#### AKADEMIA E SHKENCAVE DHE E ARTEVE E KOSOVËS ACADEMIA SCIENTIARUM ET ARTIUM KOSOVIENSIS SEKSIONI I SHKENCAVE TË NATYRËS

## RESEARCH 28 KËRKIME



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## PËRMBAJTJA

#### 612.6(05)

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## ADIPOKINES AS LOCAL REGULATORS OF OVARIAN FUNCTION

#### Abstract

The hypothalamus, pituitary gland, and ovaries work together with hormones to control the intricate female reproduction system. This intricate interaction of hormones results in ovarian cyclicity, leading to critical events such as ovulation, fertilization, and pregnancy. When it comes to ruminants, these processes are mostly controlled by estrogen from ovarian follicles and progesterone from the corpus luteum (CL). Within this framework, ovarian physiology unfolds with distinctive local regulatory mechanisms. The CL, a temporary endocrine structure formed post-ovulation, plays a crucial role during the estrous cycle and pregnancy. Adipokines are a type of cytokines that are released by adipose tissue. They have a big effect on many biological processes, such as reproduction, energy balance, food intake and immune response. This review delves into the realm of novel adipokines and their receptors within the ovaries of cycling and pregnant cows. The study reveals that the level of adipokines change a lot during the estrous cycle and pregnancy. The changing levels of adipokines and their receptors in the CL suggest their they play a part in the local systems that control how the ovary functions. Furthermore, the findings show that the investigated adipokines are expressed in the bovine CL in a way that is different and separate during the estrous cycle and pregnancy. However, further investigations are required to elucidate the detailed molecular mechanisms of regulation. Understanding the role of adipokines in ovary function may lead to the development of targeted therapies that can improve fertility and reproductive function in both animals and humans.

Keywords: ovary function; corpus luteum; adipokines; gene expression; reproduction.

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#### Introduction

The intricate orchestration of females in domestic ruminants has very complex reproductive systems that are controlled by hormones that come from the hypothalamus, pituitary gland, and ovaries. This dynamic interaction involves hormones like GnRH (gonadotropin-releasing hormone), LH (luteinizing hormone), and FSH (follicle-stimulating hormone), alongside steroid hormones such as estrogen and progesterone. This hormonal choreography results in ovarian cyclicity, ultimately leading to crucial events like ovulation, fertilization, pregnancy, and parturition [1, 2]. The pivotal control lies in the dominance of estrogen produced from ovarian follicles and progesterone from the corpus luteum (CL) [3, 4]. Remarkably, no other organs in the body undergo such rapid and dramatic functional and structural changes. These changes encompass cell proliferation, differentiation, and transformation, culminating in the formation, function, and regression of the CL. However, the complexity of cow fertility extends beyond the well-known interactions of reproductive hormones. Hormones, growth factors, peptides, cytokines, steroids, prostaglandins, and more that are released locally play a big role in fertility [5-9]. In addition, adipokines are a group of cytokines that come from adipose tissue and affect different tissues in autocrine, paracrine, and endocrine ways helping to keep the body homeostasis [10]. Over the last decade, studies have increasingly implicated adipose tissue in regulating energy balance, food intake, ovarian physiology, and immune status in domestic animals [11-13].

Adipokines are a special group of cytokines that are made, controlled, and released by adipose tissue [14-16]. They include adiponectin, vaspin, visfatin, resistin, chemerin, leptin, and apelin. Originating from the discovery of adipokines in 1994, numerous studies, predominantly related to metabolic disorders in humans, have been published [17, 18]. Their presence and expression span various tissues, influencing biological processes such as insulin sensitivity, food intake, and inflammation [19, 20, 21]. Their established role in energy metabolism and maintaining metabolic homeostasis is widely acknowledged [10, 22]. More recently, attention has turned to the involvement of adipokines in the regulation of fertility and the development of reproductive disorders [17, 23, 24]. Adipokines like adiponectin and leptin have been studied a lot, and their effects on the reproductive axis have been seen in humans, pigs, mice, and cows [18]. These adipokines may function as metabolic sensors, adjusting reproductive processes in response to changes in energy balance.

Studies have also shown that adipokines affect parts of the ovary, such as granulosa, theca, and luteal cells [12]. In addition, adipokines affect the processes involved in steroid production, changing the expression of progesterone and prostaglandins, which are important for controlling the lifespan of the corpus luteum [25]. Consequently, adipokines emerge as potential contributors to the regulation of CL function during the estrous cycle and pregnancy.

## Adipokines and Ovarian Function

#### Adipokines and Signaling Pathways

Adipokines, a group of hormones and signaling molecules released by adipose tissue engage in diverse communication pathways throughout the body. Some adipokines, such as tumor necrosis factoralpha (TNF- $\alpha$ ) and interleukin-6 (IL-6), activate the nuclear factor kappa-light-chain-enhancer of activated B cells (NF-KB) pathway. This is an important part of inflammation and immune function. Leptin and resistin, among other adipokines, initiate the JAK/STAT pathway asociated with inflammation and immunity. Adiponectin, another adipokine, stimulates AMP-activated protein kinase (AMPK) activity, playing a pivotal role in regulating cellular metabolism and energy balance. Additionally, adiponectin, leptin, and resistin influence insulin signaling, a critical factor in glucose and lipid metabolism. Furthermore, adiponectin and leptin can activate mitogen-activated protein kinases (MAPKs), essential for processes like cell proliferation, differentiation, and apoptosis. In essence, adipokines' signaling through these pathways carefully controls the body's metabolism of glucose and lipids, as well as inflammation, the immune system, and various other important physiological processes [26, 27]. GRP78 (78 kDa glucose-regulated protein), also known as HSPA5 (heat shock protein family member 5) or binding immunoglobulin protein, has been demonstrated to interact with vaspin. Adiponectin mostly works on two receptors, called adiponectin receptor 1 (AdipoR1) and adiponectin receptor 2 (AdipoR2) on the outside of the body. Visfatin is an enzyme that is made of the NAMPT gene (nicotinamide phosphoribosyltransferase). It was first found in lymphocytes in human peripheral blood. Resistin, which is also known as adipose tissue-specific secretory factor (ADSF), is a cysteine-rich peptide hormone that comes from adipose tissue and is made by the RETN gene [12, 14]. However, our understanding of the receptors for visfatin and resistin remains limited.

## Adipokines Throughout Various Phases of the Estrous Cycle

Recent investigations [28] have shown that vaspin and HSPA5, both in terms of mRNA and protein expression, are mostly found in the ovarian structures, such as ovarian follicles, oocytes, and the corpus luteum (CL) [28]. These studies show that vaspin is very important for blood in angiogenesis, proliferation, and luteal cell apoptosis within the porcine ovary [29]. Consistent findings indicate similar expression patterns for vaspin and HSPA5 in the porcine CL, with heightened levels in the middle and late stages (Figure 1), hinting at their involvement in CL steroidogenesis and luteolysis [28, 30]. Conversely, adiponectin has been identified as a key player in oocyte maturation, granulosa cell proliferation, and steroid secretion in the ovaries [23]. Additionally, adiponectin influences angiogenic factors during porcine CL development [31]. Adiponectin levels are higher during the follicular stage, especially in the cumulus-oocyle complex and theca cells of dominant follicles [32]. Interestingly, the study reveals heightened adiponectin expression during the bovine CL regression stage, followed by a subsequent decrease during the onset of CL growth (Figure 1) [33, 34]. Adiponectin receptor 1 exhibits a similar pattern (Figure 2b), with increased expression during the early and middle luteal lifespan [30, 33]. Adiponectin receptor 2 shows high expression levels in the initial days, followed by a significant change in the late stages. Although these results are still preliminary, they suggest that there may be a link between adiponectin and the inhibition of progesterone production, which is notable given the heightened progesterone production during the middle stages of CL. Additionally, adiponectin is highly expressed in porcine ovarian granulosa cells, it causes genes and proteins to be expressed in a way that looks like the ovarian follicle changing during periovulatory remodeling. Specifically, it increases the level of cyclooxygenase-2 (COX-2) and prostaglandin E (PGE) [35].

Numerous investigations have underscored a robust correlation between resistin and female reproductive function [36]. In a recent study, resistin was found to lower progesterone (P4) levels, and raise estradiol (E2) levels. It also changed several pathways, such as steroidogenic acute regulatory protein (STAR), cholesterol side-chain cleavage enzyme,  $3\beta$ -hydroxysteroid dehydrogenase, and estrogen synthetase, by activating protein kinase A and mitogen-activated protein kinase 1 [37]. Resistin demonstrated inhibitory effects on steroidogenesis in theca and granulose cells collected from the ovarian follicles of cycling cattle [38].



Figure 1. Schematically presented relative mRNA expression of vaspin, heat shock protein 5 (HSPA5), adiponectin, adiponectin receptor 1 (AdipoR1), adiponectin receptor 2 (AdipoR2), and resistin (RETN) in the bovine corpus luteum (CL) during the different stages(D=days) of the estrous cycle. Adapted from Thaqi et al. [30].

### Adipokines Throughout Various Phases of Pregnancy

Exploring adipokines during pregnancy is an evolving area with a limited understanding of their expression and roles in this physiological state. Although much remains to be unraveled, some studies affirm their presence in the pregnant corpus luteum (CL). Vaspin expression in the CL during pregnancy appears consistent, lacking a discernible regulation pattern. HSPA5, on the other hand, is responsible for making vaspin receptors. Its mRNA level goes down in early pregnancy stages (M1-2, M3-4), then up in later stages (M5-7), subsequently down again after month 7 (Figure 2) [30]. Adiponectin is consistently expressed throughout pregnancy, with AdipoR1 and AdipoR2 exhibiting slight and similar pattern expressions, respectively. Resistin, on the other hand, sees a significant upregulation in the initial months of pregnancy (Figure 2) [30].

Interestingly, findings also indicate an increase in resistin during the regression stage of the CL and the early months of pregnancy (Figure 2) [30]. Noteworthy is the identification of resistin in human placental tissue, notably in trophoblastic cells and the amniotic membrane [39]. Throughout pregnancy, heightened resistin and adipokine levels are commonly associated with increased insulin resistance [40]. However, because there is no identified resistin-specific receptor, the role and mechanisms of resistin in ruminants remain largely unknown. Additionally, the observed increase in resistin during the regression stage of the CL and the initial months of pregnancy (Figure 2) underscores the need for further exploration [30]. The presence of resistin in human placental tissue further highlights its potential significance in reproductive processes, particularly within trophoblastic cells and the amniotic membrane [39]. As research in this area progresses, a more comprehensive understanding of adipokines during pregnancy in ruminants, including their specific roles and implications, will likely emerge.



Adipokines expression in CL during different stages of pregnancy

Figure 2. Schematically presented relative mRNA expression of vaspin, heat shock protein 5 (HSPA5), adiponectin, adiponectin receptor 1 (AdipoR1), adiponectin receptor 2 (AdipoR2), and resistin in the bovine corpus luteum (CL) during different stages (M=month) of pregnancy. Adapted from Thaqi et al. [30].

## Adipokines During Induced Luteolysis

Regression of CL is an inherent process in the female reproductive system, primarily triggered by the absence of pregnancy. As previously mentioned, the pivotal event instigating CL regression involves a decline in circulating progesterone and other hormones [41]. Prostaglandin F2 $\alpha$  (PGF2 $\alpha$ ) plays a crucial role in luteolysis, initiating vasoconstriction and reducing blood flow to the CL. Released by the uterus, PGF2 $\alpha$  acts locally on receptors within the CL [42, 43]. Vaspin exhibits heightened mRNA levels at 0.5 h and 24 h after prostaglandin F (PGF) application, suggesting potential involvement in the luteolysis process (Figure 3). In contrast, HSPA5 reaches peak abundance at 2, 4, and 12 h, gradually declining to its lowest point at 48 h [44].

Vaspin and HSPA5in terms of mRNA and protein expression, are both highly expressed in porcine ovary structures, specifically in the ovarian follicles, oocytes, and the CL. These proteins and mRNA may help in angiogenesis, proliferation, and luteal cell apoptosis [28, 29]. Adiponectin's mRNA levels remain consistently expressed across all time points, with a noted downregulation at 48 h (Figure 3) [44].





Additionally, adiponectin is suggested to influence angiogenic factors in developing porcine CL [31]. In contrast, the expression of adiponectin receptor 1 remains at low levels without significant changes. Following PGF application, adiponectin receptor 2 (AdipoR2) experiences an upregulation specifically at the 24 h time point (Figure 3)[44]. Notably, resistin (RETN) demonstrates elevated levels at 0.5 h, 2 h, 4 h, and 12 h, followed by a substantial decrease at 64 h (Figure 3)[44].

## Adipokine Importance in Ovarian Function and CL Regression

Numerous studies have elucidated the intricate relationship between metabolism-related factors, hormones, and ovarian function [43, 44]. It is crucial to recognize that adipose tissue functions as an endocrine organ in addition to its conventional role in fat storage. Its connection to metabolites, especially insulin, strongly suggests a regulatory role in local regulation [45,46]. The strong link between energy balance and the female reproductive tract shows how imbalances in energy homeostasis can cause a number of reproductive pathophysiological phenomena. Notably, adipokines have been linked to conditions like polycystic ovarian syndrome and endometriosis [47, 48]. In this context, examining emerging cytokine families, such as adipokines, holds significant promise. Adipokines with their dual characteristics, proinflammatory (resistin, visfatin) and anti-inflammatory (vaspin, adiponectin), emerge as potential players in CL inflammation. Unfortunately, limited data exist on the impact of adipokines on CL regression across species, restricting a comprehensive understanding of their role. Our research pioneers the exploration of adipokine expression during experimentally induced CL regression. While existing studies hint at the indirect influence of adipokines on local ovarian function, their direct involvement in CL regression requires further validation [27, 49, 50].

