptahydrate, 0.04 mg of oxalic acid, and 1.50 mL of hydrogen peroxide were added to the reaction mixture.

The photo-Fenton reaction was carried out in a UV reactor. 0.04 mg of ferrous sulfate heptahydrate and 0.04 mL of hydrogen peroxide were added to 100 mL of the samples while maintaining the time intervals at the beginning and also after each 10 mL sample collection. As in previous experiments, the samples were stirred all the time using a magnetic stirrer to ensure homogeneous dispersion. All samples were filtered through a 0.45 μm PTFE filter and analysed by HPLC-UV.

Oxidation by aeration and ozone was applied to 100 mL water samples containing metribuzin at concentrations of 20, 50, and 100 mg/L. An air/ozone (Sander ozonizer s 500) flow rate of 2.5 L/minwas applied to the samples throughout the study. Samples were collected at 3-minute intervals in 10 mL volumes and analysed by HPLC-UV after filtration through a 0.45 μm PTFE filter.

HPLC-UV method

The mobile phase consisted of ultrapure water and acetonitrile in a 50:50 ratio, with the flow rate set at 1.0 mL/min, and an injection volume of 10 μL; isocratic elution was employed. The temperature was maintained at 50 °C ± 0.5 °C. The determination of the optimum wavelength for metribuzin was conducted by measuring the absorption spectrum using a Thermo Spectronic Genesys 8 UV-VIS spectrophotometer, with 294 nm selected based on the obtained results. The repeatability of conditions was confirmed through a series of measurements performed using the same method, in the same laboratory, by the same personnel, and with identical equipment. By conducting three replicate analyses of solutions at three concentrations (25, 50, 100 mg/L) over a day, the relative standard deviation (RSD) of the peak area was calculated from the measured values, which was ≤ 0.03.

RESULTS AND DISCUSSION

Figure 1 show the time course of the Fenton reaction, ferrioxalate system, and photo-Fenton reaction applied to a 100 mg/L aqueous solution of metribuzin over time in minutes.

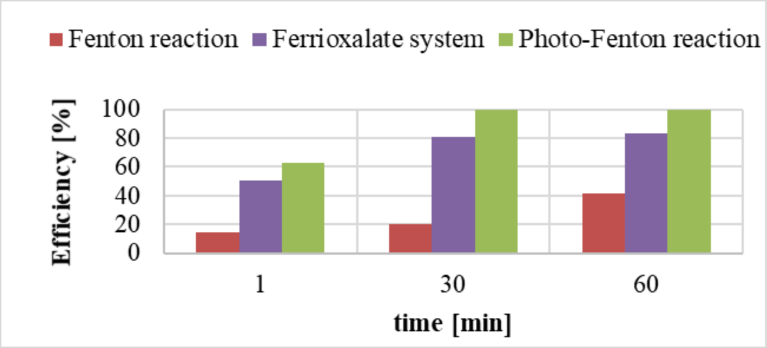


Fig. 1 - Comparison of the removal efficiency of metribuzin at a concentration of 100 mg/L by the Fenton reaction and its modifications

Initial observations indicate that the photo-Fenton reaction starts with the highest efficiency in the first minute, achieving approximately 62.72 % removal, while the Fenton reaction shows the lowest efficiency of approximately 14.65 %. By the 30th minute, the photo-Fenton reaction reaches 100 % removal efficiency, demonstrating its efficiency compared to the ferrioxalate system at approximately 80.76 % and the Fenton reaction at approximately 20.06 %. Figure 2 compares the removal efficiency of metribuzin at a concentration of 50 mg/L using the Fenton reaction, the ferrioxalate system and the photo-Fenton reaction over time in minutes.