Furthermore, the multifaceted nature of CL regression underscores the imperative for continued research in this field. This process involves the activation of various apoptotic pathways within the CL, coupled with diminished blood supply due to vasoconstriction caused by PGF and alterations in the expression of local growth factors, including angiogenic, luteolytic, and extracellular matrix remodeling factors [42, 51-55]. Understanding these complexities is essential for advancing our knowledge of reproductive physiology in dairy cattle and enhancing our ability to manage and optimize their reproductive processes. Therefore, ongoing research is not just a scientific pursuit but a practical necessity for the sustainable improvement of dairy cattle reproduction practices.

## Conclusions

Adipokines are found in the bovine CL at different times during the estrous cycle and during pregnancy, which shows how important they are for controlling CL function. The fact that adipokine mRNA levels change between stages suggest that they have different regulatory effects. The unique ways that adipokines and their receptors are expressed in the CL shows that they play a big role in the local systems that control CL activity. Nonetheless, further research is needed to fully comprehend the complex rules and mechanisms that control how adipokines work in the CL. Understanding these nuances holds promise for developing targeted therapies to enhance fertility and reproductive function in bovine species, animals, and humans.

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#### Granit Thaqi, Anila Hoda, Bajram Berisha

#### ADIPOKINET SI RREGULLATORË LOKAL TË FUNKSIONIT TE VEZORES

#### Përmbledhje

Sistemet riprodhuese të shtazëve rregullohen nga një ndërveprim kompleks hormonal që përfshin hipotalamusin, gjëndrën e hipofizës dhe vezoret. Ky ndërveprim i ndërlikuar i hormoneve rezulton në realizimin e ciklit ovarian, duke çuar në ngjarje kritike te fushës se riprodhimit si ovulacioni, fekondimi dhe shtatzënia. Te ripërtypësit, këto ngjarje rregullohen kryesisht nga dominimi i estrogjenit qe sekretohet nga folikulat dhe progesteroni nga trupi i verdhë (corpus luteum). Brenda këtij kuadri, fiziologjia e vezores përveç aspektit endokrin varet edhe nga mekanizma të veçantë rregullues lokalë (parakrin). Trupi i verdhe (CL), një strukturë e përkohshme endokrine e formuar pas ovulacionit, luan një rol vendimtar gjatë ciklit estral dhe shtatzënisë. Adipokinet, një klasë citokinash të çliruara nga indi dhjamor, është konstatuar te kenë ndikim të rëndësishëm në procese të ndryshme biologjike, duke përfshirë ekuilibrin e energjisë, marrjen e ushqimit, përgjigjen imune dhe riprodhimin. Ky punim revyal fokusohet veçanërisht ne aspektin parakrin te adipokineve të reja dhe receptorëve të tyre te specia e gjedhit. Hulumtimi zbulon ndryshime të rëndësishme në nivelet e ekspresionit të adipokineve gjatë gjithë ciklit estral dhe shtatzënisë, duke përfshirë edhe regresionin e indukuar luteal (luteolizë). Dinamika e ekspresionit të adipokineve dhe receptorëve të tyre në CL sugjeron pjesëmarrjen e tyre në mekanizmat lokalë që rregullojnë aspekte te veçanta te funksionit te vezores. Si përfundim, rezultatet sugjerojnë se adipokinat e hulumtuara tregojnë nivele te ndryshe te ekspresionit në CL të gjatë fazave te ndryshme te ciklit estral dhe shtatzënisë. Megjithatë, kërkohen hulumtime të mëtejshme për të sqaruar mekanizmat e hollësishëm molekularë të rregullimit te tyre ne indet e vezores. Prandaj, te kuptuarit e plotë të rolit të adipokineve në funksionin e vezores mund të çojë në zhvillimin e terapive të synuara që mund të përmirësojnë fertilitetin dhe funksionin riprodhues si te shtazët ashtu edhe te njerëzit.

## Flamur Sopaj<sup>1</sup>

## FENTON AND ELECTROFENTON PROCESSES FOR PERSISTENT ORGANIC POLLUTANTS REMOVAL FROM AQUATIC ENVIRONMENT

#### Abstract

Wastewater treatment is one of the most important issues concerning environmental protection, hence human health and normal natural habitat development. Wastewater treatment plants have solved a significant part of the water pollution problem. These water treatment techniques, as effective as they are, some of the pollutants still break through all the treatment stages only to be reintroduced into the natural waters. These methods - despite their conveniences - also have some practical complications. Researchers have conducted further studies to overcome these drawbacks, resulting in new and swift methods capable of destroying any recalcitrant organic chemical. The most distinguished of these methods are the Fenton and electro-Fenton processes. This review discusses the fundamentals of each method, their application and the variables that influence them. The Fenton process can destroy organics by hydroxyl radicals (OH) produced by Fenton's reagent ( $H_2O_2 + Fe^{2+}$ ), however, it cannot produce complete mineralization of organics. The ability of Electro-Fenton to sustain the electrochemical generation of Fenton's reagent not only speeds up pollutant degradation but also achieves complete mineralisation, ensuring that no harmful chemicals remain in the treated solution. The Fenton process and the electro-Fento treatment depends on a number of factors, including pH, catalyst concentration Fe<sup>2+</sup>, H<sub>2</sub>O<sub>2</sub> concentration, temperature, current intensity, and electrode material. The parameters can be optimised to increase the output of organic degradation.

Keywords: Fenton, electro-Fenton, organic pollutants, efficiency, degradation

### Introduction

As the industry is developed continuously for human life comfortability purposes, worldwide pollution pushes forward to the most remote areas as well as towards the highest extents. Environmental

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pollution appears in various forms, but probably the most dangerous is that of chemical nature. Chemical pollutants are substances used for a variety of human needs in order to facilitate, improve, enhance, or even make possible certain processes in everyday life, which, when transported in the environment, many of them disturb its normal course. Chemical pollutants can be classified into two main groups, namely organic <sup>1–3</sup> and inorganic <sup>4–6</sup> pollutants. They are transported into the different environmental areas through the atmosphere, precipitations, winds, soil washout, traffic, and many other ways <sup>5,7,8</sup>.

The most efficient way to cope with chemical pollution is to prevent it from happening completely in the first place, but since this is impossible, there can be found solutions for less pollution production in industrial processes. The reduction of the number of pollutants emitted in the environment is one of the most important means to defy the pollution, but it becomes even more so when complemented with the treatment methods for the wastes generated, nonetheless.

In order to eliminate the produced waste chemicals (organic substances, being the group of pollutants this review focuses on), one of the first methods developed is microbiological digestion, during which process bacteria destroy organic pollutants using them as food, thus transforming them to carbon dioxide (CO<sub>2</sub>), water (H<sub>2</sub>O), and other minerals or gaseous oxides depending on the heteroatoms being part of the organic molecule <sup>9</sup>. Microbiological digestion is currently the most common way to remove organic pollutants in water. It can be done aerobically, anaerobically, or a mix of the two, depending on the concentration of the organics in the wastewater <sup>10</sup>. This treatment method is very well established and studied, however, there are some factors restricting its efficiency, such as its taking a relatively long time to degrade pollutants and its sensitivity to organics with bactericidal properties, such as antibiotics <sup>11</sup>.

Some other techniques are not effected much (as compared to microbiological digestion) by the toxic nature of chemical compounds to be removed. One can mention adsorption and membrane filtration as alternatives to aerobic or anaerobic digestion <sup>12,13</sup>. These two techniques are proven to be very efficient in removing organics from polluted waters, but as separation techniques, the removed pollutants will have to be deposited, and it will be only a matter of time for these compounds to require further treatment. It is thus important to focus on destructive methods as they give a final solution to the problem. Aiming for this type of organic treatment, many other destructive methods for pollutant

removal have emerged. Outstanding water treatment methods are advanced oxidation processes (AOP), which make use of hydroxyl radicals ('OH) a very reactive species with a high redox potential of  $E^{\circ}$ = 2.8 V/SHE in acidic media at 25°C. These radicals react indiscriminately with organic substances, transforming them into CO<sub>2</sub>, H<sub>2</sub>O, and ions NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, and other species determined by the heteroatoms present in the molecule structure. In this review, two main AOPs will be discussed: the Fenton and the electro-Fenton processes.

#### Fenton process

The Fenton process has its origins since 1876 from the experiment performed by Henry John Horstman Fenton on the oxidation of tartaric acid to 2,3,-di-hydroxyl-maleic acid, using a mixture of Fe and H<sub>2</sub>O<sub>2</sub>. It is known that Fe<sup>2+</sup> reacts with H<sub>2</sub>O<sub>2</sub> producing 'OH, which further reacts with organic substances through a sequence of reactions, leading to molecular fragments formations and even final mineral species CO<sub>2</sub>, H<sub>2</sub>O, and various ions when the molecule contains heteroatoms. Only at pH 3 can the Fenton process occur effectively, the general schema is presented in figure 1.



Figure 1. Schema of Fenton process.

As presented in figure 1, hydroxyl radicals, once formed, destroy organic molecules in the wastewater.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO' + OH^-$$
(1)

Fenton's reaction requires only small quantities of iron salts because iron (II) is regenerated from the so-called Fenton-like reaction between excess hydrogen peroxide and iron (III) formed by reaction (1):

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+$$
(2)

This is not a direct reaction, as iron (III) firstly forms an adduct with hydrogen peroxide, reaction (3), and then this species gives the regenerated iron (II) and hydroperoxyl radical HO<sub>2</sub> (reaction (4)):

$$Fe^{3+} + H_2O_2 \leftrightarrow [Fe(HO_2)]^{2+} + H^+$$
(3)

$$[Fe(HO_2)]^{2+} \rightarrow Fe^{2+} + HO_2^{\bullet}$$
(4)

Hydroxyperoxyl radicals (HO<sub>2</sub><sup>•</sup>) produced in this reaction have less oxidation power compared to <sup>•</sup>OH and do not react strongly with organic molecules <sup>14</sup>. Reaction (2) is much slower than Fenton's reaction (1), and consequently Fe<sup>2+</sup> regeneration due to this reaction is not very rapid. However, Fe<sup>2+</sup> ion can be regenerated through some other paths involving very rapid reactions such as: Fe<sup>3+</sup> reduction by HO<sub>2</sub><sup>•</sup> reaction (5), a reaction (6) with an organic radical formed during initial organic molecule degradation by <sup>•</sup>OH, and another reaction (7) with a superoxide anion (O<sub>2</sub><sup>•</sup>) <sup>15,16</sup>.

$$\mathrm{Fe}^{3+} + \mathrm{HO}_{2}^{\bullet} \longrightarrow \mathrm{Fe}^{2+} + \mathrm{O}_{2} + \mathrm{H}^{+}$$
(5)

$$Fe^{3+} + R^{\bullet} \rightarrow Fe^{2+} + R^{+}$$
(6)

$$\operatorname{Fe}^{3+} + \operatorname{O}_{2}^{\bullet-} \to \operatorname{Fe}^{2+} + \operatorname{O}_{2} \tag{7}$$

There are also some other reactions of species that contribute to  $Fe^{2+}$  regeneration, these are outlined in the following <sup>17</sup>:

$$H_2O_2 + OH \to H_2O + HO_2^{\bullet}$$
(8)

$$\mathrm{HO}_{2}^{\bullet-} \leftrightarrow \mathrm{H}^{+} + \mathrm{O}_{2}^{\bullet-} \tag{9}$$

$$\mathbf{RH} + \mathbf{OH} \to \mathbf{R}^{\mathbf{+}} + \mathbf{H}_2\mathbf{O} \tag{10}$$

$$ArH + OH \to ArHOH$$
(11)

$$ArHOH^{\bullet} + O_2 \rightarrow ArOH + HO_2^{\bullet}$$
(12)

A schema of ring opening during organic reactions with hydroxyl radical is shown below <sup>18</sup>:



Although these reactions enable the Fenton process to proceed for a period of time, some of them also play a negative role towards the Fenton reaction rate. In the reactions (2) and (8)  $Fe^{3+}$  and 'OH react with H<sub>2</sub>O<sub>2</sub> destroying it in competition with reaction (2). The organic radical R<sup>•</sup> participates in  $Fe^{2+}$  regeneration but also in  $Fe^{2+}$  oxidation by reaction (13), along with dimerization reaction (14):

$$\mathbf{R}^{\bullet} + \mathbf{F}\mathbf{e}^{2+} + \mathbf{H}^{+} \longrightarrow \mathbf{R}\mathbf{H} + \mathbf{F}\mathbf{e}^{3+} \tag{13}$$

$$\mathbf{R}^{\bullet} + \mathbf{R}^{\bullet} \longrightarrow \mathbf{R} - \mathbf{R} \tag{14}$$

Some other reactions involved in the complex Fenton's chemistry are also <sup>17,19</sup>:

$$Fe^{2+} + OH \rightarrow Fe^{3+} + OH$$
(15)

$$\operatorname{Fe}^{2+} + \operatorname{HO}_{2}^{\bullet} + \operatorname{H}^{+} \to \operatorname{Fe}^{3+} + \operatorname{H}_{2}\operatorname{O}_{2}$$
(16)

$$Fe^{2+} + O_2^{\bullet-} + 2H^+ \rightarrow Fe^{3+} + H_2O_2$$
 (17)

$$O_2^{\bullet} + HO_2^{\bullet} + H^+ \rightarrow H_2O_2 + O_2$$
(18)

$$HO_2 \cdot + HO_2 \cdot \longrightarrow H_2O_2 + O_2 \tag{19}$$

$$HO_2 \cdot + \circ OH \to H_2O + O_2 \tag{20}$$

$$O_2^{\bullet-} + O_H \to O_H^{\bullet-} + O_2$$
(21)

$$OH + OH \to H_2O_2$$
(22)

The inhibiting role of these reactions restricts the values of several experimental variables. For example, reaction (15) lowers the amount of  $Fe^{2+}$  ions in the medium. This reaction, along with reaction (8), is the main parasitic reaction that lowers the oxidation power of Fenton reagent. Other reactions (18-22) are not significant because there are not many radical species in the solution compared to other molecules.

Experimental data has proven that radical scavengers significantly influences the rate of Fenton's reaction. Such species are chloride, sulphate, and nitrate ions <sup>20</sup>. Anyways, in many studies this behaviour has not been observed. The presence of some other oxidizing agents has also been pointed out <sup>21</sup>. There have been some experimental works that have brought some evidence of the existence of high-oxidation state iron complexes under certain conditions <sup>22</sup>. So, the formation of the mononuclear Fe<sup>4+</sup> oxo-complex was proposed <sup>23</sup>, which can oxidize organics only by electron transfer:

$$\operatorname{Fe}^{2+} + \operatorname{H}_2\operatorname{O}_2 \to [\operatorname{Fe}(\operatorname{OH})_2]^{2+} \to \operatorname{Fe}^{3+} + {}^{\bullet}\operatorname{OH} + \operatorname{OH}^{-}$$
(23)

Thus, researchers found a connection between hydroxyl radical and ferryl ion-complex mechanisms, which one or the other taking the lead depending on the condition of the experiment. The co-generation of 'OH and high-oxidation state oxo-iron complex has been demonstrated by time-resolved laser flash photolysis spectroscopy <sup>24</sup>:

$$[Fe^{3+}-OOH]^{2+} \rightarrow (Fe^{3+}-O\bullet - Fe^{4+}=O) + OH$$
(24)

The  $[Fe^{3+}-OOH]^{2+}$  is an excited state species and the overall reaction can be interpreted as an intra-ligand reaction. On the basis of these results, it has been proposed that ferryl formation in secondary reactions under classical Fenton condition should be considered. An example of the degradation of an organic molecule by Fenton process is given in the figure 2. The degradation of MB is very quick, and it is accelerated greatly when the Fenton reagent is increased.



Figure 2. Degradation of methyl blue by Fenton process at different [H2O2] = [Fe2+], V = 150 ml, [MB] = 0.01 mM, pH = 3.

The Fenton process efficiency depends on many experimental variables, such as: pH,  $[Fe^{2+}]$ ,  $[H_2O_2]$ , and temperature. The concentrations of  $Fe^{2+}$  and  $H_2O_2$  are the most fundamental parameters. The pH of the solution strongly influences the efficiency of the process. The most favorable pH values for the Fenton reaction to proceed are 2.8 < $pH \ge 3.0$ , and this is why at these values the majority of the total iron species in the medium are present in the form of  $Fe^{2+}$ . When the pH is lower than 2.8, the predominant species of iron present in the solution is  $Fe^{3+}$  as  $[Fe(H_2O)_6]^{3+}$  or barely  $Fe^{3+}$ , deteriorating reaction efficiency. At pH = 1 oxygen concentration does not change, and this is probably because of the stabilisation of  $H_2O_2$  with  $H^+$  in  $H_3O_2^+$  (solvation of  $H^+$ with  $H_2O_2$ ) which reduces the reaction with Fe<sup>2+</sup>. The Fenton's reaction will also slow down when the pH exceeds the value of pH 3.5. In the case of pH > 5.0, iron ions will precipitate as  $Fe(OH)_3$  thus, the catalyst will be removed from the solution, and consequently, the Fenton reaction efficiency slows down. At pH = 4.0 hydroperoxy complexes such as  $[Fe(HO_2)_2]^+$  and  $[Fe(OH)(HO_2)]^+$  are the dominant forms of iron. Temperature is another influencing parameter. The rate of Fenton's reaction increases with the temperature, but simultaneously the degradation of hydrogen peroxide in O2 and H2O does. The optimum concentrations of catalyst Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub> depend on each other, and experiments are done on the basis of the optimisation of their ratio instead of studying them separately.

There are some advantages <sup>25,26</sup> related to the Fenton treatment of polluted waters. Among them, we can mention the following advantages:

- Simple to operate.
- Easy to handle chemicals.
- Small to no energy consumption.

Disadvantages can be highlighted in the following:

- Relatively high cost and risks related to the transport and storage of H<sub>2</sub>O<sub>2</sub>.
- High amounts of chemicals to acidify the effluents at a favourable pH for the Fenton reaction and neutralize the effluent after the treatment.
- High iron sludge quantities at the end of treatment.
- The complete mineralization is not attained because of the formation of some iron (III) complexes with carboxylic acids that cannot be destroyed by bulk hydroxyl radicals.

Anyways, some of these drawbacks can be reduced. Solid ironcoating catalysts like zeolites, alumina, iron-modified clays, and ionexchange resins can prevent iron sludge. On the other hand, to improve the efficiency of Fenton's process, it can be coupled with other techniques, such as biological oxidation, membrane filtration, coagulation, and light assisted Fenton (photo-Fenton) processes.

## **Electro-Fenton process**

An enhancement of the Fenton process was achieved with the introduction of electrochemical generation of  $H_2O_2$  and electrochemical regeneration of Fe<sup>2+</sup> from Fe<sup>3+</sup> formed in the Fenton reaction. This extension method of organic degradation is known as electro-Fenton. An electrochemical cell facilitates the electrochemical treatment without the need for specific, costly, and potentially dangerous reagents. This allows for a high level of compliance with environmental regulations. During the electro-Fenton process, not only was Fenton's reagent generated as the oxidizing reagent for organic destruction, but also other processes taking place in the electrolytic cell contributed to the pollutant's degradation. Organic pollutants can also be oxidized directly on the anode or by other oxidant species created on the anode at high potentials. Organic pollutants are broken down by oxidant species (not Fenton reagent) and direct oxidation on the anode. This is known as anodic oxidation, and it happens at the same time as the electro-Fenton process.



Figure 3. Schema of electro-Fenton process.

#### Anodic oxidation

There are two main ways that molecules can be oxidized during the anodic oxidation of organic pollutants: directly through an electrochemical reaction where an electron moves from the electrode (anode) to the molecule, and indirectly through oxidants produced on the anode, which is also known as mediated oxidation <sup>27</sup>. The direct electrochemical oxidation occurs below the oxygen onset potential, and it subsides above it. At the oxygen evolution potential, organic oxidation proceeds in competition with the oxygen evolution reaction (OER). Thus, the degradation of pollutants will depend on the mechanism of OER, which strongly varies with the electrode (anode) material <sup>27,28</sup>. Generally, anodes exhibiting a high overpotential for OER show better efficiency in organic degradation. Researchers have studied a variety of electrode materials to understand their electro-catalytic properties and how they affect organic oxidation efficiency <sup>29–31</sup>.

One of the anodes representing low overpotential for OER is iridium dioxide IrO<sub>2</sub>, based dimensionally stable anode  $(DSA)^{32}$ . It is thought that oxygen evolution on these kinds of anodes happens in three steps. During water discharge, the oxidation state of the metal oxide changes based on simple reaction.(25)-(27)<sup>33</sup>. The first step is the charge transfer by the discharge of water, with the formation of active species on active sites of the anode surface:

$$M + H_2O \rightarrow MO_x(OH) + H^+ + e^-$$
(25)

$$MO_x(OH) \to MO_{x+1} + H^+ + e^-$$
(26)

$$\mathrm{MO}_{\mathrm{x}+1} \to \mathrm{MO}_{\mathrm{x}} + \frac{1}{2} \,\mathrm{O}_{2(\mathrm{g})} \tag{27}$$

Thus, firstly the  $IrO_2$  is oxidised to  $IrO_3$  via hydroxyl radicals, then it oxidizes organic molecules, but also the wasting reaction (27) takes place to certain extent.

At high oxygen evolution potential electrodes, the organic oxidation process follows a different mechanism. The most remarkable high oxygen evolution overpotential electrode is boron-doped diamond (BDD)<sup>27,31</sup>. This electrode is prepared by chemical vapour deposition of methane mixed with metallic boron or B(OCH<sub>3</sub>)<sub>3</sub> as a dopant <sup>34</sup>, on titanium or other materials. The water discharge on the BDD electrode is considered to develop through a path giving hydroxyl radicals as intermediate species. A simplified mechanism for the organics oxidation on boron-doped diamond electrodes has also been proposed <sup>35</sup>. First, the discharge of water molecules produced hydroxyl radicals physisorbed on BDD surface as very reactive oxidizing agents (reaction (91)):

$$BDD + H_2O \rightarrow BDD(HO') + H^+ + e^-$$
(28)

Then,

$$BDD(HO^{\bullet}) + R \rightarrow BDD + ROH^{\bullet} (or R^{\bullet} + H_2O)$$
(29)

The oxygen evolution reaction also occurs,

$$BDD(HO') \rightarrow BDD + \frac{1}{2}O_2 + H^+ + e^-$$
(30)

Since the BDD electrode has a high overpotential for oxygen evolution, the process enables the formation of lower quantities than on DSA-type anodes. However, OER results in a significant loss of electrical energy. Hydroxyl radicals generated cannot oxidize diamond neither are they chemically adsorbed on the diamond surface, but they are physically adsorbed. The fact that they are weakly adsorbed on the electrode surface lets them be quasi-free so that they can react with other substances that are found in the vicinity of the electrode. So the oxidation of organic pollutants by hydroxyl radicals takes place only at the electrode surface because the diffusion coefficient of hydroxyl radicals is very low because of their high reactivity <sup>17</sup>. The pollutant's degradation takes place in the bulk solution also via other oxidants generated on the anode, such as  $S_2O_8^{2-}$ , OCl<sup>-</sup>, and other species depending on the supporting electrolyte used <sup>27</sup>

#### Electro-Fenton

The degradation of organic pollutants can be achieved in an even more effective way by combining anodic oxidation with the Fenton reagent (H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup>), generated electrochemically chemistry <sup>36,37</sup>. As described in one of the previous studies, Fenton's reagent (H<sub>2</sub>O<sub>2</sub> + Fe<sup>2+</sup>) is used to produce very reactive hydroxyl radicals •OH that are used to eliminate toxic organic compounds from contaminated waters. To bring about the Fenton process, H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup> are added in the reactor, and the concentration of targeted molecules is monitored until the total consumption of the oxidizing agents. The complete mineralization of pollutants is not achieved because of the Fe<sup>3+</sup> inactivation by ligand action of carboxylic acids <sup>38</sup>, but also because of the Fenton's reagent consumption. Whereas in the electro-Fenton method, Fenton's reagent is produced directly during pollutant degradation <sup>37</sup>. Fe<sup>2+</sup> is added to the solution in a catalytic quantity as a soluble iron salt, and it is continuously regenerated on the cathode surface via the one-electron transfer, (reaction (102)) from Fe<sup>3+</sup> formed during Fenton's reaction <sup>39</sup>:

$$\mathrm{Fe}^{3+} + \mathrm{e}^{-} \to \mathrm{Fe}^{2+} \tag{31}$$

On the other side  $H_2O_2$  is electro-generated at the cathode from the two-electron reduction of oxygen in acidic media (pH 3) according to the reaction (32):

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{32}$$

Compressed air (or oxygen) is bubbling into the solution to introduce the oxygen required for this reaction. The oxygen reduction process includes the dissolution of oxygen gas in the solution, its transportation to the cathode and finally the reduction to hydrogen peroxide. Some oxygen also comes from the naturally occurring oxygen dissolution in water according to Henry's law and the oxygen evolution on the anode from water discharge (reaction (33)):

$$H_2O \rightarrow \frac{1}{2}O_2 + OH^- + e^-$$
(33)

As soon as  $H_2O_2$  and  $Fe^{2+}$  are produced as described above, they react following the Fenton's reaction (reaction (1)) to give hydroxyl radicals, which in turn oxidize organics. Afterwards,  $Fe^{3+}$  generated in reaction (1) is reduced to  $Fe^{2+}$  according to reaction (31). On the other hand,  $H_2O_2$  keeps being produced electrochemically at the cathode. Therefore, the electrochemical cell continuously supplies the Fenton's reagent in a catalytic manner.