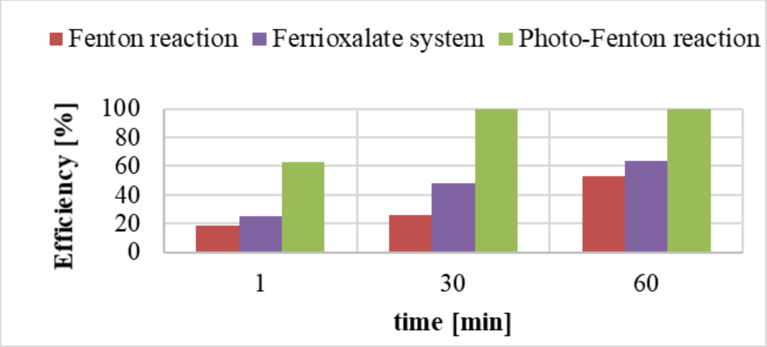


Fig. 2 - Comparison of the removal efficiency of metribuzin at a concentration of 50 mg/L by the Fenton reaction and its modifications

After 1 minute, the photo-Fenton reaction shows the highest removal efficiency of approximately 62.43 %, significantly exceeding the Fenton reaction with approximately 18.29 % and the ferrioxalate system with 25.44 %. Within 60 minutes, both the photo-Fenton reaction and the ferrioxalate system reach 100 % removal efficiency, while the Fenton reaction reaches approximately 52.90 %, demonstrating the higher efficiency of the photo-Fenton method over time. Figure 3 shows the removal efficiency of metribuzin at a concentration of 20 mg/L using the Fenton reaction, the ferrioxalate system and the photo-Fenton reaction over time in minutes.

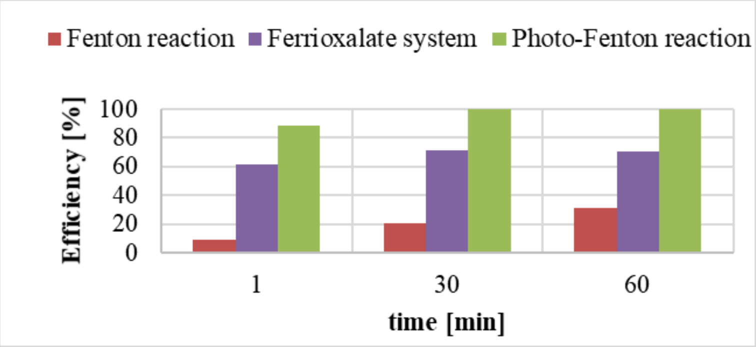


Fig. 3 - Comparison of the removal efficiency of metribuzin at a concentration of 20 mg/L by the Fenton reaction and its modifications

Initially, the photo-Fenton reaction shows the highest removal efficiency in the first minute, reaching about 88.47 %, while the Fenton reaction shows the lowest efficiency of about 9.20 %. By the 30th minute, the photo-Fenton reaction has reached 100 % efficiency, indicating its higher efficiency in degrading metribuzin compared to the ferrioxalate system with about 70.92 % and the Fenton reaction with about 20.56 %. Figure 4 compares the efficiency of metribuzin removal with concentration 100 mg/L using aeration oxidation versus ozone oxidation over time in minutes.

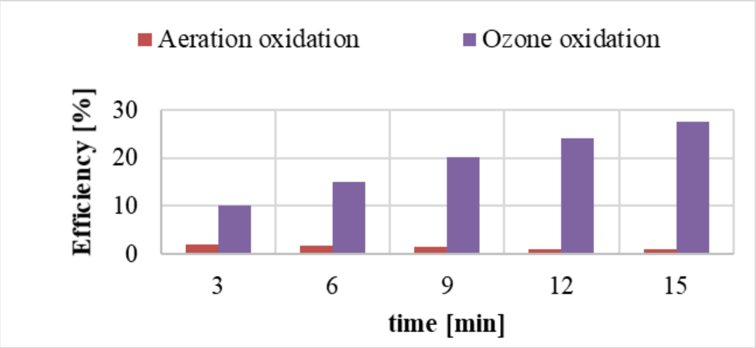


Fig. 4– Comparison of the removal efficiency of metribuzin at a concentration of 100 mg/L by Aeration oxidation and Ozone oxidation

At the 3-minute mark, ozone oxidation shows a significantly higher efficiency of approximately 10.07 % in removing metribuzin compared to aeration oxidation, which has an efficiency of around 1.97 %. This suggests that ozone oxidation is more effective at degrading metribuzin in water samples within the early minutes of treatment, highlighting the potency of ozone as an oxidizing agent in water purification processes. Figure 5 shows the removal efficiency of metribuzin with a concentration of 50 mg/L from water by aeration compared to ozone oxidation, measured over several minutes.