Apart Fenton's reagent's electrogeneration reactions, on the electrodes may be developed also other parasitic reactions. The strength of these reactions depends on how the electrochemical cell is set up and other operational factors like the electrode potentials and the generated species. For example, in an undivided cell  $Fe^{2+}$  can be electrochemically oxidized to  $Fe^{3+}$  at the anode:

$$\mathrm{Fe}^{2+} \to \mathrm{Fe}^{3+} + \mathrm{e}^{-} \tag{34}$$

The  $Fe^{3+}$  can precipitate in the very vicinity or in the pores of three-dimensional cathodes as  $Fe(OH)_3$  because of the basic conditions created by water reduction <sup>37</sup>.

Hydrogen peroxide accumulation in the system and its stability depend on working conditions. Some usual parasitic reactions are reactions (34) and its decomposition to oxygen and water  $^{40}$  (reaction (35)):

$$2H_2O_2 \rightarrow O_2 + 2H_2O \tag{35}$$

A parasitic reaction related to the cell configuration is its oxidation on the anode if an undivided cell is used. This reaction involves hydroperoxyl radicals as intermediates:

$$H_2O_2 \rightarrow HO_2^{\bullet} + H^+ + e^-$$
(36)

$$\mathrm{HO}_{2}^{\bullet} \to \mathrm{O}_{2} + \mathrm{H}^{+} + \mathrm{e}^{-} \tag{37}$$

So, all possible parasitic reactions make the accumulation of hydrogen peroxide lower than the levels expected from its electrogeneration. It is worth noting that all parasitic and regeneration reactions of  $H_2O_2$  and  $Fe^{3+}$  involved in the Fenton's chemistry can account for the electro-Fenton process also. However, some parasitic reaction, such as those between 'OH and  $H_2O_2$ , 'OH and  $Fe^{2+}$  which are the most important ones, are reduced or eliminated. The degradation of sulfamethazine (SMT) by the electro-Fenton process using an electrolytic cell with a carbon felt cathode and platinum anode is shown in figure 4. The degradation of SMT decreases rapidly with time, as well as with current intensity. Because of the parasitic reactions we talked about above, it is clear that current intensities higher than 300 mA don't make a big difference in the rate of degradation.



Figure 4. The effect of current intensity on the kinetics of degradation of SMT using the Pt/Carbon felt electrode couple during electro-Fenton process. Vs = 300 mL, pH = 3, [Na2SO4] = 50 mM, [Fe2+] = 0.2 mM.

## Experimental parameters governing the electro-Fenton process

When it comes to the electro-Fenton process, the solution pH, catalyst concentration, electrode material, applied current, temperature, and oxygen or air feed rate are the most important factors that affect it.*Effect of pH* 

Electro-Fenton process efficiency is strongly dependent on solution pH, as already discussed for Fenton's chemistry. It has been shown that the optimal pH value is 2.8-3, where a maximum generation of hydroxyl radicals was observed <sup>41</sup>. For pH > 3.5, the rate of mine-ralization of organics starts to slow down because a part of Fe<sup>3+</sup> precipitates in the form of Fe(OH)<sub>3</sub>. At pH < 1 it becomes very slow since Fe<sup>2+</sup> forms complexes with H<sub>2</sub>O<sub>2</sub> and SO<sub>4</sub><sup>2-</sup>. The type of acid used to adjust the pH value and the type of supporting electrolyte both affect how quickly pollutants break down because acids and salt anion are involved in the oxidation process. At low pH. the formation of iron complexes with Cl<sup>-</sup> and ClO<sub>4</sub><sup>-</sup> is also possible, whereas SO<sub>4</sub><sup>2-</sup> apart from the complexion action scavenges hydroxyl radicals too <sup>42</sup>.

### Catalyst concentration

The catalyst is one of two fundamental reagents of the electro-Fenton process, and its importance is crucial<sup>43</sup>. The rate of the degradation reaction increases with the catalyst concentration until a given value, owing to the intensification of Fenton's reaction (1). Then after a certain concentration, a reverse effect is observed because of the parasitic reaction (15) which consumes hydroxyl radicals in competition with organic oxidation. Thus, an optimal concentration of catalyst is required to attain the maximum rate of contaminants oxidation. This optimum concentration depends on the nature of the cathode utilized, in the process. If a carbon felt cathode is utilized the optimum concentration for Fe<sup>2+</sup> is 0.1-0.2 mmol L<sup>-1</sup> at pH = 3<sup>44</sup>.

## Applied current

Fenton's reaction, driven by electrical current, makes electro-Fenton a remarkable method for polluted water treatment. The current

applied produces and maintains  $H_2O_2$  and  $Fe^{2+}$  concentrations during electrolysis <sup>37</sup>. The variation of current affects the production rate and the concentration of  $H_2O_2$  and  $Fe^{2+}$  and consequently the rate of degradation of organic molecules. When the current intensity is increased, the quantity of  $H_2O_2$  in the solution increases owing to the acceleration of reaction (32). An increase in current intensity results in more effective  $Fe^{2+}$  regeneration, too (31). Since the concentration of both  $H_2O_2$ and  $Fe^{2+}$  is increased with the current intensity, the quantity of hydroxyl radicals will be higher, and as a consequence, faster organic removal is achieved. Nevertheless, the acceleration of organic degradation reaction rises until a certain current intensity, beyond which no improvement in the efficacy of the process is observed <sup>31</sup>. This limiting degradation current is a consequence of parasitic reactions that compete with  $O_2$  reduction to  $H_2O_2$  namely the hydrogen evolution reaction on the cathode. At high current intensities, mass transport of O<sub>2</sub> and Fe<sup>3+</sup> towards the cathode becomes the rate-determining step of the electrochemical reactions of the production of  $H_2O_2$  and  $Fe^{2+}$ , thus, any increase in current intensity beyond this limit will lead to a loss of energy without any improvement in the treatment process. Low current intensities give pollutants removal with higher electricity effectiveness but longer electrolysis, and if the current intensity is considerably low, no significant remediation of water is attained.

## Temperature and oxygen or air feed

Oxygen is fed continuously in the solution by introducing compressed air or oxygen. This provides a saturated solution with oxygen to reach maximum  $H_2O_2$  production. Temperatures up to 35-40°C enhance hydroxyl radical formation, but higher temperatures also help break down hydrogen peroxide and speed up other parasitic reactions.

#### Electrode material

Since the electro-Fenton process generates the principal reagents (oxidants), the electrode material plays a crucial role. Many cathodes have been studied so far for their performance in the electro-Fenton technology for water treatment, such as: graphite <sup>37</sup>, carbon-PTFE O<sub>2</sub> gas diffusion <sup>45</sup>, carbon felt <sup>31</sup>, reticulated vitreous carbon (RVC) <sup>46</sup>, carbon sponge, <sup>37</sup> and carbon nanotubes <sup>47</sup>. In figure 5, it can be clearly

seen that the chemical nature of the cathode and its physical properties greatly affect the value of degradation rate constants of SMT. Glassy carbon with a porosity of CS45 ppi is the most effective, and stainless steel (SS0 is the least.



Figure 5. The effect of current intensity (50- 500) mA and the cathode material on the kinetics of degradation of SMT during electro-Fenton process. Cathodes: glassy carbon of different porosities (CS30-CS100, carbon felt CF, and stainless-steel SS), platinum anode. Vs = 300 mL, pH = 3, [Na2SO4] =50 mM, [Fe2+] = 0.2 mM.

A cathode material for electrochemical water treatment must have some characteristics that make them it fit for the electro-Fenton process. To get a high hydrogen peroxide yield, a cathode needs to have a high hydrogen evolution overpotential, high current efficiencies, low catalytic activity for hydrogen peroxide decomposition, chemical and physical stability, good electrical conductivity, and low cost. Some materials like mercury support  $H_2O_2$  production, however, they are very toxic, so not useful for water treatment.

Carbon is a very appropriate material for environmental applications, as it does not show any toxic effect on living beings and repre-
sents all the characteristics required for electrochemical water remediation. Since oxygen is poorly soluble in water, three-dimensional large surface area cathodes are needed to obtain reasonable current efficiencies in pollutant removal. These electrodes are GDEs that have a thin, porous structure that lets oxygen flow through its pores and when they are biased under cathodic potential allow fast O<sub>2</sub> reduction to have H<sub>2</sub>O<sub>2</sub> accumulation owing to a high number of active sites on their surface. Carbon particles, bonded with PTFE in a cohesive layer, comprise GDEs. Carbon felt is a three-dimensional, large, specific surface cathode where the Fenton's reagent generation takes place very rapidly. In comparison with GDEs, there is a lower accumulation of the H<sub>2</sub>O<sub>2</sub> because its H<sub>2</sub>O<sub>2</sub> generation ability is lower than that of GDEs <sup>48</sup>. Contrarily, the regeneration of Fe<sup>2+</sup> at carbon felt is faster than at GDEs <sup>49</sup> leading to lower accumulation of H<sub>2</sub>O<sub>2</sub> because hydroxyl radicals are immediately produced through Fenton's reaction.

Anode material is another source of oxidants that participate in the oxidation of organic matter. Different anodes used in direct anodic oxidation can be used for electro-Fenton. When a high overpotential oxygen evolution anode is used, hydroxyl radicals can be generated from the water discharge along with other oxidants like  $S_2O8^{2-}$ , ClO<sup>-</sup>, depending on the supporting electrolyte present in the solution. In fact, the supporting electrolyte always plays an important role in pollutant degradation <sup>27</sup> in extents varying from anode material. An anode providing a high concentration of hydroxyl radicals is boron doped diamond (BDD), which is widely being used in environmental studies and also for the particular case of electro-Fenton, thanks to its distinguished performance for water remediation <sup>45</sup>. Nobel metals represent interesting materials to be used for water remediation owing to their resistivity in the very oxidizing medium in the electrochemical reactor for organic contaminants destruction. Platinum is one of the preferred anodes as it does not leave toxic ions in the solution <sup>39,49</sup>. Organics are oxidized directly on its surface by electron transfer or by hydroxyl radicals generated in low quantities, or by other oxidants in the bulk. Parasitic reactions restrict the efficiency of oxidation on anodes too. Beyond a given potential, O<sub>2</sub> evolution prevails greatly, reducing the organics oxidation at the anode.

# Conclusion

Methods for wastewater contaminated with organic pollutants have had a crucial role in environmental protection. Billions of cubic meters of water are cleaned to obtain environmentally friendly waters, so that they can be discharged in natural streams. There are, however, micropollutants that are more recalcitrant, which can go through processes in wastewater treatment plants without any change. Advanced and electrochemical oxidation processes, appear effective even in destroying these recalcitrant micropollutants. The Fenton process enables very effective organic oxidation using far fewer chemicals and equipment compared to those used in wastewater treatment plants currently in use. The electro-Fenton process is an even more advanced technology for organic pollutant destruction. It can completely mineralize any organic matter soluble in water media, owing to the sustained Fenton's reagent production directly in the electrochemical reactor. This process can be outstandingly effective and convenient when the electrical energy is provided by alternative sources, such as wind turbines and solar energy via solar panels.

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#### Flamur Sopaj

# PROCESET FENTON DHE ELEKTRO-FENTON PËR LARGIMIN E NDOTËSVE REZISTENT ORGANIKË NGA MJEDISI UJOR

#### Përmbledhje

Trajtimi i ujërave të ndotura industriale dhe komunale, është një nga çështjet më të rëndësishme në lidhje me mbrojtjen e mjedisit, rrjedhimisht shëndetin e njeriut dhe zhvillimin normal të habitatit natyror. Impiantet e trajtimit të ujërave të ndotura kanë zgjidhur një pjesë të madhe të problemit të ndotjes së ujit. Këto teknika të trajtimit të ujit, sado efektive që janë, disa nga ndotësit ende mund të kalojnë nëpër të gjitha fazat e trajtimit dhe arrijnë përsëri në ujërat natyrore. Këto metoda – pavarësisht nga lehtësitë e tyre – kanë edhe disa ndërlikime praktike. Për të kapërcyer këto të meta, janë kryer studime të mëtejshme që çojnë në metoda të reja dhe të shpejta, të afta për të shkatërruar çdo kimikat organik rezistent. Më të dalluara nga këto metoda janë procesi Fenton dhe elektro-Fenton. Procesi Fenton mund të shkatërrojë substancat organike me anë të radikaleve hidroksile 'OH të prodhuar nga reagenti Fenton (H<sub>2</sub>O<sub>2</sub> + Fe<sup>2+</sup>).

 $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + OH^{\bullet}$  $HO^{\bullet} + RH \rightarrow R^{\bullet} + H_2O \rightarrow \rightarrow OO_2 + H_2O$ 

Megjithatë procesi Fenton nuk mund të shkaktoj mineralizimin e plotë të ndotësve organikë. Ky proces mund të realizohet në mënyrë efeketive vetëm në pH rreth 3. Përqendrimet e Fe<sup>2+</sup> dhe  $H_2O_2$  janë parametrat më themelorë. Efikasiteti i procesit është i lidhur ngushtë me pH të tretësirës. Vlerat më të favorshme të pH për të vazhduar reaksionin Fenton janë  $2,8 \le pH \ge 3,0$  sepse në këto vlera shumica e specieve totale të hekurit në mjedis janë të pranishme në formën e Fe<sup>2+</sup>. Kur pH është më i ulët se 2,8, specia mbizotëruese e hekurit e pranishme në tretësirë është  $Fe^{3+}$  si  $[Fe(H_2O)_6]^{3+}$  ose  $Fe^{3+}$ , duke përkeqësuar efikasitetin e reaksionit. Në pH = 1, përqendrimi i oksigjenit nuk ndryshon, dhe kjo ndoshta për shkak të stabilizimit të H<sub>2</sub>O<sub>2</sub> me H<sup>+</sup> në H<sub>3</sub>O<sub>2</sub><sup>+</sup> (hidratimi i H<sup>+</sup> me H<sub>2</sub>O<sub>2</sub>) që redukton reaksionin me Fe<sup>2+</sup>. Reaksioni Fenton gjithashtu do të ngadalësohet kur pH tejkalon vlerën e pH 3.5. Në rastin e pH > 5.0, jonet e hekurit do të precipitojnë si Fe(OH)3, kështu që katalizatori do të hiqet nga tretësira dhe rrjedhimisht efikasiteti i reaksionit Fenton ngadalësohet. Në pH = 4.0, komplekset hidroperoksi si  $[Fe(HO_2)_2]^+$  dhe  $[Fe(OH)(HO_2)]^+$  janë format dominuese të hekurit.