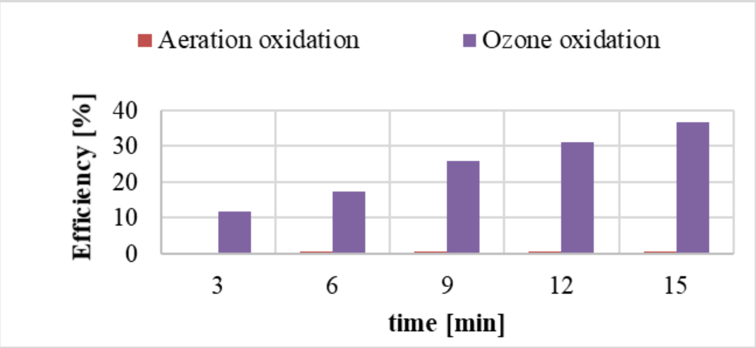


Fig. 5– Comparison of the removal efficiency of metribuzin at a concentration of 50 mg/L by Aeration oxidation and Ozone oxidation

Initially, after 3 minutes, ozone oxidation shows significantly higher removal efficiency, approximately 11.70 %, in contrast to the lower oxidation efficiency of aeration, which is approximately 0.48 %. These data highlight the superior ability of ozone oxidation to rapidly degrade metribuzin, indicating its effectiveness in water treatment processes compared to aeration methods. Figure 6 shows the removal efficiency of metribuzin at a concentration of 20 mg/L through aeration and ozonation over time measured in minutes.

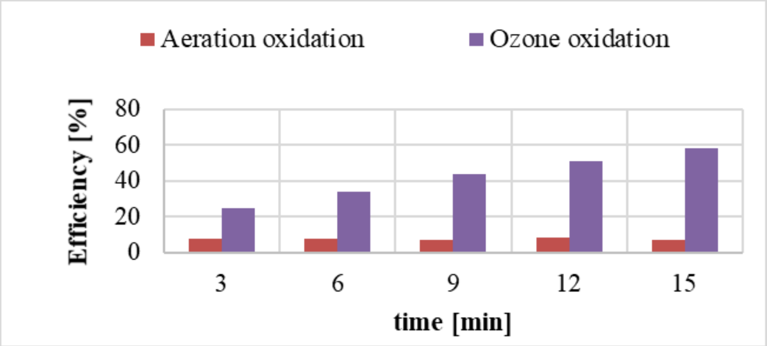


Fig. 6– Comparison of the removal efficiency of metribuzin at a concentration of 20 mg/L by Aeration oxidation and Ozone oxidation

From the outset at the 3-minute mark, ozone oxidation is significantly more effective, achieving approximately 24.57 % metribuzin removal, compared to aeration oxidation's 7.60 %. As time progresses, the gap in efficiency widens, with ozone oxidation reaching about 43.74 % removal by the 9-minute mark, further highlighting ozone's superior performance in breaking down metribuzin in water treatment processes compared to aeration methods.

Figure 7 shows the chromatograms from the HPLC-UV analysis. Chromatogram (a) shows only metribuzin (at retention time 2.74 min), in chromatograms (b) and (c) we can observe a gradual loss of metribuzin (at retention time 2.74 min), but degradation products are formed. The image displays three HPLC-UV chromatograms labeled a), b), and c). Chromatogram a) represents a pure metribuzin standard with a retention time (RT) of approximately 2.74 minutes, indicated by a single sharp peak. Chromatogram b) shows the results after treating metribuzin with the ferrioxalate system for 1 minute, where multiple smaller peaks appear at various retention times, suggesting the presence of intermediate degradation products. Chromatogram c) presents the outcome after 60 minutes of treatment with the ferrioxalate system, where the main peak for metribuzin has significantly decreased in size, indicating substantial degradation, and the other peaks, which are likely degradation products, have either changed in size or new peaks have emerged, pointing to further progress in the degradation process.