Procesi electro-Fenton duke qenë në gjendje të prodhoj në mënyrë të vazhdueshme reagjentin Fenton në mënyrë elektrokimike, jo vetëm që siguron një degradim më të shpejtë të ndotësve, por edhe një mineralizim të plotë, duke mos lënë kimikate të dëmshme në tretësirën e trajtuar. Procesi elektro-Fenton është një kombinim i shumë proceseve anodike dhe katodike të cilat qojnë në oksidim direct të ndotësit në anodë ose nga produktet e gjeneruara në të, ose oksidimin e ndotësit në mënyrë indirekte ka reagjenti Fenton i gjeneruar në katodë. Ky process mzund të paraqitet me reaksionet në vazhdim:

Reaksionet kryesore që zhvillohen në anodë kur përdoret një anodë me potencial të ulët të lirimit të  $O_2$  janë:

```
\begin{split} M + H_2O &\rightarrow MO_x(OH) + H^+ + e^- \\ MO_x(OH) &\rightarrow MO_{x+1} + H^+ + e^- \\ MO_{x+1} &\rightarrow MO_x + \frac{1}{2} O_{2(g)} \end{split}
```

 $MO_{x+1}$  pastaj vepron si oksidues i materieve organike, ose kur përdoret një anodë me potencial të lartë të lirimit të  $O_2$ :

 $BDD + H_2O \rightarrow BDD(HO^{\bullet}) + H^+ + e^{-}$ 

Then,

 $BDD(HO') + R \rightarrow BDD + ROH' (or R' + H_2O)$ 

The oxygen evolution reaction also occurs,

 $BDD(HO^{\bullet}) \rightarrow BDD + \frac{1}{2}O_2 + H^+ + e^-$ 

Janë radikalet HO<sup>•</sup> që oksidojnë molekulat organike. Gjithashtu këtu kemi prozent njëkohësisht edhe radikalet hidroksile të formuara në tretësirë nga reagjenti Fenton i formuar në mënyrë elektrokimike:

 $Fe^{3+} + e^{-} \rightarrow Fe^{2+}$  $O_2 + 2H^+ + 2e^{-} \rightarrow H_2O_2$ 

Ka disa faktorë që ndikojnë në rezultatin e trajtimit me elektro-Fenton (përveç parametrave të lidhura me rrymën elektrike, i njëjti llogari për procesin Fenton); pH, përqendrimi i katalizatorit Fe<sup>2+</sup>, intensiteti i rrymës dhe materiali i elektrodës. Këta parametra mund të optimizohen për një rezultat më të madh të degradimit të lëndëve organike. Adaptimi i kytyre variablave në vlera përkatëse me anë të matjeve eksperimentale, rezulton me një eliminim shumë efikas të ndotësve organik nga uji që trajtohet.

#### 004.3(05)

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# ARTIFICIAL INTELEGENCE AGENTS IN TELECOMMUNICATION NETWORKS

#### Abstract

In this paper we have treated the capabilities of artificial intelligence (AI) agents in the specific context of networking knowledge and troubleshooting. AI agents consist of LLM, API response from the networking environment, and the action upon response. Action can give networks an intent-based operation, thus making the traditional network operation obsolete. In this paper, we introduce different methods of how to improve basic responsiveness, correctness and chain of thought specialized for network operational tasks. Major contributions that have been added are agentic behavior for frequent network operational tasks, and action based on those tasks. The goal is to cut down on the meantime it takes to handle incidents and change related tasks. Our environment consists of large datacenter multivendor networking environment spanning multiple markets such as: APAC; EMEAR, AMER and a plethora of different services running on top of this hardware.

Keywords: AI, LLM, Network Operations, MTTR

### Introduction

Traditional operational work on a global scale network consists of multiple network operations centers spanning multiple time zones and 24/7 operational mode. Supporting these large-scale networks is difficult human resource wise as well as logistically. With recent developments in generative artificial intelligence there is a good case to employ these capabilities to augment different operational tasks with humans. [1]. Recent progress in generative models, also known as large language models, has opened up a huge window of opportunity to connect different engineering tasks to real backend systems that can handle the workflow [2]. A lot of research revolves around updating the

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generic knowledge that these models have with an up-to-date information base, since these models have inherent ability to learn from context [3]. The procedure of augmenting the search with external unstructured knowledge is also known as Retrieval Augmented Generation (RAG) [4]. Many tasks in networking can be accomplished using RAG, however, there are certain areas where you need to act based on retrieval, and that is where the concept of agent comes from [5].

An intelligent agent both retrieves information and acts on it based on the result. For example, it might fix a problem that happened during an incident, such as a packet drop, power level drop, or an application issue [6]. AI agents have evolved since their inception [5]. Initially, AI agents would have a specific task to run without collaborating with other AI agents and have no ability to adapt and learn. Then from there, the next step in evolution was multi-agent frameworks, where the agent could collaborate based on tasks and could do planning for completion of specific complex task [7]. Lastly, agents can even learn from completing tasks, so called multi-agent reinforcement learning [8]. In the networking field, AI agents would be specialized in different tasks such as design, configuration, deployment, operation, and monitoring. Each of these specialized tasks require different set of knowledge and metrics [2]. AI agents used in design should be able to work with multi-modal capabilities. To do this, they need foundational models for vision, so that when they take in image data, they can turn into text or vice-versa. Whereas AI agents used for configuration and deployment must possess multi-vendor knowledge, understanding how certain designs convert into specific vendor configurations. And finally, AI agents used in operation and monitoring would need to be as realtime as possible with abilities to react upon changes and events [9].

# AI agents' implementations

Some recent state-of-the-art (SoTA) methods will be described in detail, along with limitations and networking applications. The first method we discussed, the Chain of Though method [10], came from Google Brain Lab and helped LLM get better at reasoning by giving them intermediate reasoning tasks. Also, this can be understood by giving the initial question plus a few examples of how few simpler queries can be solved, it will improve overall performance as shown in the paper [10] for different arithmetic, common sense, and symbolic

reasoning tasks. This can be particularly useful in tasks such as troubleshooting an incident when you have past solutions and can give the model few examples on solved incidents to solve the new incident, thus improving the immediate response.

Standard Prompting Model Input	Chain-of-Thought Prompting Model Input
Q: Roger has 5 tennis balls. He buys 2 more cans of tennis balls. Each can has 3 tennis balls. How many tennis balls does he have now?	Q: Roger has 5 tennis balls. He buys 2 more cans of tennis balls. Each can has 3 tennis balls. How many tennis balls does he have now?
A: The answer is 11. Q: The cafeteria had 23 apples. If they used 20 to	A: Roger started with 5 balls. 2 cans of 3 tennis balls each is 6 tennis balls. 5 + 6 = 11. The answer is 11.
make lunch and bought 6 more, how many apples do they have?	Q: The cafeteria had 23 apples. If they used 20 to make lunch and bought 6 more, how many apples do they have?
	Nedel Output
	A: The cafeteria had 23 apples originally. They used
A: The answer is 27.	20 to make lunch. So they had 23 - 20 = 3. They bought 6 more apples, so they have 3 + 6 = 9. The answer is 9.

### Figure 1 Chain-of-Thought prompting



Figure 2 Self-Ask prompting



Figure 3 Re-Act prompting

The next method that is an improvement upon the previous one is self-ask method [11], which improves the original reasoning capabilities of foundation model by asking itself a follow-up questions which can be augmented by search engine results. The same research shows that as the model size increases, the reasoning capabilities remain unchanged. Unlike the CoT method, self-ask automatically generates the follow-up (decomposition) questions through LLM and then comes up with the final answer. This means that you did not have to work as hard to make the answer as well as ingesting in any intermediate tasks results from search engines. In the networking field, it can be easily applicable to a range of scenarios. For example, when asking for a description of an output from a device, whether it is a show command or log message, additional data can be included from search engine, thus improving the performance of an answer. Additionally, a query for topology of a certain part of the network diagram information can provide definitive answer to the model to appropriately answer by having an intermediate step to ask for tooling or function call.

The third method is Re-Act [6] which includes, in comparison to previous methods, also decision-making process. The method uses the CoT-SC [12] in cases where it underperforms, thus making overall performance greater in certain scenarios. What is also novel in this method is API interaction for specific intermediate tasks.

Another method worth mentioning that is distinct improvement upon the previously mentioned methods is the Reflexion method [13], thediagram and algorithm are shown below:



Figure 4 Reflection diagram and algorithm

Reflexion has huge opportunities for use in the networking field due to capabilities to its cope with complex reasoning and planning. These algorithms can be particularly useful in designing and optimizing existing as well as greenfield deployments. Furthermore, the algorithm can enhance troubleshooting scenarios.

# Experimental results

To experiment with the application of these agents, we have taken several actual example tasks from network operation, such as break-fix and corrective actions during change and incident management. The following table shows savings in minutes spent using appropriate AI agents compared to manually executing these tasks:

Feature	Time using AI agent (Mins) *	Time via manual process (Mins)
Search for device scheduled changes to estimate impact	1 min	20 min
Search for isolation events	1 min	20 min
Packet Loss	1 min	20 min
Get L2 Routing Instance & UUID information	1 min	10 min
List services for customers	1 min	10 min
Config search	1 min	15 min
Console info	1 min	5 min
Spare search	1 min	15 min
Log search	1 min	15 min
Tools URL search	1 min	10 min
Device traffic	1 min	20 min
Paths for L2 virtual circuits	1 min	30 min
Mirror traffic	1 min	20 min

Table 1 Network Tasks using AI reasoning vs. manual proces

These results show great impact on improving daily tasks as well as adopting AI agents for other tasks, such as business processes revolving around deployment and operation. An important factor to consider, which we have not included in this research, is the cost of replacing the manual process. Hosting large language models with big context size, memory requirements, storage and indexing cost is another important element in decision-making to make a greater adoption of AI agents.

### Conclusions

Based on experimental results from deploying different types of AI agents, we have concluded that for each specific task, there is one distinct method's performance over the other. Among all the methods, CoT has greatly improved the results and speed of performing tasks. While more complex methods can be costly to implement, they are best suited for more complex tasks. Agents seem to be the next natural evolution in network operation due to the ease of development and interaction with engineers of different levels of network expertise, it can have a greater adoption compared to the advanced tools where a higher degree of ramp-up and learning is required.

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#### Fatos Peci, Enver Hamiti

### AGJENTET INTELIGJENT NË RRJETAT TELEKOMUNIKUESE

#### Përmbledhje

Në këtë punim trajtohet roli i agjentëve të inteligjencës artificiale (AI) në rrjetet globale të telekomunikacionit, veçanërisht në fushën e njohurive dhe diagnostikimit (troubleshooting) të rrjeteve. Autorët përshkruajnë se si agjentët e bazuar në modele të avancuara gjuhësore (LLM) dhe API-të e rrjetit, mund të krijohet një mjedis operimi "bazuar në qëllim" (intent-based), duke zëvendësuar në një masë të madhe operimet tradicionale. Këta agjentë jo vetëm që marrin informacion nga një burim i jashtëm (p.sh. databazë apo sistem gjurmimi), por edhe zbatojnë veprime konkrete në rrjet, gjë që ndikon drejtpërdrejt në zvogëlimin e kohës mesatare të reagimit ndaj incidenteve dhe ndryshimeve (MTTR).

Në rrjete globale me shkallë të gjerë, ekzistojnë shumë qendra operimi që funksionojnë 24/7 dhe shpërndahen në zona të ndryshme kohore. Kjo kërkon angazhim të madh njerëzor e logjistik, duke e bërë kështu shumë tërheqës përdorimin e modeleve gjeneruese AI, për t'i ndihmuar operatorët në detyra të ndryshme. Modelet e mëdha gjuhësore mund të mbushin hendekun mes inxhinierit që ka nevojë për informacione specifike dhe sistemeve kompjuterike, duke marrë kështu rolin e një "ndihmësi inteligjent". Një nga konceptet kryesore është "Retrieval Augmented Generation" (RAG), ku modelit i ofrohet një bazë e jashtme e të dhënave për të gjeneruar përgjigje më të sakta. Mirëpo, kur kërkohet të ndërmerren veprime mbi rezultatet e këtij kërkimi, hyn në lojë ideja e "agjentit", i cili jo vetëm nxjerr informacion, por edhe reagon, për shembull duke rikonfiguruar një element të rrjetit për të zgjidhur një problem të identifikuar.

Punimi prezanton disa detyra reale nga operimi i rrjetit: diagnostikimi i rënies së paketave (packet loss), kërkimi i pajisjeve (sipas ndryshimeve të planifikuara), etj. Tabela e prezantuar tregon se si përdorimi i agjentëve AI e ul ndjeshëm kohën nga gjysëm ore ose disa minuta, në vetëm 1 minutë. Për shembull, për kërkimin e pajisjeve që preken gjatë ndryshimeve, nga 20 minuta, zbret në 1 minutë nëpërmjet një agjenti AI. Kjo tregon një potencial të madh për të kursyer kohë, veçanërisht në ambientet e gjera shumë-vendore (multivendor), me lokacione në rajone të shumta (APAC, EMEAR, AMER), ku ka larmi të madhe shërbimesh dhe pajisjesh.

Studimi tregon se në rrjete moderne, metodat e bazuara në "Chain-of-Thought" ofrojnë përfitime të dukshme në shumë skenarë, sidomos për detyra me kompleksitet mesatar. Metodat më komplekse si Reflexion apo Re-Act mund të përdoren për raste më të vështira, meqenëse kërkojnë fuqi llogaritëse dhe kohë ekzekutimi më të madhe. Në përgjithësi, agjentët e inteligjencës artificiale përfaqësojnë një evoluim të natyrshëm në operimin e rrjeteve, duke i fuqizuar inxhinierët e rrjetit me mjete të reja dhe efikase, si dhe duke reduktuar kohën e nevojshme për diagnostikim, ndryshime dhe përgjigje ndaj inçidenteve. Me zhvillimin e mëtejshëm të këtyre metodave, pritet një integrim edhe më i gjerë dhe i thellë i agjentëve AI në aspektet e dizajnit, konfigurimit dhe monitorimit të rrjeteve, duke hapur rrugën drejt një operimi më autonom dhe me kosto më të ulëta.

#### 556.55:597(05)

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# PERSISTENT ORGANIC POLLUTANTS (POPS) IN FISH FROM BATLLAVA LAKE, KOSOVO

### Dedication

This work is dedicated to Academician Nexhat Daci in recognition of his scientific and educational contributions to environmental chemistry. Throughout his career, Professor Daci has played a pivotal role in advancing our understanding of environmental pollutants and their impacts on ecosystems. His research has significantly enriched the field of environmental chemistry, providing valuable insights into the behavior, detection, and management of harmful substances in various environmental matrices. His dedication to both research and education has inspired countless students and professionals, making a lasting impact on the scientific community. This work stands as a testament to his remarkable legacy and commitment to improving environmental health through scientific excellence.

#### Abstract

The study presented here focuses on the analysis of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) in fish samples collected from Batllava Lake, one of Kosovo's artificial lakes. The lake's diverse flora and fauna are rich in various fish species and other organisms. In October 2024, 10 fish samples of species *Sander lucioperca* were collected from the lake for analysis. Organochlorine compounds were quantified using gas chromatography coupled with electron capture detection (GC/EDC) and mass spectrometry (GC/MS). To prepare the samples, fish tissues were dried and homogenized with anhydrous Na<sub>2</sub>SO<sub>4</sub> to remove water. The OCPs and PCBs were then extracted using an ultrasonic extraction method with a mixture of n-Hexane and DCM as the solvent. A Florisil column was employed for a secondary clean-up procedure. The study revealed that organochlorine pesticides and PCB

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markers were detected in almost all of the fish samples from Batllava Lake. Total PCB ( $\Sigma$ PCB) concentrations in fish ranged from < MDL to 1.87 µg/kg.  $\Sigma$ OCP concentrations in fish ranged from < MDL to 0.31 µg/kg. The presence of pesticides likely reflects their historical usage and their high persistence in the environment. PCBs, on the other hand, may have originated from atmospheric deposition or localized sources near the lake. Ongoing monitoring of organochlorine pollutants in Batllava Lake's fish samples is essential and should be conducted by the relevant authorities. This monitoring is essential for developing informed management strategies aimed at preventing further contamination of this vital water resource.

Keywords: Batllava Lake, OCPs, PCBs, Fish samples, Gas chromatography

### Introduction

Persistent Organic Pollutants (POPs), including organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) are widely recognized environmental contaminants with significant ecological and health risks [1-5]. These compounds are characterized by their high stability, bioaccumulation potential, and persistence in the environment, often leading to long-term contamination of aquatic ecosystems, particularly in lakes [1,2]. They are released into the environment through agricultural runoff, industrial discharges, combustion processes, and wastewater effluents, and can spread over long distances via atmospheric deposition, further increasing their environmental footprint [3,4].

Pesticides, including OCPs, are extensively used in agriculture to control pests and diseases. However, their uncontrolled application and persistence in the environment make them a significant concern for water quality, particularly in regions with intensive agricultural practices [5]. These chemicals can accumulate in sediments, water, and aquatic organisms, posing serious threats to both aquatic life and human health through the food chain [6,7]. PCBs are synthetic organic chemicals that were once widely used in industrial applications due to their insulating properties. Although their production has been banned in many countries, PCBs continue to persist in the environment, especially in aquatic ecosystems, due to their hydrophobic nature and resistance to degradation [8,9]. PCBs are commonly detected in the sediments and biota of lakes and rivers, where they pose risks to aquatic organisms and the populations relying on these ecosystems for food [10,11].

Aquatic ecosystems, particularly lakes, are important reservoirs for these pollutants, which accumulate in sediments, water, and biota [12]. The bioaccumulation of POPs in aquatic organisms, especially fish, represents a major route of human exposure [13]. Local populations dependent on these water bodies for drinking water, fishing, and recreation face increased health risks due to the consumption of contaminated water and fish [14].

This study aims to assess the presence and concentrations of these pollutants in fish samples from Batllava Lake, and to evaluate the potential risks posed to local populations relying on these ecosystems for their water supply and food.

# Experimental part Sample collection and preparation

In this study, 10 fish samples were collected from Batllava Lake in October 2024 following the guidelines outlined in ISO 23893-1:2007 [15]. The samples represented most common fish species in the lake: *Sander lucioperca*. The samples were transported in plastic bags at a temperature of +4°C. Only the fish tissues, which are the consumable parts, were analyzed [16-20]. To ensure uniform distribution of contaminants, the fish tissues were homogenized. The tissues were typically freeze-dried and ground into a fine powder before extraction [21].

# Treatment of fish samples for GC analysis

The fish tissue samples were first homogenized with anhydrous sodium sulfate (1/10, m/m), followed by extraction using an ultrasonic bath with around 10 g of fresh tissue. The extraction solvent was a 50 ml mixture of n-hexane and dichloromethane (3/1, v/v). The extract was initially cleaned up by shaking with 15 g of silica gel, which had been previously impregnated with 45% sulfuric acid to hydrolyze macromolecules. A further clean-up step involved using an open glass column filled with 5 g of Florisil, deactivated with 5% water. The organo-chlorine compounds were eluted from the column with 10 ml of a n-hexane/dichloromethane mixture (4/1, v/v). The final extract was concentrated to 1 ml by using rotary evaporator (DW-2000ADQ Multi rotary evaporator) before being analyzed using GC/MS for qualitative analysis and GC/ECD for quantitative analysis [21,22].

# GC/MS Analysis of pollutants in fish samples

Qualitative determination of pesticide residues and PCB markers in the fish samples from Batllava Lake was performed using a Shimadzu GC/MS-Q2020 Nexius system. The instrument was equipped with a Shimadzu AOC-20i autosampler and a split/splitless injector, set to split mode at 280°C. A 30-meter long Rtx-5ms fused silica column (0.25 mm i.d.  $\times$  0.25 µm film thickness) was used for the separation. The oven temperature program was as follows: 150°C for 2 minutes, increased to 280°C at a rate of 5°C per minute, and then held at 280°C for 4 minutes. A 1 µl injection volume was used. The MS detector operated in scan mode (50-500 m/z) initially, followed by SIM mode. Three ions were selected for each pesticide and PCB, with the most abundant ion serving as the quantifier and the others as qualifiers for confirmation [23]. The analytical method was validated, and parameters such as accuracy, repeatability, reproducibility, linearity, limit of detection (LOD), and limit of quantification (LOQ) were assessed. The validation followed European Commission standards [23], and the parameters evaluated included specificity, matrix effect, linearity, LOD, LOO, accuracy, and precision.



Figure 1. GC/MS chromatogram of Sander lucioperca sample by using scan mode.

# GC/ECD Analysis of OCPs and PCBS

OCPs and PCBs were analysed by using a Varian GC 450 instrument equipped with an electron capture detector (ECD) and a Rtx-5 capillary column (30 m long  $\times$  0.25 mm i.d.  $\times$  0.25 µm film thickness). Helium was employed as the carrier gas, and nitrogen was used as the make-up gas. Manual injections were performed in split mode (1:50) at a temperature of 280°C. The OCPs were identified according to the EPA 8081 standard [24] and included HCH isomers ( $\alpha$ -,  $\beta$ -, and  $\delta$ -), DDT-related compounds (4,4-DDE, 4,4-DDD, 4,4-DDT), Heptachlors (Heptachlor and Heptachlor epoxide), Chlordanes ( $\alpha$  and  $\gamma$  isomers), Aldrin-related compounds (Aldrin, Dieldrin, Endrin), Endosulfans (I, II, and Endosulfane sulfate isomer), Methoxychlor, and Mirex. For PCBs, the analysis focused on seven specific PCB markers (IUPAC Nos. 28, 52, 101, 118, 138, 153, and 180). Quality assurance protocols were implemented, which included the determination of limit of detection (LOD), limit of quantification (LOQ), precision, reproducibility, and accuracy of the method. Five calibration points with concentrations of 5, 10, 25, 50, and 100 ng/µL were used for both pesticides and PCBs. Qualitative analysis was performed using the external standard method [23,25].



Figure 2. GC/ECD chromatogram of OCPs and PCB markers in fish sample of Batllava Lake

### Results and discussion

The analysis of organochlorine pesticides (OCPs), their residues, and polychlorinated biphenyls (PCBs) was conducted on fish samples from Batllava Lake. Organochlorine pollutants are highly stable compounds that can persist in the environment for many years after their application. The fish species *Sander lucioperca* was selected as a representative sample of the fish population in Batllava Lake.

Table 1 presents the total concentrations of OCPs in fish samples from Batllava Lake. OCPs concentrations in fish ranged from < MDL to 0.31 µg/kg of fresh fish. The observed concentration levels are likely attributed to the historical use of pesticides in the watershed area. The distribution of OCPs was relatively consistent across all samples, indicating a common source of contamination. However, it was observed that certain pesticides appeared at higher levels in some samples, which may be related to specific characteristics of the fish, such as age, weight, and sex. In all fish samples, the OCP levels did not exceed the Maximum Residue Limits (MRLs) established by Codex Alimentarius 2010 [26] for any of the individual OCPs analyzed.

Organochlorine	Mean	Min	Max	Median	STDEV
Pesticide					
a-HCH	0.052	0.010	0.112	0.045	0.044
β-НСН	0.045	0.020	0.062	0.050	0.014
Lindane	0.017	0.000	0.037	0.011	0.014
δ-НСН	0.016	0.000	0.037	0.015	0.016
Heptachlor	0.130	0.010	0.386	0.031	0.171
Aldrin	0.085	0.010	0.140	0.086	0.052
Heptachlor	0.055	0.010	0.120	0.049	0.039
epoxide					
y-Chlordane	0.009	0.000	0.020	0.010	0.008
Endosulfan I	0.257	0.000	0.772	0.075	0.347
a-Chlordane	0.002	0.000	0.010	0.000	0.004
<i>4,4'-DDE</i>	0.007	0.000	0.012	0.010	0.006
Dieldrin	0.012	0.010	0.020	0.011	0.004
Endrin	0.003	0.000	0.010	0.000	0.005
Endosulfan II	0.317	0.010	0.810	0.314	0.299
4.4'-DDD	0.000	0.000	0.000	0.000	0.000
Endrin aldehid	0.038	0.010	0.130	0.022	0.045
<i>4,4'-DDT</i>	0.000	0.000	0.000	0.000	0.000
Endosulfan	0.319	0.010	1.020	0.202	0.383
sulfat					
Methoxychlor	0.036	0.010	0.130	0.020	0.046
Endrin keton	0.017	0.000	0.037	0.011	0.014
Mirex	0.004	0.000	0.012	0.000	0.006

Table 1. OCPs in fish samples from Batllava Lake ( $\mu g/kg$ ).

The profile of OCPs (Figure 3) in the fish samples was as follows: Endosulfan sulfat > Endosulfan II > Endosulfan I > Heptachlor > Aldrin > Heptachlor epoxide >  $\alpha$ -HCH >  $\beta$ -HCH. Their presence may be attributed to the bioaccumulation process and/or recent usage of these chemicals. It is important to note that the pesticide profile could be linked to the specific period during which these chemicals were applied [11,14]. Additionally, the individual physical-chemical properties of each pesticide and their residues could influence the observed profile.



Figure 3. Profile of OCPs in fish samples of Batllava Lake.



Figure 4. Lindane and its isomers in fish samples of Batllava Lake.