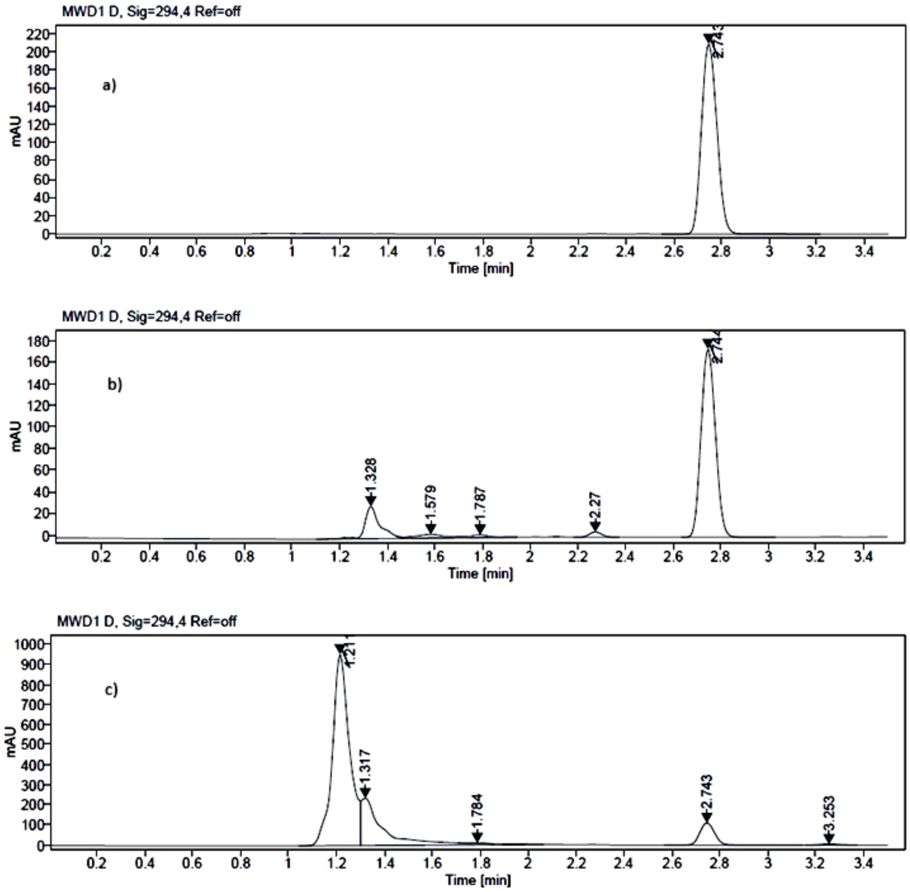


Fig. 7 – Removal efficiency of metribuzin with a concentration of 50 mg/L by the ferrioxalate system (a) at the beginning (b) after 1 minute (c) after 30 minutes

CONCLUSION

In this work, the effectiveness of various advanced oxidation processes (AOPs) in removing the herbicide metribuzin from water was examined. The study shows that among the methods tested, which include the Fenton reaction and the ferrioxalate system, the photo-Fenton reaction is the most efficient at removing metribuzin across different concentrations. Moreover, a comparison between aeration oxidation and ozone oxidation revealed that ozone oxidation significantly surpasses aeration in breaking down metribuzin, underscoring its viability for water treatment applications. These findings emphasize the significance of advanced oxidation techniques in water purification and treatment technologies. Additionally, it is crucial to consider the degradation products formed during these processes, which may also be harmful to the environment. This underscores the importance of comprehensive evaluations to ensure the environmental safety of the treated water.

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