Figure 4 illustrates the profile of Lindane and its isomers in fish samples from Batllava Lake. Lindane and its isomers were detected in nearly all fish samples, with an average concentration of 0.13  $\mu$ g/kg.  $\alpha$ -HCH was found at higher levels due to its tendency to bioaccumulate in adipose tissues. This profile may be a result of the stability of HCHs and their bioaffinity in living organisms. The total concentration of HCHs ( $\Sigma$ HCHs) was found to be below the maximum allowable limit for fish samples according to Codex Alimentarius 2010 [26].



Figure 5. Heptachlores in fish samples of Batllava Lake.

Figure 5 displays the presence of Heptachlors in fish samples from Batllava Lake. Both Heptachlor and its degradation product, Heptachlor epoxide, were detected in 83.6% of the analyzed samples. Heptachlor epoxide was found at higher concentrations (mean concentration of 0.055  $\mu$ g/kg) in all samples, which is likely due to the historical use of Heptachlor. The total concentration of Heptachlors ( $\Sigma$ Heptachlors = 0.18  $\mu$ g/kg) was below the maximum allowable limit for fish samples, according to Codex Alimentarius 2010 [26].

Figure 6 presents the levels of Chlordanes in the fish samples. Both  $\alpha$  and  $\gamma$  isomers of Chlordanes were detected in 63% of the analyzed samples. The total concentration of Chlordanes ( $\Sigma$ Chlordanes = 0.011 µg/kg) was below the maximum permissible limit for fish samples according to Codex Alimentarius 2010 [26].



Figure 6. Chlordanes in fish samples of Batllava Lake.



Figure 7. Aldrines in fish samples of Batllava Lake.

Figure 7 depicts the profile of Aldrin's in fish samples from Batllava Lake. The total concentration of Aldrin's was measured at 0.15  $\mu$ g/kg. It is possible that Aldrin's were applied in the area in recent years under an unapproved brand. The degradation products of Aldrin were found at elevated concentrations in all samples, likely as a result of its previous use. The overall concentration of Aldrin was within the allowable limits for fish samples, in compliance with Codex Alimentarius 2010 [26].

The profile of DDT and its related compounds (DDD, DDE, and Methoxychlor) in fish samples from Batllava Lake is shown in Figure 8. DDTs were found in 23% of the samples. Among the related compounds, Methoxychlor (0.036  $\mu$ g/kg) and DDE (0.007  $\mu$ g/kg) were detected at higher concentrations in all samples. However, DDE and DDT were not found in the fish samples. Despite the presence of these contaminants, the total concentration of DDTs in the fish samples was below the permissible limits set by Codex Alimentarius 2010 [26], indicating that the levels of these pollutants are within acceptable regulatory standards.



Figure 8. DDTs in fish samples of Batllava Lake.

Figure 9 presents the profile of Endosulfans in fish samples from Batllava Lake. The average concentration of Endosulfans was 0.68  $\mu$ g/kg, with Endosulfan sulfate (0.319  $\mu$ g/kg) being identified at higher concentrations in all the fish samples. Despite the presence of Endosulfans, the total concentration was found to be below the permissible limits for fish samples, in compliance with Codex Alimentarius 2010 [26], indicating that the levels of these contaminants are within the accepted regulatory standards.



Figure 9. Endosulfanes in fish samples of Batllava Lake.

Mirex was detected in all the analyzed fish samples from Batllava Lake, with an average concentration of 0.004  $\mu$ g/kg. This indicates the widespread presence of Mirex in the lake's ecosystem, although the concentration remains relatively low across all samples. Continuous monitoring of such pollutants is important to assess potential long-term environmental impacts and ensure the protection of aquatic life and human health.

Elizabeta et al. (2011) conducted research on OCPs in Ohrid Lake, North Macedonia, using fish samples [27]. The concentrations of OCPs found in fish samples from Ohrid Lake ranged from 0.452 to 14.725  $\mu$ g/kg, which are higher than the values we found in fish samples from Batllava Lake (from < MDL to 0.31  $\mu$ g/kg).

Table 2 illustrates the total concentrations of PCB markers in fish samples from Batllava Lake. PCBs were detected in all analysed fish samples, with an average total concentration of 2.53  $\mu$ g/kg, which is two to three times higher than the concentrations of organochlorine pesticides (OCPs) found in the same species. The presence of PCBs may be linked to nearby industrial activities around the lake, such as mechanical operations, as well as maintenance work on electrical transformers and generators. The distribution of PCBs was nearly uniform across all samples, suggesting a common source of contamination affecting the entire lake ecosystem.

РСВ	Mean	Min	Max	Median	STDEV
markers					
<b>PCB 28</b>	1.878	0.012	5.794	0.395	2.624
<b>PCB 52</b>	0.018	0.002	0.060	0.015	0.021
PCB 101	0.039	0.004	0.067	0.041	0.025
PCB 118	0.076	0.019	0.132	0.081	0.042
PCB 153	0.022	0.003	0.044	0.019	0.016
PCB 138	0.023	0.010	0.030	0.023	0.007
PCB 180	0.000	0.000	0.000	0.000	0.000

Table 2. PCBs in fish samples from Batllava Lake (µg/kg).

Figure 10 presents the profile of PCBs in fish samples from Batllava Lake. PCB 28 was detected at higher levels (1.87  $\mu$ g/kg), with its origin likely attributed to atmospheric deposition. The presence of heavier PCB congeners, such as PCB 138 and PCB 153, suggests a potential terrestrial origin. Additionally, the discharge of wastewater from nearby industries and mechanical operations may have contributed to the observed concentrations and distribution of PCBs in the lake's fish samples.

Aurel et al. (2014, 2017, 2020) compared the concentrations of various pollutants found in water samples collected from different ecosystems of Albania [28-30]. The values found by Nuro et al. (2014, 2017, 2020) are similar compared to the values we found in Batllava Lake for PCBs, ranging from < MDL to 1.87  $\mu$ g/kg.



Figure 10. Profile of PCBs in fish samples of Batllava Lake.

### Conclusions

The aim of this study was to investigate the presence of organochlorine pesticides, their residues, and PCB markers in fish samples from Batllava Lake. The analysis of these contaminants followed EU protocols for fatty food samples. Organochlorine pesticides and their residues were detected in nearly all fish samples from the lake, with the presence of pesticide residues likely linked to their previous use in the surrounding agricultural areas. Degradation products of pesticides were found at higher concentrations, and the pesticide profile in the samples was as follows: Endosulfan sulfat > Endosulfan II > Endosulfan I > Heptachlor > Aldrin > Heptachlor epoxide >  $\alpha$ -HCH >  $\beta$ -HCH. These concentrations and the distribution patterns can be associated with the historical use of these chemicals in agriculture and their individual physical-chemical properties. Pesticide levels in all samples were found to be below the allowed limits set by EU legislation. PCBs were present at concentrations 2 to 3 times higher than organochlorine pesticides in the same fish samples. The higher levels of volatile PCBs in all samples suggest an origin linked to atmospheric deposition, while the presence of heavier PCB congeners could be attributed to terrestrial sources, such

as agricultural machinery and local industrial activities. The detection of both organochlorine pesticides and PCBs in the fish samples from Batllava Lake highlights the need for continuous monitoring by responsible institutions to assess and mitigate environmental contamination in the area.

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#### Ilirjana Osmani, Arben Haziri, Majlinda Daci, Bledar Murtaj, Aurel Nuro

## NDOTËSIT ORGANIKË TË QËNDRUESHËM (POPs) NË PESHQI NGA LIQENI I BATLLAVËS, KOSOVË

#### Përmbledhje

Ndotësit organikë të qëndrueshëm (POP), duke përfshirë pesticidet organoklorinike (OCP) dhe bifenilët e polikloruruara (PCB) janë ndotës mjedisorë të njohur gjerësisht me rreziqe ekologjike dhe shëndetësore. Këto komponime karakterizohen nga stabiliteti i tyre i lartë, potenciali i bioakumulimit dhe qëndrueshmëria në mjedis, shpesh duke çuar në ndotje afatgjatë të ekosistemeve ujore, veçanërisht në liqene. Ato kalojnë në mjedis përmes rrjedhjeve bujqësore, shkarkimeve industriale, proceseve të djegies dhe rrjedhjeve të ujërave të zeza dhe mund të përhapen në distanca të largta nëpërmjet depozitimit atmosferik, apo edhe nëpërmjet shpërlarjes së tokës. Ekosistemet ujore, veçanërisht liqenet, janë rezervuarë të rëndësishëm për këta ndotës, të cilët grumbullohen në sedimente, ujë dhe biota. Bioakumulimi i POP-ve në organizmat ujorë, veçanërisht peshqit, përfaqëson një rrugë kryesore të ekspozimit të njeriut. Popullata lokale të varura nga këto ekosisteme ujorë për ujë të pijshëm, peshkim dhe rekreacion përballen me rreziqe shëndetësore për shkak të konsumit të ujit dhe peshkut të kontaminuar.

Prandaj ky studim ka synuar të vlerësojë praninë dhe përqendrimet e këtyre ndotësve në mostrat e peshqve nga liqeni i Batllavës, dhe të vlerësojë rreziqet potenciale të paraqitura për popullsinë lokale që mbështetet në këto ekosisteme për furnizimin e tyre me ujë dhe ushqim.

Qëllimi i këtij studimi ishte të hulumtojë praninë e OCP-ve, mbetjeve të tyre dhe markerëve të PCB-ve në mostrat e peshkut nga liqeni i Batllavës. OCP-të dhe mbetjet e tyre u gjetën në pothuajse të gjitha mostrat e peshkut nga liqeni, dhe prania e mbetjeve të pesticideve ka të ngjarë të lidhet me përdorimin e tyre të mëparshëm në zonat bujqësore përreth. Produktet e degradimit të pesticideve u gjetën në përqendrime më të larta dhe profili i pesticideve në mostra ishte si vijon: Endosulfan sulfat > Endosulfan II > Endosulfan I > Heptaklor > Aldrin > Heptaklor epoksid >  $\alpha$ -HCH >  $\beta$ -HCH. Këto përqendrime dhe modelet e shpërndarjes mund të lidhen me përdorimin historik të këtyre komponimeve në bujqësi dhe me vetitë e tyre individuale fiziko-kimike. Nivelet e pesticideve në të gjitha mostrat u gjetën nën kufijtë e lejuar të përcaktuar nga legjislacioni i BE-së. PCB-të ishin të pranishme në përqendrime 2 deri në 3 herë më të larta se OCP-të në të njëjtat mostra peshku. Nivelet më të larta të PCB-ve në të gjitha mostrat sugjerojnë një origjinë të lidhur me depozitimin atmosferik, ndërsa prania e PCB-ve më të rëndë mund ti atribuohet burimeve tokësore, të tilla si makineritë bujqësore dhe aktivitetet industriale lokale. Zbulimi i OCP-ve dhe PCB-ve në mostrat e peshkut nga liqeni i Batllavës nxjerr në pah nevojën për monitorim të vazhdueshëm nga institucionet përgjegjëse për të vlerësuar dhe zbutur ndotjen mjedisore në këtë ekosisteme ujor.

#### 517(05)

## Razim Hoxha<sup>1</sup>

## GENERALIZATION OF REVERSES OF THE TRIANGLE INEQUALITY

#### Abstract

In this paper we establish the recently results of reverses of the triangle inequality and generalization with positive linear functionals. Some of these results are given and analyzed. Based on these results, we obtain some improvements and generalizations of the reverses triangle inequality.

Keywords: Triangle inequality, reverse inequality, generalization, Lebesgue integral.

## Introduction

There are a lot of reverses of the triangle inequalities in recente literature. Some of these results are given in [2], [3] and [4].

First of all, let's remind on the classical triangle inequality (see [4] and [2]).

Let  $z_1, \ldots, z_n$  be complex numbers. Then the following inequality holds:

$$\left|\sum_{i=1}^{n} z_{i}\right| \leq \sum_{i=1}^{n} |z_{i}| \tag{1.1}$$

There also exist analogues of the triangle inequality (1.1).

Let *f* be a continuous complex (real) function of real variable x on a segment [a,b], then the following inequality holds:

$$\left| \int_{a}^{b} f(x) dx \right| \leq \int_{a}^{b} |f(x)| dx$$
 (1.2)

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which is continuous version of the triangle inequality (1.1).

Now, we give the opposites of the triangle inequality.

Also, let's remind on classical reversed triangle inequality (1.1) and (1.2).

In [4], the following result is obtained.

**Theorem 1.1.** Let *a* be a real number and let  $0 < \theta < \frac{\pi}{2}$ . If  $z_1, ..., z_n$  are complex numbers such that  $a - \theta \le \arg z_i \le a + \theta$ , (i = 1, ..., n), then the following inequality holds:

$$\left|\sum_{i=1}^{n} z_{i}\right| \ge (\cos\theta) \sum_{i=1}^{n} |z_{i}|$$
(1.3)

Proof. We have

$$\begin{vmatrix} \sum_{i=1}^{n} z_i \\ = \begin{vmatrix} e^{-ia} \sum_{i=1}^{n} z_i \end{vmatrix} \ge \operatorname{Re}\left(e^{-ia} \sum_{i=1}^{n} z_i\right) \\ = \sum_{i=1}^{n} |z_i| \cos(-a + \arg z_i) \ge (\cos\theta) \sum_{i=1}^{n} |z_i|$$

There exists the continuous version of a reverse inequality (1.2). If *f* is a complex – valued integrable function on [*a*, *b*] and  $-\theta < \arg f(x) < \theta$  for  $0 < \theta < \frac{\pi}{2}$ , then the following inequality holds:

$$\left| \int_{a}^{b} f(x) dx \right| \ge \cos \theta \int_{a}^{b} |f(x)| dx$$
(1.4)

Also, in [4], the following inequality is proved.

**Theorem 1.2.** Let *a* be a real number and let  $0 < \theta < \frac{\pi}{2}$ . If  $z_1, ..., z_n$  are complex numbers such that

$$a < argz_i < a + \theta, i = 1, ..., n$$
 (\*)

then the following inequality holds:

$$\left|\sum_{i=1}^{n} z_{i}\right| \ge \max\left(\frac{\sqrt{2}}{2}, \cos\theta\right) \sum_{i=1}^{n} |z_{i}|$$
(1.5)

Now, if we apply Theorem 1.1 and (\*) Theorem 1.2, we obtain a similar result in the following form.

**Theorem 1.3.** Let be  $z_1, ..., z_n$  complex numbers in a sector of the complex plane with the origin as its vertex of angle  $\theta$ , where  $0 \le \theta \le \pi$ . Then the following holds:

$$\left|\sum_{i=1}^{n} z_{i}\right| \ge \left(\cos\frac{\theta}{2}\right) \sum_{i=1}^{n} |z_{i}|$$
(1.6)

**Proof.** If we apply Theorem 1.1, then we have that if it (\*) holds for  $0 \le \theta \le \pi$ , then (1.6) holds. In fact, this result is the same as Theorem 1.1 since it (\*) can be rewritten in the form

$$\left(a + \frac{\theta}{2}\right) - \frac{\theta}{2} < \arg z_i < \left(a + \frac{\theta}{2}\right) + \frac{\theta}{2}$$

## The Generalization of Reverses of the Triangle Inequality with Positive Linear Functional

First, we give a generalization of the triangle inequality with a positive linear functional.

Let E be a nonempty set and L be a linear class of functions  $g: E \rightarrow R$  having the following properties:

- (1)  $f, g \in L \Rightarrow (af + bg) \in L$  for  $a, b \in R$
- (2)  $1 \in L$ , i. e. if f(t) = 1 ( $\forall t \in E$ ), then  $f \in L$ .

Let's consider the positive linear functional A:  $L \rightarrow R$ , which satisfies conditions.

- (I) A(af + bg) = aA(f) + bA(g), for f, g L, and a, b R
- (II) If  $f \in L$  and  $f(t) \ge 0$  on E, then  $A(f) \ge 0$

Further, let's consider the class:

 $\overline{L} = \{f: E \rightarrow C/Ref \in L, Imf \in L\}$ 

Let *A* be a positive linear functional and let the functional  $\overline{A}: \overline{L} \to C$  is defined by

$$\overline{A}(f) = A(\text{Ref}) + iA(\text{Imf}) = \text{Re}(\overline{A}(f)) + i\text{Im}(\overline{A}(f))$$

Then,  $\overline{A}$  is a complex linear functional on  $\overline{L}$ , i. e.

$$\overline{A}(af + bg) = a\overline{A}(f) + b\overline{A}(g)$$
, for f,  $g \in \overline{L}$ , a,  $b \in C$ 

In [4] the following inequality is proved:

**Theorem 2.1.** If  $f \in \overline{L}$ , and  $|f| \in L$  then the following inequality holds:

$$|\overline{A}(f)| \le A(|f|) \tag{2.1}$$

**Proof.** For arbitrary  $\theta \in \mathbb{R}$ , we have

$$\operatorname{Re}\left(e^{i\theta}\overline{A}(f)\right) = \operatorname{Re}\left(\overline{A}\left(e^{i\theta}f\right)\right) = A\left(\operatorname{Re}\left(e^{i\theta}f\right)\right) \le A(|f|)$$

Suppose that  $\overline{A}(f) = re^{it}$ . Set in previous consideration  $\theta = -t$ , we get

$$|\overline{A}(f)| = r = \operatorname{Re}(e^{-it}\overline{A}(f)) \le A(|f|)$$

Then, we'll state the abstract reversed triangle inequality, i.e. we obtain the following inequality:

**Theorem 2.2.** If  $f \in \overline{L}$ , and  $a - \theta < argf(x) < a + \theta$ ,  $0 < \theta < \frac{\pi}{2}$ , then

 $|\overline{A}(f)| \ge (\cos\theta)A(|f|) (2.2)$ 

Proof. We have

$$\begin{aligned} |\overline{A}(f)| &= \left| e^{-ia}\overline{A}(f) \right| \ge \operatorname{Re}\left( e^{-ia}\overline{A}(f) \right) = A\left( \operatorname{Re}\left( e^{-ia}f \right) \right) \\ &= A\left( |f|\operatorname{Re}\left( e^{i(\operatorname{arg} f - a)} \right) \right) = \end{aligned}$$

 $= A(|f|\cos(\arg f - a)) \ge A(\cos\theta|f|) = (\cos\theta)A(|f|).$ 

In addition for

$$a < argf(x) \le a + \theta$$
, for  $0 \le \theta \le \pi$ 

it holds

$$|\overline{A}(f)| \ge \left(\cos\frac{\theta}{2}\right)A(|f|) (2.3)$$

Now, by introducing two parameters, we obtain the following result:

**Theorem 2.3.** If  $f \in \overline{L}$ ,  $|f| \in L$ ,  $a + \phi_1 < \arg f(x) < a + \phi_2$  and  $0 < \phi_2 - \phi_1 < \pi$ , then the following inequality holds:

$$|\overline{A}(f)| \ge \cos \frac{\varphi_2 - \varphi_1}{2} \cdot A(|f|)$$
 (2.4)

Proof. Since

$$\left(a + \frac{\phi_1 + \phi_2}{2}\right) - \frac{\phi_2 - \phi_1}{2} \le \arg(x) \le \left(a + \frac{\phi_1 + \phi_2}{2}\right) + \frac{\phi_2 - \phi_1}{2}$$

Then, the inequality obviously follows from the result of Theorem 2.2.

Now we obtain the following result, i e., the generalization of reverses of the triangle inequality:

**Theorem 2.4.** Let  $f \in \overline{L}$  and  $t \in E$ ,  $0 < \varphi_{1\varphi} < \varphi_2 < \frac{\pi}{2}$  and  $a + \varphi_1 \le argf(t) \le a + \varphi_2$ . Then the following of the triangle inequality holds

$$|\overline{A}(f)| \ge \sqrt{\sin^2 \varphi_1 + \cos^2 \varphi_2} \cdot A(|f|)$$
(2.5)

Proof. We have

$$|\overline{A}(f)| = |e^{-ia}\overline{A}(f)| = \left\{ \left( \operatorname{Re}\left( e^{-ia}\overline{A}(f) \right)^2 \right) + \left( \operatorname{Im}\left( e^{-ia}\overline{A}(f) \right)^2 \right) \right\}^{\frac{1}{2}} = \left\{ \left( (A|f|)\cos(\arg f - a) \right) \right\}^2 + \left( (A|f|)\sin(\arg f - a) \right)^2 \right\}^{\frac{1}{2}} \ge \\ \ge (A|f|)\left\{ \cos^2\varphi_2 + \sin^2\varphi_1 \right\}^{\frac{1}{2}}$$

Using **Theorem 2.3.** and **Theorem 2.4.** we obtain the following inequality

$$|\overline{A}(f)| \ge \max\left\{\cos\frac{\varphi_2 - \varphi_1}{2}, \sqrt{\sin^2\varphi_1 + \cos^2\varphi_2}\right\} \cdot A(|f|) (2.6)$$

In [3], the following inequality is proved:

**Theorem 2.5.** Let  $f: [a, b] \rightarrow C$  strongly measurable such that the Lebesgue integral

$$\int_{a}^{b} |f(x)| dx \text{ exists and is finite. Let}$$
$$0 < \varphi_1 < \arg f(x) < \varphi_2 < \frac{\pi}{2}, \text{ for a.e. } x \in [a,b]$$

Then the following inequality holds

$$\left| \int_{a}^{b} f(x) dx \right| \ge \sqrt{\sin^2 \varphi_1 + \cos^2 \varphi_2} \cdot \int_{a}^{b} |f(x)| dx \ (2.7)$$

with equality if and only if

$$\int_{a}^{b} f(x)dx = (\cos\varphi_{2} + i\sin\varphi_{1})\int_{a}^{b} |f(x)|dx$$

Now, if we apply Theorem 2.5, we can obtain a similar result in the following form.

**Theorem 2.6.** Let,  $f: [a, b] \rightarrow C$  strongly measurable, such that the Lebesgue integral

$$\int_{a}^{b} |f(x)| dx \text{ exists, and it is finite. Let}$$
$$a + \varphi_1 < \arg f(x) < a + \varphi_2, \text{ and } 0 < \varphi_2 - \varphi_1 < \pi, \text{ for a.e. } x \in [a, b]$$

Then the following inequality holds:

$$\left|\int_{a}^{b} f(x)dx\right| \ge \cos\frac{\varphi_2 - \varphi_1}{2} \int_{a}^{b} |f(x)|dx| (2.8)$$

**Proof.** Now we are going to compare the result obtained in Theorem 2.5. and Theorem 2.6. Then, the following inequality is valid:

*b*]

$$\cos\frac{\varphi_2-\varphi_1}{2} \ge \sqrt{\sin^2\varphi_1+\cos^2\varphi_2}$$

for  $0 < \varphi_1 < \operatorname{argf}(x) < \varphi_2 < \frac{\pi}{2}$ .

Let's fix  $\alpha = \varphi_2 - \varphi_1$ . Now, consider the function *F* defined as

$$F(\varphi_1) = \sin^2 \varphi_1 + \cos^2(\varphi_1 + \alpha) - \cos^2 \frac{\alpha}{2}$$

We are going to prove that, for each  $\alpha \in \left(0, \frac{\pi}{2}\right)$ , the function *F* is negative for each  $\varphi_1 \in \left(0, \frac{\pi}{2} - \alpha\right)$ 

Indeed, we calculate the first derivative of function F:

 $F'(\phi_1) = \sin(2\phi_1) - \sin(2\phi_1 + 2\alpha)$ 

Now, it is easy to find that the minimum of *F* is obtained for  $\varphi_1 = \left(\frac{\pi}{4} - \frac{\alpha}{2}\right)$ . In both cases (when  $\varphi_1$  tends to 0 or to  $\frac{\pi}{2} - \alpha$ ), the value of *F* ( $\varphi_1$ ) tends to  $\cos^2 \alpha - \cos^2 \frac{\alpha}{2}$  and this value is obviously negative for  $\alpha \epsilon \left(0, \frac{\pi}{2}\right)$ . So, the function *F* is negative for each  $\varphi_1 \epsilon \left(0, \frac{\pi}{2} - \alpha\right)$ .

Hence, the result of Theorem 2.5. can be improved in the following way:

$$\left| \int_{a}^{b} f(x) dx \right| \ge \cos \frac{\varphi_2 - \varphi_1}{2} \int_{a}^{b} |f(x)| dx$$
  
for  $a + \varphi_1 < \arg(x) < a + \varphi_2, \ 0 < \varphi_2 - \varphi_1 < \pi$ , for a.e.  $x \in [a, b]$ 

## Conclusions

There are a lot of results on reverses of the triangle inequalities in recent literature. Some of these results are given and analyzed (see [2], [3] and [4]). We can also find a more general abstract triangle and reversed triangle inequality, i.e. a generalization of the triangle inequality with positive linear functionals. Based on these results, we obtain some forms of reverses of the triangle inequality, i.e., we obtain some improvements and generalizations of the reverse triangle inequality.

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#### Razim Hoxha

## PËRGJITHËSIMI I KONVERZIONEVE TË PABARAZIMIT TË TREKËNDËSHIT

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Në këtë punim janë shqyrtuar pabarazimet e trekëndëshit dhe disa konverzione përkatëse të këtyre pabarazimeve. Kështu, në pikën 1. janë dhënë disa pabarazime klasike të pabarazimit të trekëndëshit dhe i konverzioneve përkatëse në rastin diskret e integral. Mandej, ne kemi vërtetuar Teoremën 1.3. dhe kemi fituar një rezultat të ngjashëm me Teoremën 1.1. Pra, kemi fituar një konverzion në rastin diskret. Në pikën 2. kemi dhënë përgjithësimin e konverzioneve të pabarazimit të trekëndëshit me funksione lineare pozitive. Pastaj, janë analizuar rezultatet e mëparshme lidhur me përgjithësimin e konverzioneve të pabarazimit të trekëndëshit. Në bazë të këtyre rezultateve, ne kemi fituar disa forma të konverzioneve të pabarazimit të trekëndëshit, që në fakt paraqesin disa përmirësime dhe përgjithësime të konverzioneve të pabarazimit të trekëndëshit. Kështu, ne kemi vërtetuar Teoremën 2.2, Teoremën 2.3. dhe Teoremën 2.4. dhe kemi fituar përgjithësime të konverzioneve të pabarazimit të trekëndëshit, me funksione lineare pozitive. Poashtu, është vertetuar edhe Teorema 2.6 dhe kemi fituar një rezultat të ngjashëm me Teoremen 2.5. d.m.th kemi fituar një konverzion të pabarazimit të trekëndëshit në rastin integral.

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